

A Study of the Effect of Etching Time on the Optical Properties of Irradiated CR-39 Polymer

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Abstract

The track etch detector, CR-39, in common usage, is highly sensitive to recording charged particles. CR-39 polymer samples were irradiated with alpha particles at different energies (2.17 MeV and 3.95 MeV) followed by chemical etching with different times (1.50, 3.00 and 6.00 h). The tracks formed in CR-39 due to irradiations were visualized by using etching technique. The optical properties of the CR-39 polymer before and after the etching processes were studied with ultraviolet-visible (UV-vis) spectroscopy. The optical band gap energy was calculated for the CR-39 polymer samples. The average value of the track diameter of irradiation at 2.17 MeV and etching time 1.5 h is fairly large compared with its value at 3.95 MeV. This is due to the production of defect levels in the band gap of polymer at the 2.17 MeV. The results revealed that the CR-39 samples at 3.00 h are insensitive to the optical variations in the fundamental absorption edge.

Keywords: CR-39 track etch polymer, etching time, alpha particles irradiations, optical band gap energy, Urbach energy

Introduction

Polyallyl diglycol carbonate, $C_{12}H_{18}O_7$, (CR-39) track detectors are the most sensitive and popular detector for recording alpha particles [1-4]. Therefore, several studies [5-13] have been carried out to determine the main factors which affect the sensitivity and the properties of the CR-39 polymer as a track detector.

The passing of alpha particles through a CR-39 sample causes ionization for almost all molecules which are close to its path in a cylindrical zone. A zone enriched with free radicals and other chemical species is created along the path of the alpha particle. This damage zone is called a latent track [14].

The latent track can be revealed through chemical etching (erosion) in the material surface by using an acid or base solution [15]. The optimum etching conditions for using CR-39 as a track detector are 6.25 M NaOH solution at 70 °C for 6 h [7]. In the chemical etching, the rate along the particle trajectory, track etch rate (V_T), is faster than the rate of etching of the undamaged surface, bulk etch rate (V_b). A pit is formed in the position of each track as etching progresses [15].

Several authors [16-20] have studied the optical properties of CR-39 irradiated with different doses of gamma rays and different ions fluences. They found that the optical band gap energy was reduced with an increase of gamma-absorbed dose and ions fluences. Thus, the present work has been verified by the UV-vis spectra of CR-39 polymer materials, which irradiated with different alpha particle energies (2.17 - 3.95 MeV) at a constant fluence and at different etching times (1.500, 3.00 and 6.00 h). Furthermore, the changes in the optical band gap energy and the etching properties (track diameter measurements) of the tracks at different etching times have been recorded.

Materials and methods

Experimental technique

Various holder collimators with different heights were used to verify normal irradiation for the INTERCAST CR-39 ($1.00 \times 1.00 \text{ cm}^2 \times 1.50 \text{ mm}$) in air by alpha-particles [21]. The density of CR-39 was 1.32 g/cm^3 . The energy of the alpha particle that emerged from the collimator was measured by using a surface-barrier semiconductor detector and a calibrated multichannel analyzer. The heights of the collimators reduced the energy of 5.486 MeV alpha-particles which emitted from the ^{241}Am - source to 3.95 ± 0.20 and $2.17 \pm 0.18 \text{ MeV}$.

The incident flux (ϕ) was calculated by the following equation;

$$\phi = \frac{A_c}{4\pi r^2} \quad (1)$$

where A_c is the activity of the ^{241}Am - source in Bq and r is the source-detector distance in centimeters.

The fluence (Φ), the total number of alpha-particles emitted from the collimator and fallen on CR-39 per unit area in a certain irradiation time (t), was;

$$\Phi = \phi t \quad (2)$$

The irradiation times were varied for different fluxes to get a constant fluence value. The value of Φ was verified at $(32058 \pm 31 \text{ incident alpha-particles per cm}^2)$ for all irradiated CR-39 samples.

After irradiations, the samples were etched chemically in 6.25 M NaOH solution at 70°C for 1.50, 3.00 and 6.00 h. The value of V_b was calculated by the mass difference Δm , as the following equation [22];

$$V_b = \frac{\Delta m}{2A_i \rho t_e} \quad (3)$$

where A_i is the etched surface area, ρ is the density of the detector and t_e is the etching time. The calculated value of V_b was $1.599 \pm 0.270 \mu\text{m/h}$.

