Scanning electron microscopy of nuclear pore filters in poly(ethylene terephthalate) and ethylene–tetrafluoroethylene copolymer

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The interior of nuclear pore filters was observed by high resolution scanning electron microscopy. In poly(ethylene terephthalate) the interior of the hole with nodules of some widths was observed and the tapering angle observed from the cross section of the hole agreed with that calculated from the ratio of etching rates. In ethylene–tetrafluoroethylene copolymer the holes lie among the fibrils. Only ~40% fission fragments penetrated and the residual remained in the 12 μm thick film from the observation of cross section of holes and from measurement of radioactive distribution of incident nuclides in the film. In either film the irregular surface was assumed to be induced by the difference of etching between the amorphous and the crystalline regions.

Keywords Scanning electron microscopy; nuclear porefiller; poly(ethylene terephthalate); ethylene–tetrafluoroethylene copolymer; fission fragments; chemical etching

INTRODUCTION

The fundamental research of nuclear tracks in polymer by chemical etching has recently increased and the applications have broadened progressively[1]. However, there are few reports of the etched holes themselves using electron microscopy[2-6]. Optical microscopic studies on nuclear tracks have insufficient resolution, while electron microscopic studies are not always convenient for polymers.

As an application of nuclear track etching, there is the preparation of porous membrane of polymer as 'Nuclepore' made of polycarbonate. The authors prepared the porous membrane of poly(ethylene terephthalate) and polyfluoro plastics with chemical resistivity. The appropriate hole density and the hole size for the films, poly(ethylene terephthalate)[6,9], poly(vinylidene fluoride)[7], and ethylene–tetrafluoroethylene copolymer[8], were determined by the irradiation condition of fission fragments and chemical etching, respectively.

This report summarizes the scanning electron microscope observations on the structure of etched tracks for poly(ethylene terephthalate) and ethylene–tetrafluoroethylene copolymer films. The reaction between the etchant and the films is discussed with the morphology of polymers. The difference in the penetrating ratio of fission fragments is determined from the cross section of penetrating hole and the residual radioactivity of the heavier nuclides.

EXPERIMENTAL

Samples used in the experiments were poly(ethylene terephthalate) (PET) (Daiya Foil, Mitsubishi Plastics Ind. Co. Ltd.) and ethylene–tetrafluoroethylene copolymer (ETFE) (Asahi Glass Co., Ltd.) films. The PET is a conventional biaxially stretched film, 9 μm in thickness, 1.4 g cm^{-3} in density, and 260°C in melting point. The ETFE is slightly monoaxially oriented film, 12 μm in thickness, 1.75 g cm^{-3} in density, about 60% in crystallinity, and 270°C in melting point.

The films were irradiated by fission fragments obtained from the thermal neutron fission of ^{235}U in a nuclear reactor. A natural uranium layer 1000 Å thick, deposited on an aluminium foil, was used as a source of fission fragments. The irradiated films were etched in 3 N NaOH solution at 45°C for PET and in 12 N NaOH solution at 125°C for ETFE. The experimental details were presented in the previous papers[6-8].

Electron micrographs were taken with scanning electron microscopes (JSM-U3 and JFSM-30, JEOL, Japan). The JFSM-30 is a high resolution scanning electron microscope using field emission source. The cross sections of films were taken by cracking the film using a knife in liquid nitrogen. An Au or Au–Pd alloy was deposited on the specimens in a vacuum evaporator.

The residual radioactivity in the film bombarded by fission fragments of about 10^{10} particles was measured after 5 days cooling using a 4096 multichannel pulse height analyser, Canberra, with a high pure Ge

