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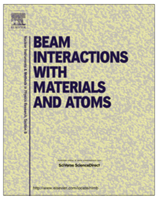

Applied-voltage dependence on conductometric track etching of poly(vinylidene fluoride) films

N. Nuryanthi [a,b], T. Yamaki [b,*], H. Koshikawa [b], M. Asano [b], S. Sawada [b], S. Hasegawa [b], Y. Maekawa [b], Y. Katsumura [a]

[a] *Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *Quantum Beam Science Directorate, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan*

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ABSTRACT

We investigated the conductometric etching of heavy-ion-irradiated poly(vinylidene fluoride) (PVDF) films to study their pore growth behavior, which was estimated from radial etch rates under the application of different voltages. The plateau of the pore diameter seen in a bulk etching region was constant at an applied voltage ranging from 0.1 to 3.0 V, while the breakthrough time varied considerably. Employing the first derivative of the conductometric curve, corresponding to the radial etch rate, R, enabled us to clearly analyze parameters reflecting the track structures (i.e., the maximum radial etch rate, R_{max}, and the time for the diameter to reach the final plateau, T_E). Interestingly, these two parameters were significantly influenced by the applied voltage. There was a trend toward increasing values of R_{max} and, in contrast, decreasing levels of T_E as the applied voltage was increased. These promotional effects of the etching process can be rationalized by considering the electrophoretic migration of dissolved species in and out of each pore. Thus, conductometric etching under different voltage conditions offers the ability to control pore geometries by optimizing the etching process in the transverse direction as well as in the thickness direction.

1. Introduction

Swift-heavy-ion irradiation provides a unique way to modify an organic material by introducing localized concentrated molecular fragments as well as free radicals and excited or ionized chemical species along the ion trajectory. These damaged areas, which are called latent tracks, can be etched out by a suitable etching solution to give uniform micrometer- to nanometer-sized pores [1]. The track-etched membranes have been used for many applications in industry and basic research [2,3].

It is very important to establish a method for obtaining etched pores with defined geometry. We have investigated the ion-track membranes of poly(vinylidene fluoride) (PVDF) for several years [4–7]. Unlike previous investigators [8,9], we employed moderate etching conditions, that is, a pure alkaline solution at high temperature without any oxidant additives (such as $KMnO_4$ or KIO_4), enabling us to precisely evaluate the process of pore evolution and growth. In a series of studies of conductometric track etching, we were able to monitor pore evolution by recording the electrical conductance through the membrane. Changes in the etch rate with an increasing pore diameter reflect the spatial distribution of ion-induced chemical and physical modifications of the polymer over the core and halo regions of the track. This provides a strong potential for analyzing the track structures in PVDF by defining the etch rates in the directions of the film thickness and track radius.

Fortunately, the conductometric etching method gave us another option for investigating the etching behavior, that is, the effect of the voltage level applied to a conductometric cell. It was previously reported that track-etching characteristics and the resulting pore geometries of polycarbonate (PC) and polyethylene terephtalate (PET) were affected by varying the applied voltage [10–14]. In our studies of PVDF-based ion-track membranes [5,6], the profiles of the conductometric curves seemed to be dependent on the applied voltage in the range from 0.3 to 2.0 V, and additionally, in a quite recent study [7], the range of the investigated voltages has been expanded to between 0.1 and 3.0 V. However, we have not yet analyzed the detailed behavior of pore growth at these different voltages, which could lead to a better understanding of the track structures.

This study examines the influence of the applied voltage on the etching characteristics of heavy-ion-irradiated PVDF films, including the pore growth as well as parameters extracted directly from the conductometric curve, during the conductometric etching process. We will characterize the radial structure of the etchable tracks using the etch rate in the transverse direction.

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* Corresponding author. Tel.: +81 27 346 9413; fax: +81 27 346 9687.
E-mail address: yamaki.tetsuya@jaea.go.jp (T. Yamaki).

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2. Experimental

PVDF films 25 μm in thickness (Kureha KF Polymer) were irradiated in a vacuum chamber ($<10^{-6}$ Torr) with 450-MeV ^{129}Xe ions from a cyclotron at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) facility, Japan Atomic Energy Agency (JAEA). The room-temperature irradiation was performed perpendicular to the surface at the fixed fluence of 3×10^7 ions/cm^2. Chemical etching was then performed in a 9 mol dm^{-3} KOH aqueous solution at 80 °C in a conductometric cell [6]. The electrical conductance was monitored using an LCR meter (HiTESTER 3522, HIOKI) at the frequency of 1 kHz. The AC voltage applied between the electrodes ranged from 0.1 to 3.0 V. Assuming cylindrical pores as previously justified by experimental and theoretical investigations [5,6], we calculated the effective pore diameter, d_{eff}, at any given time from the measured conductance by

$$d_{\text{eff}} = \sqrt{\frac{4Lg(t)}{\pi KNS}} \tag{1}$$

where $g(t)$ is the electrical conductance of the solution through the film; L is the membrane thickness; K is the specific conductivity of the KOH aqueous solution (9 mol dm^{-3} and 80 °C) [15]; N is the pore density, which corresponds to the ion fluence; and S is the area of the measured sample [16]. Scanning electron micrograph (SEM) observations were conducted with SEM JEOL 5600 after coating the sample with a 20-nm-thick gold layer in order to confirm the pore density. Other details of our experiment were described in our previous reports [5,6].