After etching, the track diameters (D) were measured by using the optical microscope which magnifies 1000 times and attached with eyepiece micrometer.

The etching time (t_R) required to etch the complete range for present alpha particles at normal incidence was determined by using the following equation [23];

$$t_R = \frac{R}{V_T} \quad (4)$$

where R is the range of alpha particles in CR-39 samples and V_T is the track etching rate. The range according to the alpha particle energy can be calculated by SRIM 2013 code [24]. The V_T -values can be calculated from a Track_Test program computer [25] by using the values of the range and V_b -value above.

The optical absorption spectra for virgin (before and after etching) and irradiated CR-39 samples at different times 1.50, 3.00 and 6.00 h were measured by using a double beam UV-vis spectrophotometer (Shimadzu 1601 PC, Japan) in the wavelength range of 200 - 800 nm.

Results and discussion

The CR-39 samples were irradiated with different alpha-particle energies 2.17 and 3.95 MeV at constant fluence (32058 ± 31 incident alpha-particles per cm^2). The energy lost by alpha particles in the CR-39 samples was mainly dominated by 2 mechanisms known as electronic stopping power (S_e) and nuclear one (S_n), which is usually expressed in $\text{eV}/\text{\AA}$. The values of S_e and S_n depend on the energy and the mass of the bombarded particle, as well as on the polymer composition. Using the calculations of the SRIM 2013 code [24], the projected range of alpha-particles in CR-39 polymer, S_e and S_n , were obtained. Also, the output calculations of this code indicated that more than 99.91 % of energy lost by the present alpha particle energies in CR-39 was due to electronic stopping power. The electronic energy loss leads to radical formation, chain scission and cross-linking of CR-39 polymer chains [26]. This was reflected in changes in the molecular structure of the polymer and changes in the optical band gap energy.

The optical absorption method used for the investigation of the optically induced transitions which can provide information about the band structure and energy gap in crystalline and non-crystalline materials [27]. **Figures 1 - 3** showed UV-vis spectra in the wavelength range of 200 - 800 nm for virgin (before and after etching) and irradiated CR-39 samples at different etching times 1.50, 3.00 and 6.00 h. It is noticed that the strongest absorption was found in the UV region for all samples, where there were higher photon energies due to electronic transitions that can take place in the material.

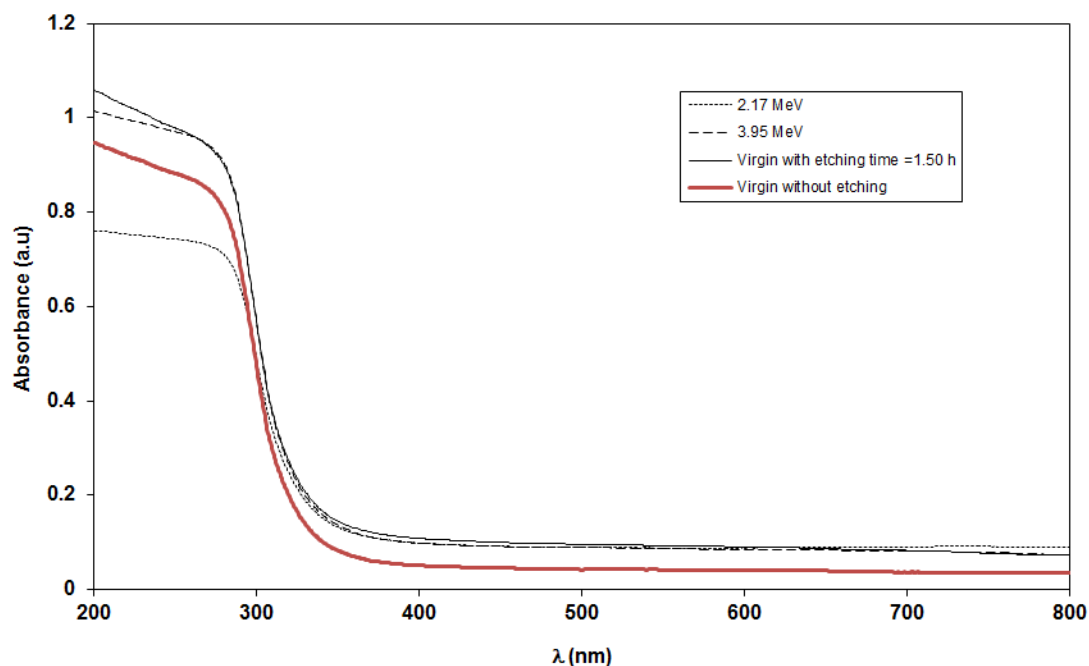


Figure 1 UV-VIS spectra of CR-39 samples virgin (before and after etching) and irradiated with alpha-particle energies 2.17 MeV and 3.95 MeV at 1.50 h etching time.