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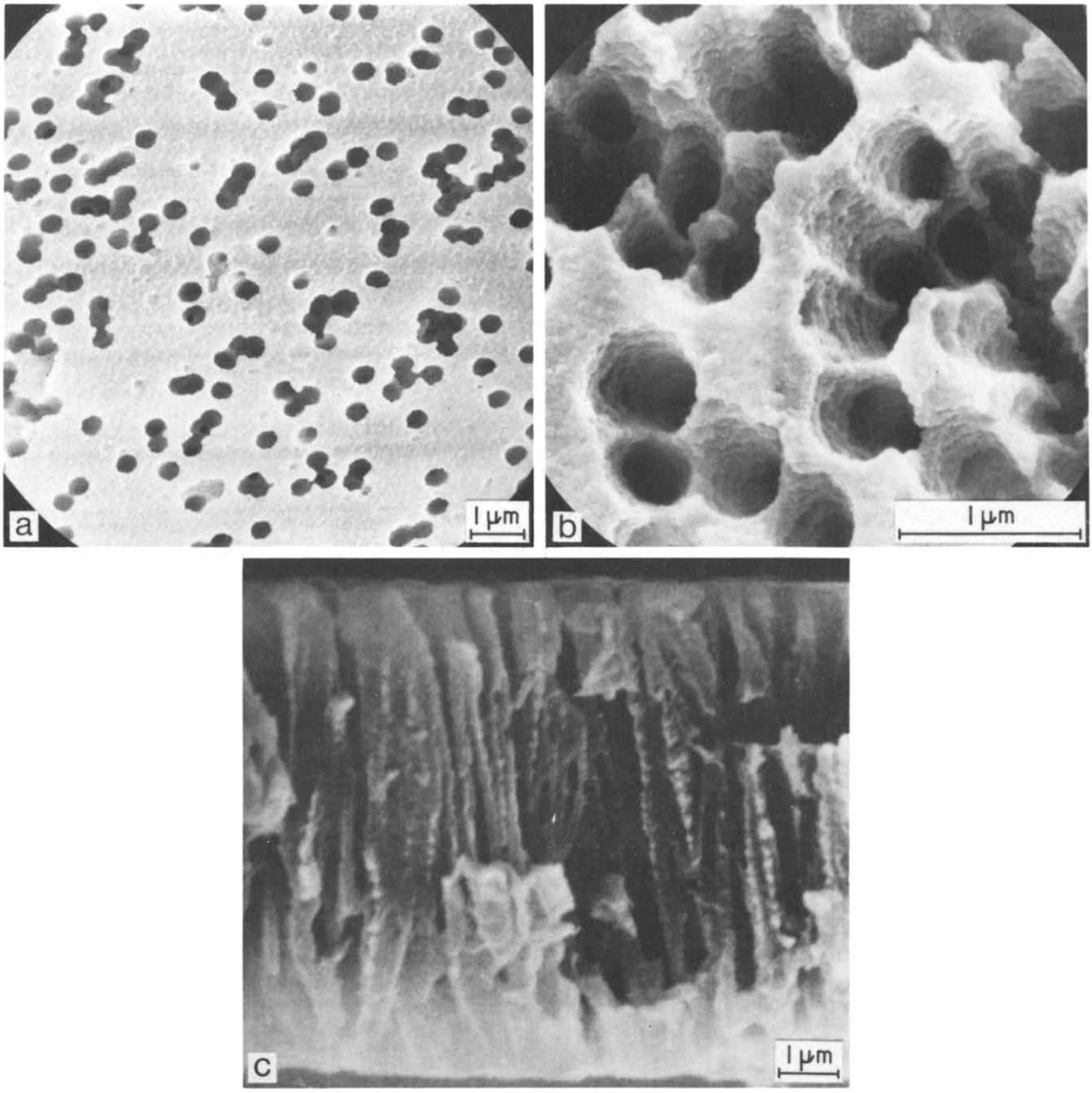

Figure 1 The scanning electron micrographs of poly(ethylene terephthalate) pore filter produced by etching in 3 N NaOH solution at 45°C after bombardment of fission fragments. (a) The feature of the top surface of the film etched for 1 h. (b) A field emission scanning electron micrograph of the top surface of the film. (c) The structure of the cross section of the film cracked using a knife in liquid nitrogen

detector and the data obtained were analysed with a computer code No. BOB 75 (JAERI).

RESULTS AND DISCUSSION

Poly(ethylene terephthalate)

Figure 1a shows a top surface of PET film after the chemical etching of fission tracks for 1 h at 45°C in 3 N NaOH solution. The number of holes is $2 \times 10^8/cm^2$ and agrees with the calculated value ($2.1 \times 10^8/cm^2$) from the irradiation conditions. The hole density can be calculated using the formula[7],

$$\rho = 2N\sigma\varphi tAS_u/S_p \qquad (1)$$

where ρ is the density, N the number of ^{235}U atoms, σ the fission cross section of ^{235}U for thermal neutrons, φ the thermal neutron flux ($2 \times 10^{13}\ s^{-1}\ cm^{-2}$), t the irradiation time (10 min), A the fraction of fission fragments entered into the film, $A = 1/70$, S_u the area of the fission source, and S_p the irradiation area, and $S_u/S_p = 0.56$ in the present experiment. The diameter of the hole which had been measured by the gas flow method was ~1300 Å for the same sample. The value measured by gas flow reflects the diameter at the interior of the hole[6]. Therefore the diameter at the surface may be larger than that of the interior.

