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Effect of UV and gamma rays on bulk etching of the Pokalon track detector

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Abstract: Solid-state nuclear track detectors (SSNTDs) find applications in many fields of science and technology. Polycarbonates like CR-39 or Lexan are most widely used for such applications. Pokalon is a relatively new member of the polycarbonate family of SSNTDs. It has the same monomer as that of Makrofol. In the present work we have studied the bulk etching characteristics of Pokalon at different temperatures and normalities of NaOH etchant with and without magnetic stirring. The effect of UV and gamma irradiation on the bulk etch rate has also been studied. From the bulk etch rate values at different temperatures, we have determined the corresponding activation energies. Measurable enhancement of the bulk etch rates with accompanying reduction in the activation energies following UV and gamma irradiation suggests chain scission and bond breaking as possible mechanisms for these changes in the etching characteristics.

Key words: Solid-state nuclear track detectors, Pokalon, chemical etching, bulk etch rate, UV, gamma irradiation

1. Introduction

Solid-state nuclear track detectors (SSNTDs) have found applications in several diverse branches of science and technology [1]. Pokalon is a relatively new entrant in the field of SSNTDs. It is an advanced version of Makrofol, originally introduced by Bayer Films Americas (Berlin, Germany), the production of which has recently been discontinued by the firm [2]. The monomer repeat unit of Pokalon is $C_{16}H_{14}O_3$. Thin films of Pokalon are presently marketed by LOFO High Tech Films (Germany). Not many reports exist in the literature on the etching characteristics of the detector. We have come across only one reported work by Sertova et al. [3] on the etching characteristics of Pokalon, wherein they quote values of 0.372 μm/h and 0.084 μm/h for the bulk etch rates at 60 °C and 40 °C, respectively, for 5 N NaOH. In view of this scarcity of reported data, we have attempted in the present work an investigation of the bulk etching characteristics of the Pokalon track detector.

Recently a new application of etched ion track detectors has emerged, wherein such etched track detectors can be used as templates for the fabrication of nanowires [4–6]. For such applications, etched track detectors with nanosized pores extending throughout the thickness of the detector are needed. In order to realize this in practice, the ratio of the track etch rate V_t and the bulk etch rate V_b has to be large.

Earlier studies on UV and gamma irradiated CR-39 track detectors [7] and Lexan and Makrofol detectors [8–11] showed that such irradiations tend to enhance the bulk and track etch rates as well as the etch rate ratio. This observed effect has been ascribed to breaking of the bonds (scission) in the polymer chain. These scissions reduce the average molecular weight and, as a result, increase the rate of chemical attack. Consequently, a

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corresponding decrease occurs in the energy needed for activating the chemical reaction responsible for the etching (the so-called activation energy).

Schiedt [12] carried out extensive studies on the effect of UV irradiation on the pore size and pore size distributions in Makrofol and Pokalon detectors. He observed no significant influence of the UV irradiation on the pore size. However, the results showed that UV irradiation has a very beneficial effect on the pore size distribution in both materials, the effect being more pronounced in Pokalon than Makrofol. Apart from this single report, similar studies on bulk etching characteristics are scarce in the case of the Pokalon detector. To this end, we have also investigated in the present work the effect of UV and gamma radiations on the bulk etch rate in Pokalon. Details of the experimental setup, the procedure, and the results obtained are described in this paper.

2. Materials and methods

A temperature-controlled (± 0.5 °C) water bath was used for chemical etching of the Pokalon track detector films. We used a Teflon-coated magnetic stirrer to ensure uniform heating of the etchant as well as speedy removal of the etched out material from the detector surfaces [13]. A platinum wire sensor was placed inside the water bath for real-time monitoring of the temperature. Pokalon pieces of dimensions 2.5 $\times$ 2.5 cm^2 and thickness 20 μm, procured from LOFO, Germany, were used in the experiments. We used aqueous solutions of AnalaR-grade sodium hydroxide with 5 N and 6 N normalities for chemical etching of the Pokalon samples. The masses of the samples were measured with a sensitive electronic balance both before and after etching. The bulk etch rate was calculated from the mass difference (ΔM) and the time of etching (t) using the following equation:

$$V_b = \left(\frac{\Delta M}{M}\right)\left(\frac{x}{2t}\right), \tag{1}$$

where M is the original mass of the track detector sheet of thickness x. The factor of 2 in the denominator is inserted to take into account the fact that the etching proceeds on both surfaces of the detector.

The effect of magnetic stirring on the measured bulk etch rates was studied by repeating the measurements after switching off the stirrer control.

Bulk etch rate measurements were carried out at four different temperatures of 29 $^{\circ}C$ (room temperature), 50 $^{\circ}C$, 60 $^{\circ}C$, and 70 $^{\circ}C$. In each case we have extracted the activation energies for bulk etching using these data and employing a linear least squares fit. The calculation is based on the Arrhenius-type relation between the bulk etch rate V_b and the etching temperature T (K):

$$V_b = V_0 exp\left(\frac{-E_a}{kT}\right). \tag{2}$$

Here E_a is the activation energy for bulk etching and k is the Boltzmann constant. Thus, a plot of $ln\,(V_b)$ vs. $(kT)^{-1}$ would yield a straight line with a negative slope equal to the activation energy.