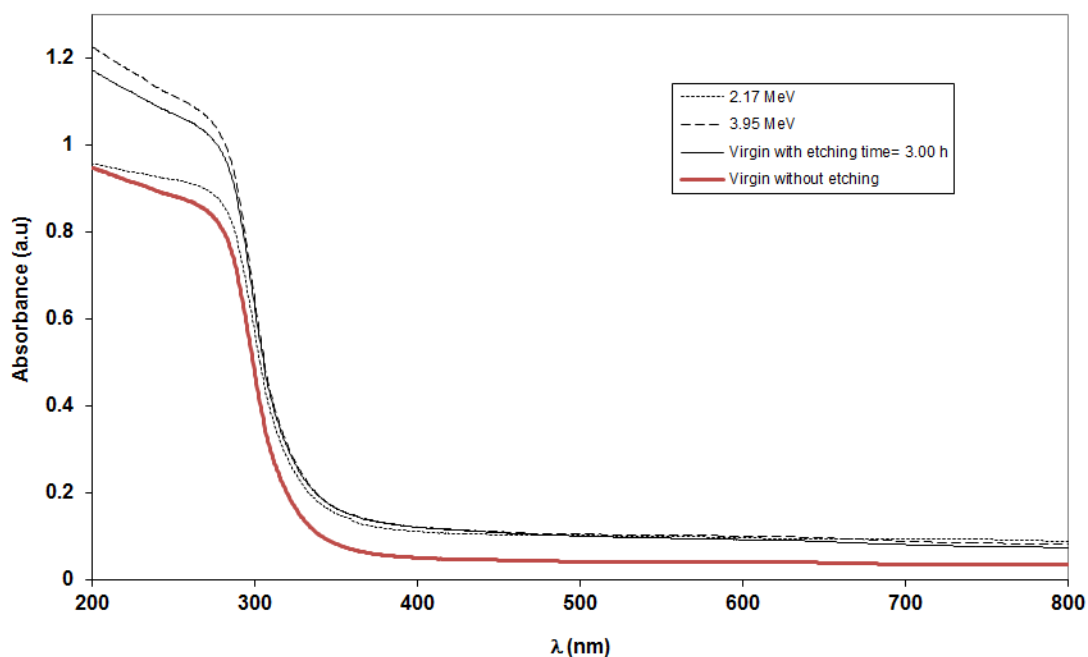


Figure 2 UV-VIS spectra of CR-39 samples virgin (before and after etching) and irradiated with alpha-particle energies 2.17 MeV and 3.95 MeV 3.00 h etching time.

