POLYVINYLIDENE FLUORIDE TRACK MICROFILTER*

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ABSTRACT

By the etching of PVDF (polyvinylidene) foils perpendicularly bombarded to their surfaces in advance with heavy ions at UNILAC (GSI Darmstadt, Germany), PVDF track microfilters are successfully manufactured and mostly evaluated by means of an optical microscope. The recipes of the elaboration, the properties as well as etching and technical parameters of the microfilters are summarized. The possible applications are also discussed briefly.

Keywords PVDF, Chemical etching, Track microfilter, Pore size

1 INTRODUCTION

Track microfilters can be generated by energetic charged particle irradiation to suitable track detecting materials and subsequent chemical etching of the irradiated detectors in appropriate chemicals[1,2]. Such filters have been used in a broad spectrum of industries, such as electronics, pharmaceutical, biomedical, quality control and analysis, water treatment, biotechnology, food and beverage, speciality chemicals, speciality gases and aerospace. But it is found that most of commonly used materials for the manufacture of track microfilters have poor physical properties, particularly, thermal properties and their resistances against aggressive chemicals. In order to extend the range of the applications, more and more efforts have been made to search for the matrixes to make track microfilters with special properties. Recently, we produced a new track microfilter — PVDF track microfilter by chemical etching of PVDF foils of 50 mm in diameter and $40\,\mu m$ in thickness which were perpendicularly irradiated to their surfaces in advance with ^{238}U heavy ions of 13.7 MeV/u. PVDF physically resembles TEFLON. Besides good mechanical property, it shows very fine resistivities against aggressive chemicals, high temperature and radiations. Particularly, its rolled and streched form possesses pizo-/pyro-electric proporties. Moreover, it is endowed with certificate of inspection in food and medicine quality control by its physiological properties which make it a good filter material.

Because of its so fine resistivity against chemicals that the chemical etching of PVDF track microfilter is more time consuming than other plastics track microfilters. One of the aims of present work is to search for a suitable recipe for increasing etching selectivity(V) as high as possible. For this purpose, we systematically investigated the

*This work was performed under the agreement of China-Germany Scientific Collaboration
Manuscript received date: 1994-10-08

etching behaviours of PVDF vs different solutions (NaOH, KOH, $KMnO_4$, $K_2S_2O_5$ and their mixtures) in different concentrations at 70 °C (for keeping its pizo-/ pyro-electric properties). Some results are plotted in Fig.1 which demonstrats that the solution of 10 mol/L KOH+0.25 FW (formula weight) $KMnO_4$ could be considered as an acceptable etchant for manufacture of PVDF track microfilter. When the PVDF foils of 40 μm thick perpendicularly bombarded with ^{238}U heavy ions of 13.7 MeV/u and etched in the etchant specified above at (70±1) °C for 5 h, one can obtain the PVDF track microfilter with penetrating through holes. With the prolongation of etching, the pore sizes of track are gradually enlarged, and the foils are normally covered by a layer of purple darkish precipitates which can be easily washed away by using a solution of $K_2S_2O_5$. For the etching of about 20 h, microholes could be observed having diameter (D) of 4~5 μm at the surface and ~4 μm in centre of foil.

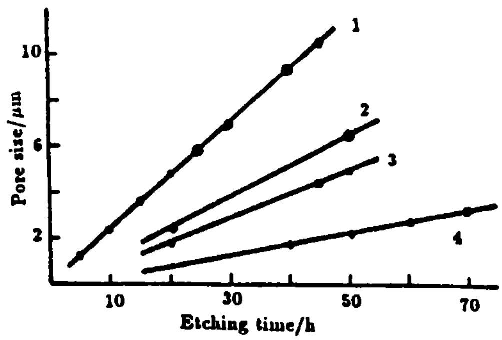

Fig.1 Pore size at surface of microfilter vs etching time at (70 ± 1)°C for different concentrations of KOH+$KMnO_4$

1. 10 mol/L KOH+0.25 FW $KMnO_4$,
2. 8 mol/L KOH+0.15 FW $KMnO_4$,
3. 7.5 mol/L KOH+0.1 FW $KMnO_4$,
4. 6 mol/L KOH+0.1 FW $KMnO_4$

2 PARAMETERS

The PVDF track microfilters produced in our etching conditions have such a kind of microholes which consist of two identical funnels standing opposite each other (Fig.2). The outer diameter (D) of microholes is larger than the inner diameter (d). The cone angle [δ=arcsin$(1/V)$] is related to the etching selectivity ($V = V_T/V_B$), i.e. the ratio of the track etch rate along the damage trails (V_T) to the bulk etch rate of matrix itself (V_B). The larger the ratio is, the smaller the cone angle is, the more "cylindrical" the microholes are. Generally speaking, the track microfilters made from plastics are mostly of funnels-like-shaped microholes with a cone angle of a few degrees. The parameters of such track microfilters are linked each other by Eq.(1)

$$d = D[1 - (L - 2V_Bt)/(2(V_T - V_B)t)] \quad (1)$$

where d is the inner diameter, D the outer diameter, V_T the track etch rate, V_B the bulk etch rate, L the original thickness of the foil, t etching time.

From Eq.(1), one can deduce following two deductions:

$$t_o = L/2V_T \quad (2)$$

$$t_d = L/2V_B \quad (3)$$

Eqs.(2,3) are etching times when microholes start to be formed in a foil and the foil will be completely dissolved, respectively. These two deductions are frequently used for the inspection of quality control in the manufacture of track microfilters.

