Development of Etching Process for Enlargement of Particle Damaged Nuclear Tracks on Polystyrene Film

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Abstract: In this study nuclear track forming property of Polystyrene film was investigated. Conventionally 6N NaOH is used to etch the particle tracks and to enlarge them. Since the chemical structure and bond energy of every polymer is different, the broken fragments and particle damaged portions of different polymer can not be properly etched by one type of etching solutions. As the organic polymers react differently with different solvent, for every SSNTD material etching solutions should be different to achieve an optimum etching condition. We have composed different etching compositions with different polarities and studied the etched nuclear tracks. We have found that different numbers of nuclear tracks were formed with different etching compositions. The bulk etch rate of Polystyrene is found to be very low as compared with the track etch rate. This fact allows the polymer to be etched for a long period of time unlike many conventional SSNTD polymers.

Key words: Polystyrene film, etching compositions, SSNTD polymers.

Introduction

Massive positively charged energetic nuclei that traverse insulating solids, produce narrow trails of radiation damaged material called latent track. This is not visible with the naked eye. This is visible by looking at a thin slice of the solid at high magnification with an electron microscope. Because of their unique characteristics solid state nuclear track detectors (SSNTDs) have made possible a number of experiments in nuclear physics and are now widely used in laboratories through out the world. The exact changes in physical and chemical properties of damaged region depend very strongly on the particle charge and speed, or the chemical structure of the detector material, the physical state of the material during irradiation and environmental conditions particularly the temperature and atmosphere. [1-12]

Solid state nuclear track detectors have unique capabilities for measuring the concentration and spatial distribution of certain radioactive elements. This area of research began with the measurement of uranium via the detection of fission fragments in samples irradiated with thermal neutrons [4]. Now a days energetic heavy particle emitting radioactivity can be easily determined by the formation of nuclear tracks [5,6] which are easily observed on a solid start nuclear track detector material such as organic polymer with suitable etching. In the present study we have exposed solid state polymer Polystyrene

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to alpha radiation and studied the optimum track developing properties under different etching variables.

Basics of SSNTD technique

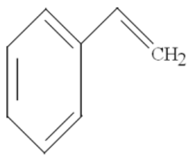
Solid-state nuclear track detector (SSNTD) technique is based on the fact that a heavy charged particle will cause extensive ionization of the material when it passes through a medium. For example, an alpha particle with energy of 6 MeV creates about 150,000 of ion pairs in cellulose nitrate. Since the range of a 6 MeValpha particle in this material is only about 40 mm that means on average 3700 ion pairs are created per micrometer, or 3–4 ion pairs per nanometer. An alpha particle ionizes almost all molecules close to its path. This primary ionizing process triggers a series of new chemical processes that result in the creation of free radicals and other chemical species. Along the path of the alpha particle, a zone enriched with free radicals and other chemical species is then created. This damaged zone is called a latent track. If a piece of material containing latent tracks is exposed to some chemically aggressive solution, chemical reactions would be more intensive along the latent tracks. Aqueous solutions of NaOH or KOH are the most frequently used chemical solutions in this regard. The overall effect is that the chemical solution etches the surface of the detector material, but with a faster rate in the damaged region. In this way, a ‘‘track’’ of the particle is formed, which may be seen under an optical microscope. This procedure is called ‘‘detector etching’’ or track visualization, and the effect itself is called the ‘‘track effect’’. The track effect exists in many materials. It is particularly pronounced in materials with long molecules, e.g., cellulose nitrates or different polycarbonates, and such materials are the most convenient ones for application and detector manufacturing. The effect is also seen in some amorphous materials like glasses, etc. However, only dielectric materials show the track effect. In conductive materials and in semiconductors, the process of recombination occurs and the latent tracks are not stable.[1-14]