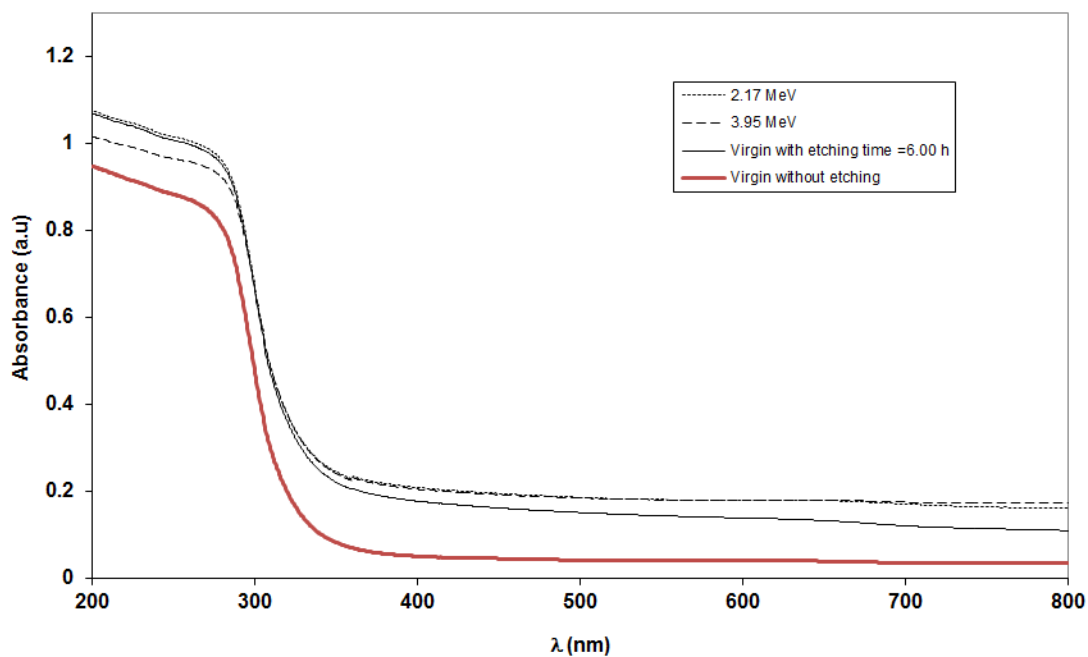


Figure 3 UV-VIS spectra of CR-39 samples virgin (before and after etching) and irradiated with alpha-particle energies 2.17 MeV and 3.95 MeV at 6.00 h etching time.

The optical absorption coefficient (α) can be calculated by the absorbance (abs) and the thickness of CR-39 material (d) as the following equation;

$$\alpha = 2.303 \frac{abs}{d} \tag{5}$$

The α values as a function of the photon energy, $h\nu$, are given by the relation [28];

$$\alpha = \beta(h\nu - E_g)^n / h\nu \tag{6}$$

where β is a constant, E_g is the value of the optical band gap energy and n depends on the type of transition (direct or indirect). Specially, n is 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively.

The usual method for the determination of the value of E_g of CR-39 samples can be determined by plotting $(\alpha h\nu)^{1/n}$ versus photon energy ($h\nu$). All samples showed that the most probable involved transition mechanism is the direct allowed transition, where $n = 1/2$. The intersection of the extrapolated line with $h\nu$ -axis represents the value of E_g . The regression coefficient of the best fit lines for the linear parts of the fundamental absorption edge of the UV-vis spectra is found to be not less than 0.99, as shown in Figures 4 - 6.

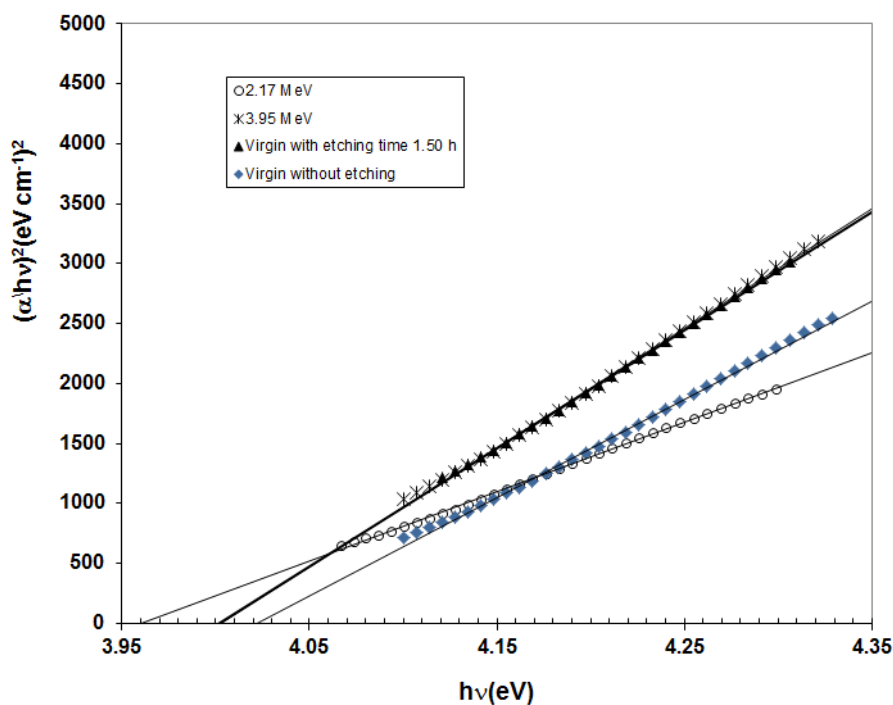


Figure 4 Calculations of the optical energy gap from extrapolation of the fitted lines (—) with $h\nu$ -axis for virgin (before and after etching) and irradiated CR-39 samples with alpha-particle energies 2.17 MeV and 3.95 MeV at 1.50 h etching time.