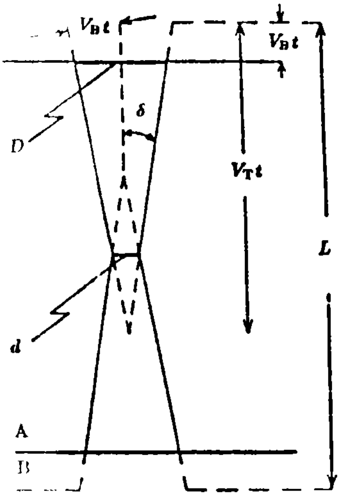

Fig.2 A scheme of the parameters used for the evaluation of the inner and outer diameter of microholes

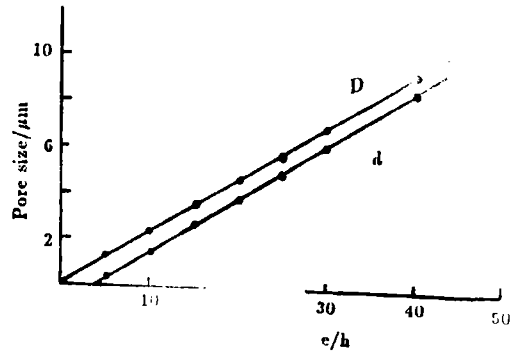

Fig.3 Pore sizes (D and d) vs etching time at (70 ± 1)°C for the solution of 10 mol/L KOH+0.25 FW $KMnO_4$

It is evident that δ i.e. V_T and V_B are the dominant parameters for producing track microfilters. V_T is interrelated to mass and energy of track forming particles. Therefore, for the etching of every batch of foils irradiated with certain heavy ion beam, one has to determine V_T beforehand to be able to estimate the etching time needed to produce diameters required by the user of the microfilters. There are several methods to be employed to derive V_T. A more practical one is the deduction of V_T by using a plot of pore sizes (D and d) vs etching time (Fig.3). From Fig.3, one can see that the inner diameter d of microfilters starts increasing linearly after after an "induction time" t_0 which is regarded as the time necessary for forming the "penetrating" microholes. With this induction time t_0 and the original thickness of foils L, the track velocity V_T can be derived through the equation $V_T = L/(2t_0)$. In this way we calculated V_T as $(5.13 \pm 0.02)\,\mu$m/h for ^{238}U heavy ions of 13.7 MeV/u at the etching condition of 10 mol/L KOH + 0.25 FW $KMnO_4$ at 70°C. For this defined etching condition the average bulk etch rate V_B is determined as $(0.2 \pm 0.1)\,\mu$m/h by measuring weight and thickness before and after etching. For the manufacture of track microfilters with the cone angle as small as possible, the reduction of foil thickness is an effective method, but it is limited from practical viewpoint. So the attention is normally paid to search for the most optimized recipes. Apart from selection of etching condition the additional (pre- or post-) treatments are usually helpful to increase etching selectivity.

3 PROPERTIES AND POSSIBLE APPLICATIONS

PVDF track microfilter presented here is the microfilter with funnel-like-shaped microholes of a few degrees of the cone angle. It possesses some unique advantages in physical, chemical and electric properties which are useful for a variety of technological applications. Some characteristics are summarized as follows:

a. Excellent resistivities against aggressive chemicals and gases, which makes it useful in the industry of speciality chemicals and gases. Fig.4 illustrates a comparison of the change of the mechanical strength between PET and PVDF track microfilters after a long contact with aggressive gases (HCl and NH_3) used in the production of semiconductor.

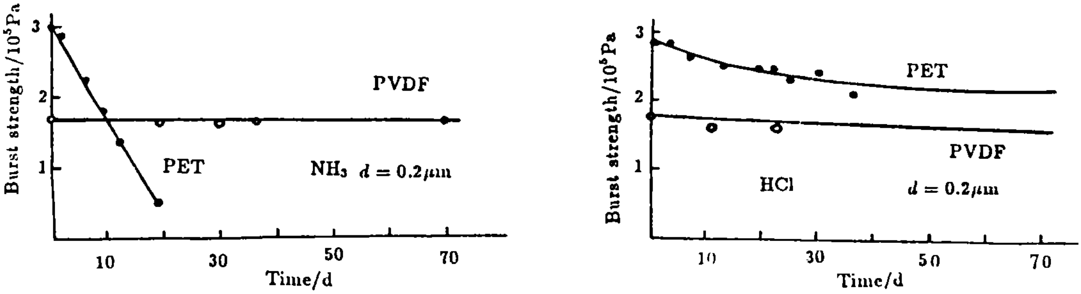

Fig.4 Change of the mechanical strength of PET and PVDF track microfilters after a long contact with aggressive gases

b. Wide working temperature, ranging from −30°C to 135°C, which allows it to be applied in cryogenic technology.

c. A low ash content which is of importance in the quantitative elemental analysis by means of neutron activation and optical spectroscopy.

d. High transparence which is sufficient for optical microscopic investigations.

e. A smooth surface which permits their use for analytical purposes, in particular, in studying the precipitate by means of optical or electron microscopy.

f. Small weight and negligible moisture absorption (<0.03% at 23°C in 24 h), which allows it to be used for gravimetrical analyses.

g. Fine air-resisting and radiation resisting property, which makes it important in a variety of applications, especially in nuclear technology.

h. Incombustibles which is useful for some special application fields.

i. Electric (pizo- / pyro-) properties, which make it acceptable in automatic control.

ACKNOWLEDGEMENT

The authors are greatful to Drs. R. Spohr and J. Vetter for their kind help of irradiation of the foils. We thank the international officers, DLR, Koeln and CNTC, Beijing, for their support.

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