Detector Material

Polystyrene

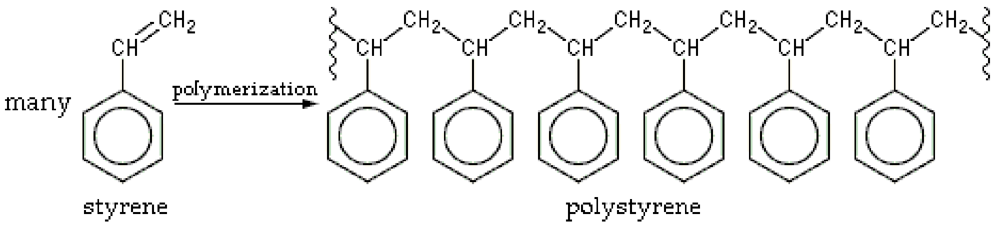
Polystyrene, abbreviated PS, $(C_8H_8)_n$ is an aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. Polystyrene is one of the most widely used plastic. Polystyrene is a thermoplastic substance, normally existing in solid state at room temperature, but melting if heated (for molding or extrusion), and becoming solid again when cooling off. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. It can be cast into molds with fine detail. Polystyrene can be transparent or can be made to take on various colors.The chemical makeup of polystyrene is a long chain hydrocarbon with every other carbon connected to a phenyl group (the name given to the aromatic ring benzene, when bonded to complex carbon substituents). It is an aromatic hydrocarbon and burns with an orange-yellow flame, giving off soot, as opposed to non-aromatic hydrocarbon polymers such as polyethylene, which burn with a light yellow flame (often with a blue tinge) and no soot. Complete oxidation of polystyrene produces only carbon dioxide and water vapor. [15,16,17].

Monomer:



Styrene

Polymer:



It is know [27] that organic solvent with alkaline solution mixture yields more track with the reduction of etching time, we have prepared three new etching solutions judging the polarities and dielectric constant of different organic solvents which are 10% acetone : 10% DMF : 6N NaOH, 10% isopropyl alcohol : 10% EtOH: 3N KOH and 25% triethanolamine : 3N NaOH solution . In total we have used five different etching solutions and they are :

a) 10% acetone : 10% DMF : 6N NaOH
b) 10% isopropyl alcohol : 10% EtOH: 3N KOH
c) 25% triethanolamine : 3N NaOH
d) 6N NaOH
e) 6N KOH

Radiation exposure of Polystyrene (PS) film

The chamber with detector configuration consisted of an open mount insulating container, 8 cm in height and 7 cm in diameter. The middle portion of the chamber was covered with a semi permeable polyethylene membrane. The membrane slows down the normal diffusion of Nobel gases into the chamber and thus discriminates in favor of radon against thoron. This configuration is generally used in the exploration to eliminate the thoron interference and water condensation. This configuration also prevents the entrance of radon daughter and is a radon only device. This detector configuration was calibrated in laboratory and used for radon measurement.

Polystyrene (PS) film of 1 cm x 1cm was hung from the bottom of the cap inside the chamber at ~6 cm above the standard solution level. The containers were filled with 5 ml of standard solution. The detectors were exposed at 714.653 Bq/ M^3 standardize radon activity obtained by standard radium nitrate solution. The containers were closed and were made airtight. As a result, the detectors are exposed only to radon. One side of each detector was covered so that only one side of the detector was exposed to radon. All of these exposures were done in airtight environment for thirty days free from any disturbance. After the exposure all of the detectors are taken out and washed with distilled water for several times. After washing the detectors were dried in room temperature and

After exposure of the plastic detectors for desired period of time the one set of detectors were etched at temperature of $60^o \pm 1^o$ C for two hours and temperature of $70° \pm 1^o$ C for four hours with 25% triethanolamine: 3N NaOH, 6N NaOH and 6N KOH etching solutions. To achieve a temperature near of 60 ^{o} and 70°C, a constant temperature water bath was used. Since the organic solvents has a very low boiling point , other set of detectors were etched at temperature of $40^o \pm 1^o$ C for two hours and temperature of $50° \pm 1^o$ C for four hours with 10% acetone : 10% DMF : 6N NaOH and 10% isopropyl alcohol : 10% EtOH: 3N KOH etching solutions.[21,22]

After etching of precise hours, detectors were picked out from the beakers and dropped in cold water, held under the flow from top with the help of a forceps for two or three minutes. After this, detectors were finally washed in distilled water soaked by tissue paper, dried in air and then kept wrapped in tissue paper for subsequent study under a microscope. Similar procedures of etching and identical etching conditions were adopted for all the detectors. Particular care was taken to keep the concentration of the solution, the temperature and the period of time identical for all occasions. After etching the detectors scanned under an optical microscope.