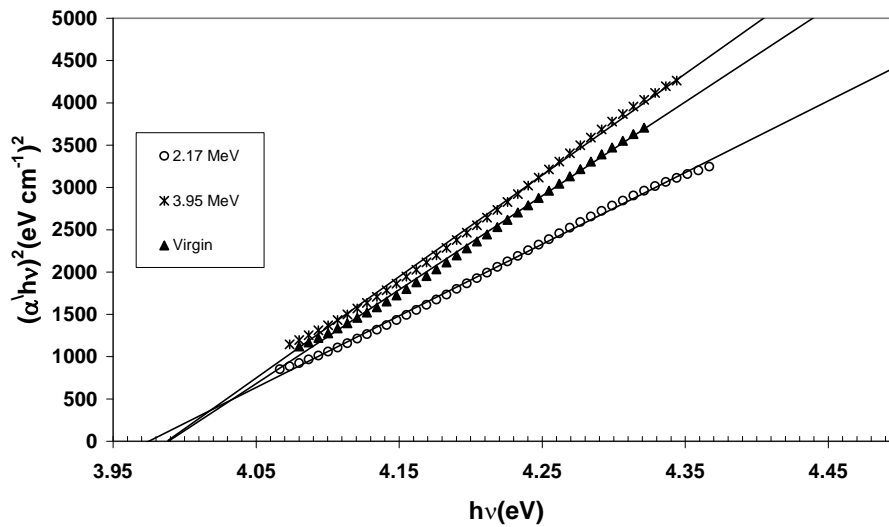


Figure 5 Calculations of the optical energy gap from extrapolation of the fitted lines (—) with $h\nu$ -axis for virgin and irradiated CR-39 samples with alpha-particle energies 2.17 MeV and 3.95 MeV at 3.00 h etching time.

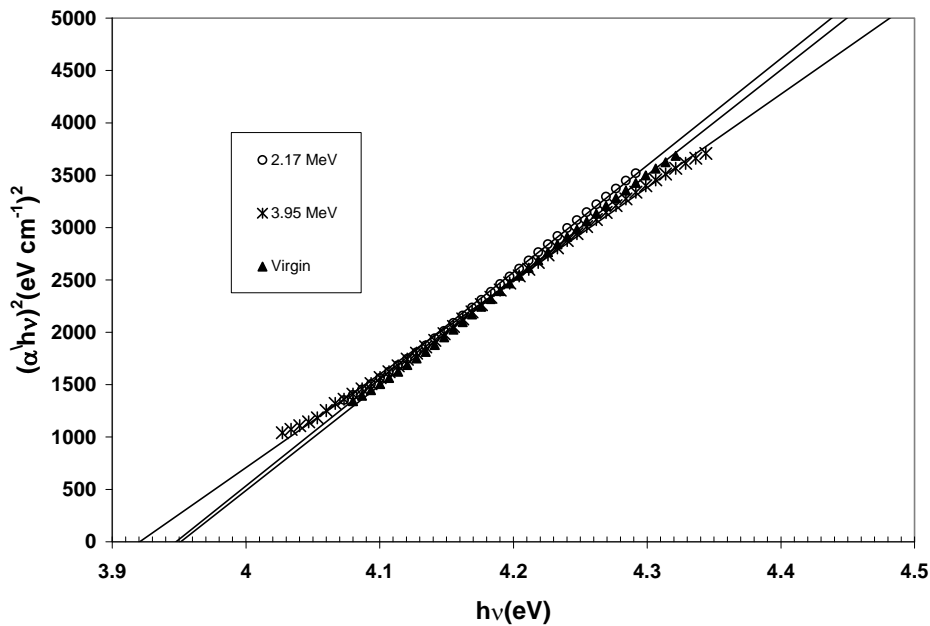


Figure 6 Calculations of the optical energy gap from extrapolation of the fitted lines (—) with $h\nu$ -axis for virgin and irradiated CR-39 samples with alpha-particle energies 2.17 MeV and 3.95 MeV at 6.00 h etching time.