Figure 1b shows the more detailed surface of the PET film by a high resolution scanning electron microscope. The interior walls of the etched holes which can be clearly observed are not smooth surfaces but have many fold-like nodules of 200 Å width. The similar irregular steps of

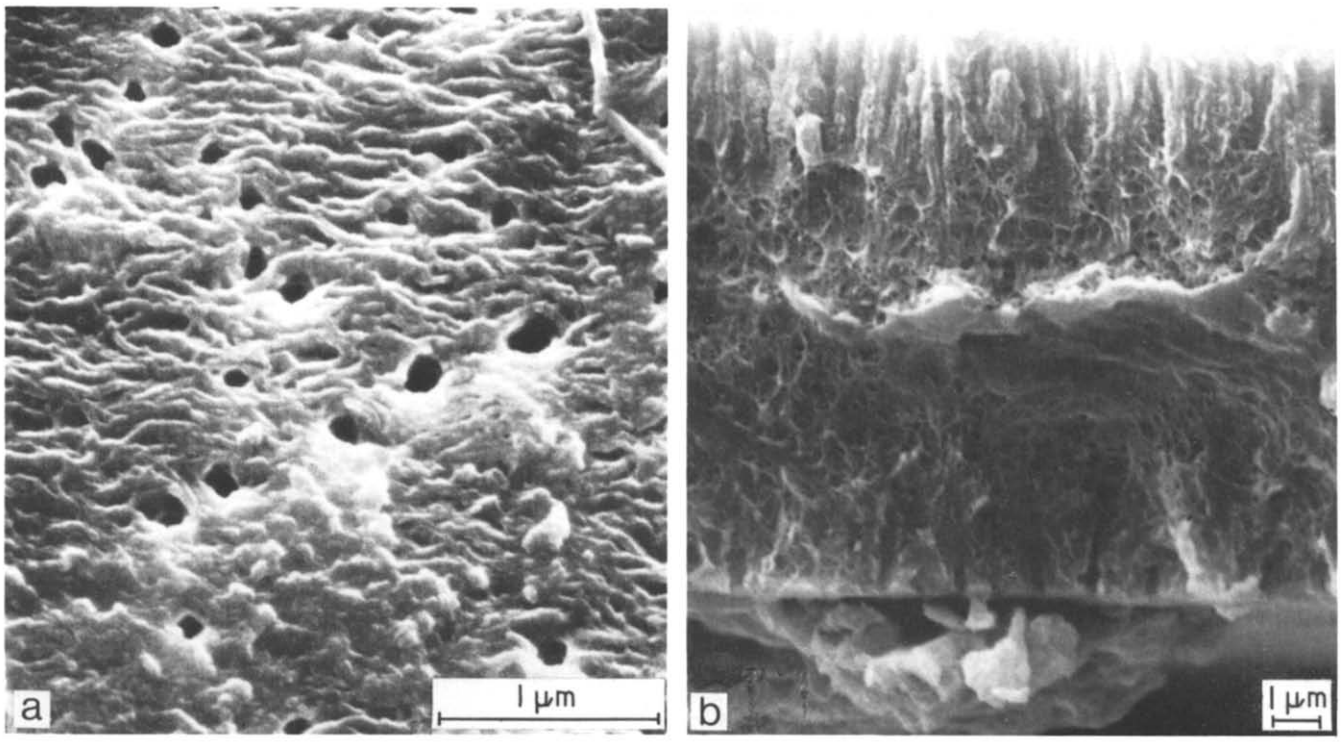

Figure 2 The scanning electron micrographs of ethylene–tetrafluoroethylene copolymer pore filter produced by etching in 12 N NaOH solution at 125°C after bombardment of fission fragments. (a) A field emission scanning electron micrograph of the top surface of the film etched for 70 h. (b) The structure of the cross section of the film etched for 250 h

inner wall on TEM observation have been reported[6].

These nodules may be the crystallite remains of the micelles of the macromolecule after chemical etching. Though it has not been clarified how the etchant attacks the microportion of tracks in the macromolecules, the amorphous regions will dissolve more quickly than the crystallites. In the study of polyethylene etched in HNO_3 solution, Palmer[10] showed that the amorphous regions were preferentially attacked and the crystallite remained. Consequently, the perforated holes etched by chemical reagent do not always show the smooth interior wall especially for the crystalline macromolecules.

Figure 1c shows the vertical section of etched film; the upward and downward directions correspond to both the surfaces, and the distance is the film thickness. The structure at the section was destroyed to some extent because the section was cracked using a knife in liquid nitrogen. The holes penetrate linearly throughout the film along the trajectory of fission fragments. The shape of the hole seems conical rather than cylindrical in form, i.e. cylindrical with a loose taper angle. The diameter is about 5000 Å at both of the surfaces and about 1300 Å at the midpoint. The author[7] elucidated the following relation among the diameter D_m at midpoint, D_a at surface of the etched perforated holes, and the etching rate,

$$\frac{V_1}{V_2}=\frac{l}{D_a-D_m} \tag{2}$$

where l is the film thickness, V_1 the etching rate along the track and V_2 the radial etching rate. However, the following relation between the cone angle (θ) of hole and V_1/V_2 holds at a constant linear rate V_1[1],

$$\theta=\sin^{-1}\left(\frac{V_2}{V_1}\right) \tag{3}$$

The values of V_1 and V_2 were determined as 690 Å min^{-1} and 25 Å min^{-1} from the gaseous flow[9]. Consequently, $\theta=2°$ is calculated from equation (3). Substituting D_a, D_m, and l in equation (2) the value of V_2/V_1 yields 0.041, then $\theta=2.4°$ is obtained from equation (3). The values of θ agree satisfactorily.