Counting charts were prepared in which there were blocks recorded with number of counts. The count of each field of view was recorded and after completion of scanning of a detector the counts were added. The total count divided by the number of blocks gave the average number of alpha track etch pits per area of the field of view. Using the actual area of field of view the number of tracks per cm^2 was calculated. [6, 8, 10]

The mathematical expression of track density could be given by:

$$\rho_T = \frac{\sum_{L}^{n} N_i}{\sum n \times A} \tag{1}$$

Where ρ_T = Track density or tracks per cm^2

$\sum_{L}^{n} N_i$ = Total number of tracks.

$\sum n$ = Total number of fields counted.

A = Area of one field.

The count on the detector should follow the Poisson distribution. Thus the probability 'P' of getting a certain result N when the true value is m would be,

$$P(N:m) = \frac{e^{-m}m^{N}}{N!} \tag{2}$$

where, variance, σ^2, is defined as such that 68.3% of the measurement results fall within $\pm\,\sigma$ of the true value m and for Poisson distribution, σ^2 = m as follows:

$$\text{Uncertainty} = \sqrt{\frac{\text{Tracks / field of view}}{\text{Area of the field of view}}}$$

$$\text{Uncertainty} = \sqrt{\frac{\text{Tracks}}{\text{cm}^2}} \tag{3}$$

After the background correction, the corrected track density was recorded and analyzed. Growth of alpha tracks formed by organic solvent based etching system and conventional etching solution are shown in figure (1), figure (2) and figure (3).

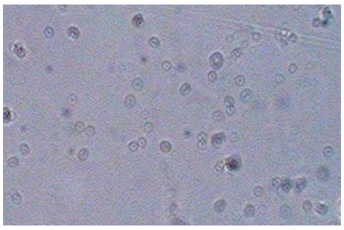


Fig. 1: *10% isopropyl alcohol : 10% EtOH: 3N KOH etching system*

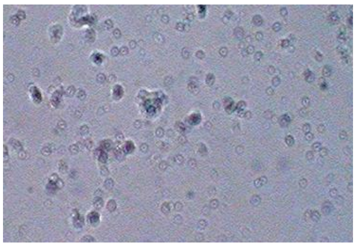


Fig. 2: *25% triethanolamine: 3N NaOH etching system*

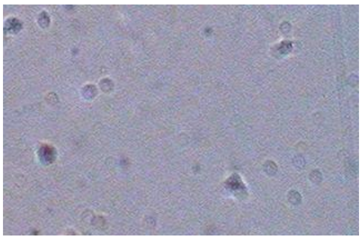


Fig. 3: *6N NaOH etching system*

Analysis of result

Tracks in each exposed detectors were counted for known areas. Using the number of tracks per field of view, track density was calculated for all the detectors. Then background correction was performed. For each etching condition separate blank test was performed .The corrected track density per field of view and track density per cm^2 (T/ cm^2) under various etching solutions and etching conditions are given in table 1 and Table 2.

Table 1: *Two Hours etching condition*

Total number of detectors.	Etching solution.	Etching temperature. ^oC	Track Density. (T/ cm^2).
10	10% acetone : 10% DMF : 6N NaOH	40^o±1^o	2070±44
10	10% isopropyl alcohol : 10% EtOH: 3N KOH	40^o±1^o	6369±80
10	25% triethanolamine : 3N NaOH	60^o±1^o	7564±87
10	6N NaOH	60^o±1^o	3105±55
10	6N KOH	60^o±1^o	3822±61

Table 2: *Four Hours etching condition*

Total number of detectors.	Etching solution.	Etching temperature. ^oC	Track Density. (T/ cm^2).
10	10% acetone : 10% DMF : 6N NaOH	50^o±1^o	19028±137
10	10% isopropyl alcohol : 10% EtOH: 3N KOH	50^o±1^o	28503±168
10	25% triethanolamine : 3N NaOH	70^o±1^o	32803±181
10	6N NaOH	70^o±1^o	17834±133
10	6N KOH	70^o±1^o	12739±113

At two hours etching time with 40^o C temperature the highest track density recorded for Polystyrene is 7564±87 (T/ cm^2) 7166±85 by 25% triethanolamine : 3N NaOH with better visibility and linearity. At the same condition the lowest track density was found 2070±44 (T/ cm^2) by 10% acetone : 10% DMF : 6N NaOH with 40^o±1^o C etching temperature. The etching solution 6N NaOH at 60^o±1^o C yielded 3105±55 (T/ cm^2) nuclear tracks.