The optical absorption coefficient near the fundamental absorption edge is exponentially dependent on the $(h\nu)$ and obeys the empirical Urbach formula [29];

$$\alpha \approx \alpha_0 \exp (h\nu/E_U) \tag{7}$$

where E_U is the Urbach energy, which corresponds to the width of the band tail of a localized state in the forbidden band gap, and α_0 is a constant. The E_U values can be calculated from the inverse of the slope of the linear part of the curve between $\ln \alpha$ and photon energy [30] as shown in **Figures 7 - 9**. The calculated values of E_U are listed in **Tables 1 - 3**.

The variations of the track diameter and the optical band gap energy for virgin (before and after etching) and irradiated CR-39 samples at different etching times (1.50, 3.00 and 6.00 h) are reported in **Tables 1 - 3**.

The etching times required to cover the whole range of alpha particles with energies 2.17 and 3.95 MeV are 2.14 and 6.77 h, respectively. The values of the etching time were calculated using Eq. 4. The etching time values give information about the reaching or not of the etching solution to the end of the alpha particle range in CR-39. Fleischer's method [31] to calculate the track etch rate was not used because the track length was not measured. Therefore, the V_T -values were calculated from the Track_Test program computer.

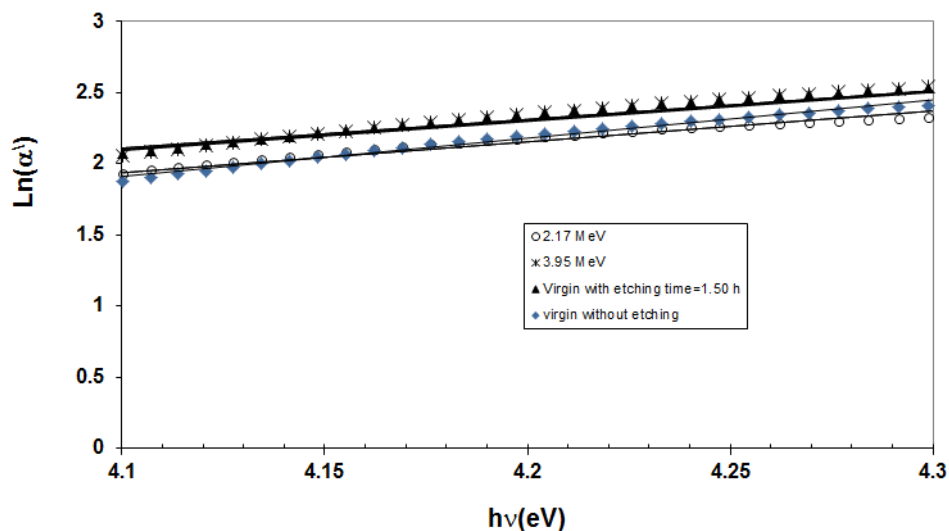


Figure 7 Variation of $\ln \alpha'$ with the photon energy for virgin (before and after etching) and irradiated CR-39 samples with alpha-particle energies 2.17 MeV and 3.95 MeV at etching time 1.50 h.

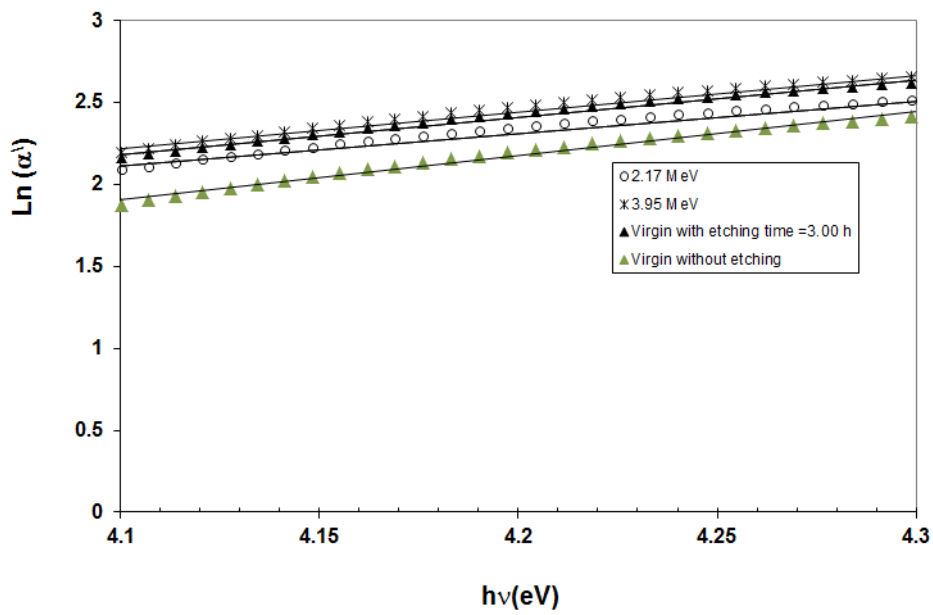


Figure 8 Variation of $\ln \alpha'$ with the photon energy for virgin (before and after etching) and irradiated CR-39 samples with alpha-particle energies 2.17 MeV and 3.95 MeV at etching time 3.00 h.