The results are presented in the next section. The errors in the quoted values arise mainly from the mass measurements and typically amount to 6%. The bulk etch rate was also measured for Pokalon samples after irradiation with UV and gamma rays. UV irradiation was carried out using an 18-W Phillips fluorescence lamp (wavelength range: 310–360 nm) for intervals of 6 h, 12 h, and 18 h in duration. Gamma irradiation was done using bremsstrahlung radiation generated using a 15-MV electron linear accelerator at the KIMS Hospital,

Thiruvananthapuram. Total doses used were 20 Gy, 50 Gy, 100 Gy, and 150 Gy. The corresponding activation energies were also determined in each case.

The transmission spectra in the UV and visible regions were recorded for the irradiated specimens using a SYSTRONICS UV-VIS spectrophotometer with an unirradiated specimen as the reference.

3. Results

The bulk etch rate values obtained with and without magnetic stirring are given in Table 1. Table 2 gives the bulk etch rate values for the Pokalon samples at different temperatures. Similar results for the irradiated samples are presented in Table 3.

Table 1. Bulk etch rates with and without magnetic stirring.

Normality	Temperature (K)	Bulk etch rate (μm/h)	
		Without stirring	With stirring
5 N	333	0.411 ± 0.025	0.490 ± 0.027
	343	0.849 ± 0.050	1.002 ± 0.065
6 N	333	0.609 ± 0.041	0.625 ± 0.043
	343	1.141 ± 0.067	1.321 ± 0.071

Table 2. Bulk etch rates for the unirradiated Pokalon samples at different temperatures (6 N NaOH).

Temperature (K)	Bulk etch rate (μm/h)
302	0.023 ± 0.002
323	0.222 ± 0.013
333	0.398 ± 0.024
343	0.776 ± 0.032

Table 3. Bulk etch rates for gamma and UV irradiated Pokalon samples (typical uncertainties: ±6%).

Temperature (K)	Bulk etch rate (μm/h)						
	UV irradiated			Gamma irradiated			
	6 h	12 h	18 h	20 Gy	50 Gy	100 Gy	150 Gy
302	0.024	0.027	0.032	0.023	0.025	0.028	0.029
333	0.425	0.447	0.472	0.403	0.417	0.436	0.462
343	0.867	0.889	0.913	0.822	0.850	0.873	0.894

The activation energies for bulk etching for the irradiated as well as UV and gamma irradiated Pokalon samples obtained in the present work are compared in Table 4.

The UV-visible transmission spectra for the gamma irradiated samples are shown in Figure 1. It is seen that the transmission is enhanced as the total gamma dose is increased from 20 Gy to 150 Gy. A similar behavior has also been observed for the UV irradiated samples.

In Figure 2, the average transmittances in the UV and visible regions have been plotted versus the corresponding activation energies for Pokalon. The plot shows a definite correlation.

Table 4. Activation energies for the Pokalon samples at different temperatures (6 N NaOH).

Sample details	Activation energy (eV)
Unirradiated	0.777 ± 0.040
UV - 6 h	0.745 ± 0.035
UV - 12 h	0.723 ± 0.034
UV - 18 h	0.698 ± 0.032
Gamma - 20 Gy	0.760 ± 0.038
Gamma - 50 Gy	0.754 ± 0.036
Gamma - 100 Gy	0.738 ± 0.034
Gamma - 150 Gy	0.715 ± 0.033

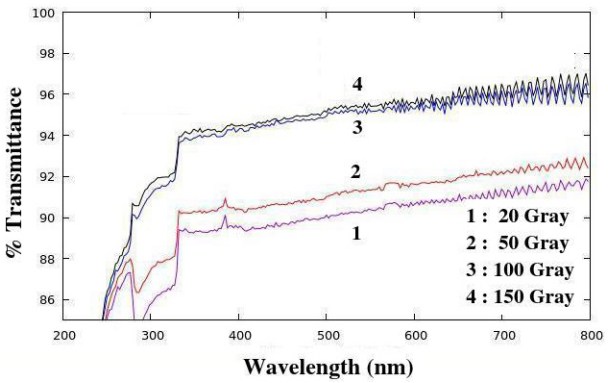

Figure 1. UV-Vis transmission spectra of the gamma irradiated specimens.

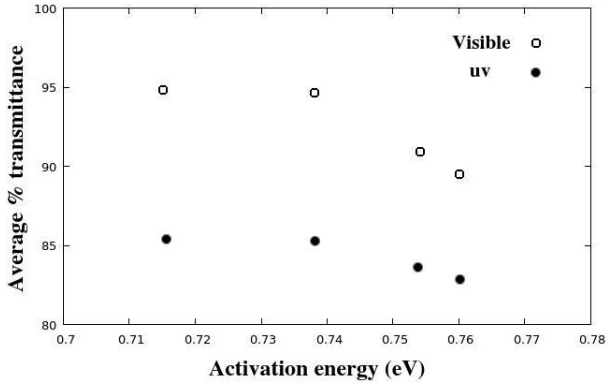

Figure 2. Average transmittance vs. activation energy for Pokalon.