Ethylene–tetrafluoroethylene copolymer

Figure 2a shows the top surface of etched tracks in ETFE film observed by the high resolution electron microscope. Our previous report[8] indicated that the radial etching rate is very small (6–8 Å h^{-1}) and that an etching time of about 250 h at 125°C in 12 N NaOH solution was necessary in order to observe the clear holes by a scanning electron microscope. Using the high resolution electron microscope, the etched tracks can be observed after 70 h etching at 125°C. The size of the hole is 1000 ± 500 Å, but the shape of most holes at the surface is not circular. The film surface shows uneven structure like fibrils, undetected on the unetched films.

It is assumed that these fibrils correspond to the crystallite which remains after chemical etching and align with the film orientation. The crystalline regions may be more resistant to chemical etching than the amorphous regions as with PET and polyethylene, and the shapes of the holes seem deformed when small. Deformation of the film by electron irradiation was not observed initially.

Figure 2b shows the section of film which has been etched for 250 h. When the hole diameter is small, they are difficult to distinguish. The holes do not penetrate the entire thickness of the film, only ~4 μm from both of the surfaces. A spread in hole diameters on the surface of ETFE is considered to be the variation of radiation damage owing to the distribution of energies and masses of fission fragments, analogous with PET[6].

The cross section in *Figure 2b* shows the difference in the number of holes on one side of the film surface to another, and the penetrating ratio of fission fragments in 12 μm thick ETFE film is shown to be $\sim 40\%$[8]. This indicates that the etchant attacks only one side of the surface of non-penetrating fragments, which is reasonable because of the distribution of the range of fission fragments. Using the data by Cusack and King[11], the ranges of the heavier and lighter fission fragments in ETFE are obtained from the following equation:

$$(1/R_c) = \sum_i (f_i/R_i)$$

where R_c and R_i are the ranges in the compound and in the element of i component, respectively and f_i the weight fraction of i component. R_i was presented in the table. According to this relation, the ranges of the heavy nuclides are shorter, about 1–4 μm in length, than the lighter nuclides in ETFE. The width of single surface dissolved from the original surface should be below 0.2 μm up to this time. Consequently, fission fragments which penetrate up to 40% are due to the lighter fragments of larger recoil energy, the residual being due to the heavier fragments trapped in ETFE film. As the surface of film is dissolved the entire thickness of the film crops out and the ratio of penetrated holes must increase.

Yoshida *et al.*[3] studied the radioactive distribution of incident fission fragments in a stack of polycarbonate films and the elution behaviour of the nuclides in etching. Here, the radioactivity in the film was measured to confirm the significance of the difference of the penetrating ratio of fission fragments in the film. The residual fission fragments in the 12 μm thick ETFE film were found to consist only of the heavier nuclides. The nuclides were assigned from the γ-spectrum as follows: ^{131}I(364, 637 keV), ^{132}Te(230 keV), ^{132}I(668, 773, 523 keV), ^{140}La(487, 815, 1597 keV), ^{141}(Ce(145 keV), ^{143}Ce(293 keV), and ^{147}Nd(531 keV), in comparison with those in 100 μm thick film where both the light and the heavy nuclides were found because enough thickness is available for retention of all the fission fragments. A shorter cooling time was practically impossible because of the radioactive protection in the reactor; however it is more suitable for detection of light nuclides. The following nuclides were detected in the thicker film: ^{95}Zr(724 keV), ^{95}Nb(765 keV), ^{97}Nb(665 keV), ^{99m}Tc(142 keV), ^{99}Mo(780, 740 keV), and ^{103}Ru(497 keV). The difference in number and kind of residual nuclides corresponds to the penetrating ratio of fission fragments in the thinner film.

Finally, compared with the etched interior surface of holes in the filters of PET and ETFE films, any essential difference appears to be absent.

CONCLUSION

The interior wall of etched holes was not smooth, the surface being covered with nodules for PET and fibrils for ETFE. These nodules and fibrils are thought to be the crystallite remaining after etching. The structure of the holes in PET is cylindrical with a tapering angle and can be explained by the ratio of etching rates radially and along the tracks. For ETFE the structure of the holes was more cylindrical than that of PET. The penetrating ratio of fission fragments in 12 μm thick ETFE film was discussed from observation of cross sections of the film and the residual radioactive nuclides.

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