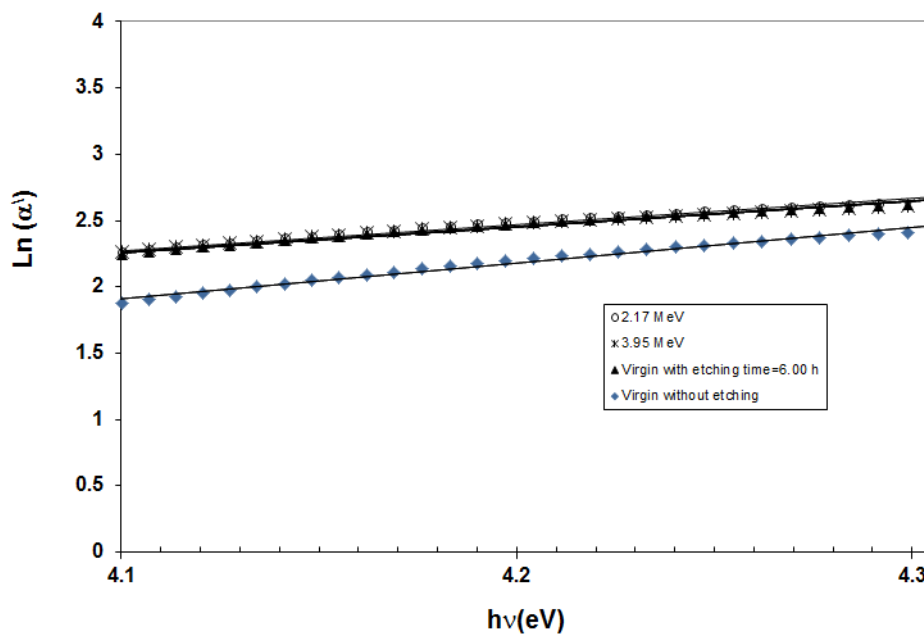


Figure 9 Variation of $\ln \alpha'$ with the photon energy for virgin (before and after etching) and irradiated CR-39 samples with alpha-particle energies 2.17 MeV and 3.95 MeV at etching time 6.00 h.

The value E_g for the virgin sample before etching has the same values after 1.50 and 3.00 h etching times, and greater than its value at 6.00 h etching time. This result reveals that the effect of etching time on the optical properties of CR-39 samples is statistically significant at 6.00 h etching time.

For the sample of energy 2.17 MeV at etching time 1.50 h, the etching time is insufficient to cover the whole range of this alpha energy. Also, the E_g has a relatively small value when compared with virgin and 3.95 MeV samples. This can be interpreted as the electronic stopping power for 2.17 MeV having the largest value (19.68 eV/Å), so the deposition in the alpha particle track will enhance scission in the molecular chains of the CR-39 samples over cross-linking, i.e. the polymer molecules may be broken into small fragments. This result reflects the formation of defects in the CR-39 track etched polymer after 2.17 MeV. Accordingly, the average value of the track diameter is large compared with its value at energy 3.95 MeV.

The E_g values for virgin samples after etching have the same values for 2.17 MeV at 3.00 and 6.00 h, as in **Tables 2** and **3**. The chemical etching has sufficient time to reach the end of the alpha particle path and progresses in all the directions in the bulk of CR-39 with the same rate [14]. This result reflects the similarity in the optical behavior for those samples. Accordingly, it was found that the measured track diameters of this energy at etching time of 3.00 and 6.00 h as in **Tables 1 - 3** are smaller than those predicted by 1.5 h with a fixed ratio of 16 %. The predicted track diameters at 3.00 and 6.00 h were 10.66 and 21.32 μm , respectively.