3. Results and discussion

3.1. Etching parameters directly extracted from conductometry curves

In Fig. 1, we compare the conductometry curves at different applied voltage levels. The characteristic etching parameters were directly identified from the curve in the following manner. At the initial stage of etching, the breakthrough time was recognized as a sudden jump in the conductance because at this point, the etching solution inside the tracks made initial contact. In contrast, the final stage involves etching beyond the width of the latent track (i.e., bulk etching). The d_{eff} did not appear to increase in the bulk-etching region, which indicates that the damage in the track was completely etched out, and the bulk etch rate was negligibly low. In other words, this final d_{eff} can be regarded as representative of the completion of the etching process. Additionally, the etching time required to reach the final d_{eff} value is extracted and defined as T_E. In the subsequent paragraphs, the dependence of these etching parameters on the applied voltage is discussed.

The final d_{eff} values were similar, suggesting that this parameter was not affected by the level of applied voltage. In this sense, the present result is consistent with our previous results [5–7]. However, in the current case, the final d_{eff} value was 265 nm, which is substantially larger than that from the previous study (150 nm) [5,6]. This difference in the diameter probably result from inhomogeneous etching in the conductometric cell, a situation that we have recently encountered [7]. This problem led to much larger pores than expected in a limited area located a few micrometers from the membrane edge. But the conductometry averages the information acquired over all the pores in the membranes, thus leading to the observation of larger pores. That is why our arguments were limited to a comparative analysis of the results and their qualitative characteristics; the inhomogeneous etching was not crucial in this framework of evaluation.

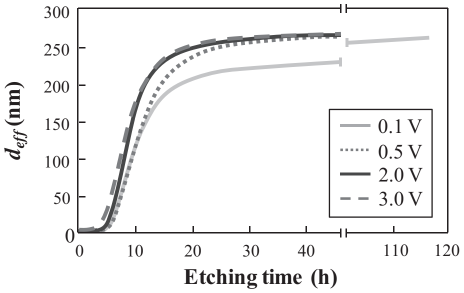

Fig. 1. Curves of the effective pore diameter, d_{eff}, versus etching time, obtained by etching in a conductometric cell using a 9 mol dm^{-3} KOH etching solution at 80 °C. The applied voltage was 0.1, 0.5, 2.0, and 3.0 V.

The applied-voltage dependence of the T_E was significant; in particular, the T_E was too long at 0.1 V to be seen at less than 48 h, the time at which the end of the etching process was reached at higher voltages. On the whole, the T_E became shorter as the applied voltage was increased, in contrast to the invariant final d_{eff} value. However, it was difficult for us to estimate an exact value of T_E because of its high statistical dispersion. Thus, this topic will be discussed further in Section 3.2.

Fig. 2 is an enlarged view of the conductometric curves in the first 8 h of etching, providing a clear comparison of the breakthrough time. The breakthrough time was shortened under higher applied voltages. For example, it was two times shorter at 3.0 V than at 0.1 V, and while no distinct difference was seen between 0.1 and 0.5 V, a prominent change was observed between 2.0 and 3.0 V. Thus, there might be a voltage threshold to overcome.

Before discussing the radial etch rate, we should mention the wide distribution of the breakthrough time, which was previously discussed for studies of conductometric etching of PET both experimentally [17] and analytically [18]. Apel et al. [17] ensured that the shape of the condutometric curve obtained in experiments with multi-track samples was not influenced by the variation in the breakthrough time for individual tracks. Zhu et al. [18] found that the degree of distribution of the breakthrough time could be decreased by track sensitization using UV light irradiation. On the other hand, we did not perform experiments with single-track samples in parallel and applied no pre-etching treatment for sensitization. In this sense, the possibility that non-simultaneous breakthrough of the tracks might alter the d_{eff} (conductance) to some extent, especially at the beginning of pore opening, cannot be entirely excluded. Our discussion about the breakthrough (in the above paragraph) and its vicinity is, therefore, limited to a relative comparison of the data at the different applied voltages.

3.2. Radial etch rates

In order to analyze pore growth, we calculated the radial etch rate using the following equation (i.e., the time derivative of Eq. (1)):

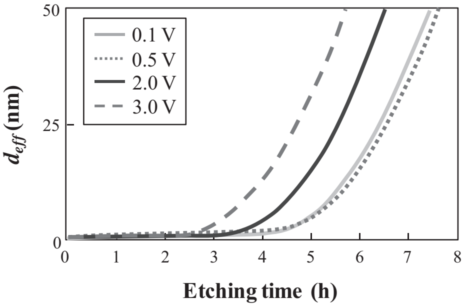

Fig. 2. Enlarged view of the conductometric curves of Fig. 1 during the first 8 h of etching enabling a clear comparison of the breakthrough time.