4. Discussion

A comparison of the bulk etch rate values obtained with and without magnetic stirring shows that stirring definitely enhances the bulk etch rate. The effect is seen to be more pronounced for the lower normality (5 N) of the etchant at both etching temperatures. At 6 N normality, subject to the uncertainties in the measurement, the effect of stirring may be less prominent at the lower temperature as compared to the higher one. The results clearly indicate that the effect of temperature on the etching rate is more pronounced than that of stirring. Similar stirring-aided enhancements of etch rates were obtained earlier in the case of LR-115 [14]. A straightforward explanation of this enhancement is the speedy removal of the etched detector material, which may otherwise stay close to the surface of the detector, thereby partially blocking the proximity of the etchant to the surface of the detector.

It is seen from the results quoted above for UV and gamma irradiated track detectors that the irradiations lead to an enhancement in the bulk etch rate of the Pokalon detector samples, as is the case for other polycarbonates. There is also a reduction in the corresponding activation energies as a result of irradiation by either UV or gamma rays. This effect can be attributed to chain scission of the carbonate linkage of the polymeric molecules, since weakening of the chemical linkage leads to an enhancement of the rate of the chemical reaction and thereby to a lowered activation energy. There is a subsequent reduction in absorption (or equivalently an enhancement in the transmittance) of the incident UV or visible radiations in the UV-Vis spectra. The correlation between the activation energies and the UV and visible transmittances of the gamma irradiated Pokalon detector corroborates this explanation.

5. Conclusions

We have measured the bulk etch rates of the Pokalon track detector under various conditions of temperature, etchant concentration, stirring of the etchant, and irradiation of the track detector with UV and gamma radiations. We have also calculated activation energies for bulk etching. Enhancement of the bulk etch rates following UV and gamma irradiations has been observed. We also observed a correlated reduction in the UV-visible absorption. These effects can be ascribed to chain scission of the polymeric molecules.

As noted in the introduction, an enhancement of the etch rate ratio following irradiation will be desirable from the point of view of the use of the etched track detector as a template for nanowire fabrication. This necessitates more detailed investigations with regard to the effect of irradiations on the track etch rate of Pokalon.

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References

[1] Fleischer, R. L.; Price, P. B.; Walker, R. M. *Nuclear Tracks in Solids: Principles and Applications*; University of California Press: Berkeley, CA, USA, 1975.

[2] L'Annunziata, M. F. *Handbook of Radioactivity Analysis*, *3rd edition*; Elsevier: Amsterdam, the Netherlands, 2012.

[3] Sertova, N.; Balanzat, E.; Toulemonde, M.; Trautmann, C. *Nucl. Instrum. Meth. B* **2009**, *267*, 1039-1044.

[4] Toimil Molares, E. M.; Brotz, J.; Buschmann, V., Dobrev, D.; Neumann, R.; Scholz, R.; Schuchert, I. U.; Trautmann, C.; Vetter, J. *Nucl. Instrum. Meth. B* **2001**, *185*, 192-197.

[5] Toimil Molares, E. M.; Hohberger, E. M.; Schaeein, C.; Blick, R. H.; Neumann, R.; Trautmann, C. *Appl. Phys. Lett.* **2003**, *82*, 2139-2141.

[6] Chakarvarti S. K.; Vetter, J. *Radiat. Meas.* **1998**, *29*, 149-159.

[7] Abdel-Haliem, A.; Seddik, U.; El-Aasser, M. R.; Rizk, R. A.; Abdel-Mongy, A. A.; Salama, T. A. In *Proceedings of* the *3rd Conference on Nuclear and Particle Physics*; Cairo, Egypt, 2001, pp. 349-355.

[8] Singh S.; Pasher S. *Radiat. Eff. Defect. S.* **2004**, *159*, 359-367.

[9] Singh S.; Pasher S. *Radiat. Meas.* **2004**, *40*, 50-54.

[10] Neerja; Singh S.; Pasher S. *Radiat. Meas.* **2007**, *42*, 135-137.

[11] Kumar, A.; Jain, R. K.; Yadav, P.; Chakraborty, R. N.; Singh, B. K.; Nayak, B. K. *J. Radioan. Nucl. Ch.* **2013**, *295*, 95-98.

[12] Schiedt, B. PhD, Ruperto-Carola University of Heidelberg, Heidelberg, Germany 2007.

[13] Chan, K. F.; Ng, F. M. F.; Nikezic, D.; Yu, K. N. *Nucl. Instrum. Meth. B* **2007**, *263*, 284-289.

[14] Yip, C. W. Y.; Ho, J. P. Y.; Koo, V. S. Y.; Nikezic D.; Yu, K. N. *Radiat. Meas.* **2003**, *37*, 197-200.