For the 3.95 MeV samples, the values of E_g at 1.50 and 3.00 h have nearly the same values for virgin samples before and after etching. This result suggests that the CR-39 samples are insensitive to the optical variations in the fundamental absorption edge. The situation at 6.00 h is different (E_g at 3.95 MeV is smaller than that for virgin samples) due to the electronic stopping power [24] having low value (13.63 eV/Å) compared with the value (19.68 eV/Å) at 2.17 MeV. Also, the etching times (1.50 - 6.00 h) were insufficient to cover the whole range of this alpha energy. Therefore, the track diameter values at 1.50 h were consistent with those predicted at higher etching times 3.00 and 6.00 h.

The estimated values of Urbach energies for virgin samples after etching times (1.50 - 6.00 h) are greater than its value before, as in **Tables 1 - 3**. This can be attributed to the etching process having enhanced the diffusion rate of π -electron to the forbidden level of the CR-39 polymer [30]. Also, there are small fluctuations in Urbach energy values for the samples (virgin and irradiated) after the etching times, as displayed in **Tables 1 - 3**. Accordingly, the CR-39 samples before and after etching show a semi-crystalline formation (i.e. a mixture of small crystalline and amorphous states within the material) with dominating amorphous content in it.

Table 1 The variations of the track diameter, electronic stopping power, optical band energy gap and Urbach energy at 1.50 h etching times for different alpha particle energies in CR-39 samples.

E_a (MeV)	The etching times required to cover the whole range of alpha particles (h)	Electronic stopping power (eV/Å)	1.50 h		
			Track diameter (μm)	Optical energy band gap (eV)	Urbach energy (eV)
2.17 ± 0.18	2.14	19.68	5.33 ± 0.25	3.960	0.46
3.95 ± 0.20	6.77	13.52	4.19 ± 0.39	4.007	0.49
Virgin after etching	-	-	-	4.006	0.49
Virgin without etching	-	-	-	4.003	0.37

Table 2 The variations of the track diameter, electronic stopping power, optical band gap energy and Urbach energy at 3.00 h etching times for different alpha particle energies in CR-39 samples.

E_a (MeV)	The etching times required to cover the whole range of alpha particles (h)	Electronic stopping power (eV/Å)	3.00 h		
			Track diameter (μm)	Optical energy band gap (eV)	Urbach energy (eV)
2.17 ± 0.18	2.14	19.68	8.94 ± 0.31	3.980	0.46
3.95 ± 0.20	6.77	13.63	7.21 ± 0.53	3.993	0.44
Virgin after etching	-	-	-	3.994	0.44
Virgin without etching	-	-	-	4.003	0.37

Table 3 The variations of the track diameter, electronic stopping power, optical band gap energy and Urbach energy at 6.00 h etching times for different alpha particle energies in CR-39 samples.

E_a (MeV)	The etching times required to cover the whole range of alpha particles (h)	Electronic stopping power (eV/Å)	6.00 h		
			Track diameter (μm)	Optical energy band gap (eV)	Urbach energy (eV)
2.17 ± 0.18	2.14	19.68	17.82 ± 0.51	3.952	0.50
3.95 ± 0.20	6.77	13.63	16.10 ± 0.70	3.926	0.51
Virgin after etching	-	-	-	3.957	0.52
Virgin without etching	-	-	-	4.003	0.37

Conclusions

The track registration and optical properties of CR-39 track etch polymer irradiated with a fixed fluence of alpha particles at different energies (2.17 MeV and 3.95 MeV) and etching times (1.50 - 6.00 h) were investigated. The electronic stopping power for 2.17 MeV has a fairly large value. Therefore, the optical band gap energy has a small value in comparison with its value at 3.95 MeV at the etching time of 1.50 h, due to the formation of defects in the CR-39 samples. The chemical etching solution for 2.17 MeV samples at 3.00 and 6.00 h has reached the end of the alpha particle path and progresses in all the directions in CR-39 with the same rate. Accordingly, virgin samples and the samples at 3.00 and 6.00 h have the same values of the optical energy band gap and the track diameters are smaller than those predicted by 1.5 h with fixed ratio of 16 %. The E_g for 3.95 MeV samples has nearly the same values of virgin samples at 1.50 and 3.00 h etching times. This result suggested that the CR-39 samples at 3.00 h are insensitive to the optical variations in the fundamental absorption edge, i.e. optically stable. The Urbach energy behavior showed that the CR-39 samples before and after etching times show a semi-crystalline formation with dominating amorphous content on it.

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