On the other hand at four hours etching time with 70^o±1^o C temperature the highest track density was achieved by 25% triethanolamine: 3N NaOH etching solution and the track density was recorded as 32803±181 (T/ cm^2). This etching system yielded clearer and larger tracks even greater in diameter than the conventional 6N NaOH etching solution. At 4 hour etching time the lowest track density was obtained 6N KOH etching system and the tracks were recorded as 12739±113 (T/ cm^2). Another etching solution 10% isopropyl alcohol: 10% EtOH: 3N KOH yielded non linear but isolated clear tracks on this polymer. From present study of alpha tracks it is observed that for different etching solution the growth rate of nuclear tracks are different. We have also observed that the addition of organic solvents have great effect in track development. Since the detector material is organic, the organic solvents enhances the power of etching solution which gives better number of tracks with better visibility and linearity . It is also found that the optimum temperature is also depended and varies with the etching solution. Different etching solutions works better in different etching temperature. As for polystyrene the optimum etching solution is found to 25% triethanolamine: 3N NaOH with 4 hour of etching time and 50^oC temperature. Other organic solvent based etching solutions including inorganic 6N KOH also can be used with there respective temperature and etching time. One thing is observed from this study is that all organic solvent based etching solution yielded more tracks than conventional 6N NaOH solution. This phenomenon clearly shows that the etching of radiation damaged portion of the organic detector is greatly affected by the polarity of the solvent as we have etched the detectors with etching solution of different polarities.

Analysis of track development

The track is formed as a three-dimensional structure. The cross-section of the post-etch surface I′ and the cone is a circle with a diameter D, i.e., the radius of the track opening. If t is the etching time then the track depth is given by:

$$L = (V_t - V_b)\, t \tag{4}$$

Here V_b is bulk etch rate and V_t is the track etch rate.

We know

$$\sin^2\delta + \cos^2\delta = 1$$

Or, $$\cos^2\delta = 1 - \sin^2\delta$$

Or, $$\cos\delta = \sqrt{1-\sin^2\delta}$$

Or, $$\cos\delta = \sqrt{1-\frac{V_b^2}{V_t^2}}$$

Or, $$\cos\delta = \sqrt{\frac{V_t^2 - V_b^2}{V_t^2}}$$

Therefore, $$\tan\delta = \frac{\sin\delta}{\cos\delta} = \frac{\frac{V_b}{V_t}}{\sqrt{\frac{V_t^2 - V_b^2}{V_t^2}}}$$

$$\tan\delta = \frac{V_b}{\sqrt{V_t^2 - V_b^2}}$$

We know,

$$\tan\delta = \frac{D/2}{L} = \frac{h}{\sqrt{L'^2 - h^2}} \quad (5)$$

and by combining the equations (4) and (6), the diameter of the track opening can be obtained as

$$D = 2h\sqrt{\frac{V-1}{V+1}} \quad (6)$$

Here,

$$V = \frac{V_t}{V_b}$$

If V is very very greater then 4, equations (6) becomes

$$D \cong 2h$$

If the track etch rate is very large, which is the case when heavy ions or fission products are used for the irradiation, the removed layer would be directly related to the track-opening diameter which is easily measurable.

Conclusion

In order to study the nuclear tracks formed in organic polymer polystyrene we have used solid state nuclear track detector technique. We have compared the nuclear tracks formed in this polymer with different etching solutions and other etching variables. The conventional etching solutions yielded tracks in poly styrene film but organic solvent based etching solution 25% triethanolamine: 3N NaOH yielded more tracks. From our present study it is observed that at higher temperature with more etching time, more nuclear tracks are formed. But with a suitable etching solution for a particular polymer, temperature and time could be reduced. The conventional 6N NaOH and 6N KOH solution yielded nuclear tracks in polystyrene film but it seems that both of them developed tracks with better visibility with organic solvent and alkali mixture. 25% triethanolamine: 3N NaOH etching system contains organic base triethanolamine. This etching solution yielded clear tracks on polystyrene, but fewer in number at lower temperature. As we have studied the nuclear track forming property of Poly(methyl 2-

methylpropenoate) with various etching solution, we have found the results are satisfactory compared to the conventional SSNTD allyl diglycol carbonate film. With suitable etching solution such 25% triethanolamin: 3N NaOH polystyrene film seems to be sensitive in developing radiation damaged nuclear tracks.

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