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Nuclear Instruments and Methods in Physics Research B 236 (2005) 501–507
NIM B Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Making porous membranes by chemical etching of heavy-ion tracks in β-PVDF films

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Received in revised form 11 January 2005
Available online 15 June 2005

Abstract

Production of porous membranes using heavy ion bombardment and subsequent chemical etching of poly(vinylidene difluoride) (PVDF) films has been reported several years ago. However, porous membranes with pore diameter in the nanometer scale requires a better understanding of the chemical etching mechanism. In this work PVDF foils irradiated with Sn ions (2.85 MeV per nucleon) were exposed to several etching conditions which involved permanganate oxidation in different alkaline environments. The solution of KOH 9 mol L^{-1} and saturated in $KMnO_4$ was the best etching reactant for PVDF. Functional groups created in the alkaline and oxidative attack by permanganate were studied by FT-IR and UV–vis spectroscopy. The spectroscopic data reveals that the formation of pores occurs by a two-step mechanism: (i) double bonds as a result of dehydrofluorination induced by alkaline media and (ii) oxidation of these double bonds in permanganate solution. The etching temperature and time can be attuned to prepare track-etched membrane with a desired pore diameter in the range of few hundred nanometers. Temperatures ranged between 55 °C and 65 °C were optimal to produce cylindrical pores. Temperatures higher than 85 °C induce conical-shaped track-etched pores while temperatures lower than 50 °C slow down the chemical attack. The addition of a phase-transfer agent enhances the chemical attack and allows the decrease of the etching temperature and/or time.

PACS: 42.70.Jk; 61.82.Pv; 68.37.Hk; 61.80.−x; 81.05.Lg

Keywords: PVDF; Tracks; Etching; Pores

1. Introduction

PVDF (poly(vinylidene difluoride)) is one of the most resistant polymers commercially available. Its bi-axial β-phase has additional interesting technological features such as piezo- and pyroelectric

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0168-583X/$ - see front matter
doi:10.1016/j.nimb.2005.04.027

properties. Production of track-etched membranes using heavy ion bombardment and subsequent chemical etching of PVDF films has been reported several years ago [1]. However, there is a renewal interest to make track-etched membranes with pore diameter in the nanometer scale.

Track membranes with pore diameters at molecular dimensions have direct application in molecule and ion sensing through resistive-pulse sensor method [2]. Another interesting application comes from the introduction of chemical selectivity in order to confer a molecular recognition in the selective-permeation function. Specific chemical interactions between solute and the modified nanopore walls can alter the transport properties [3]. Additionally, Apel has recently reviewed novel applications of track membranes as template for the synthesis of micro- and nanowires and tubes, textured surfaces and bodies with special optical properties [4].

However, most of the advances in this field have been done on commercial track-etched membranes modified with a gold deposition by electroless plating method to reduce the pore diameter [5]. Thus, this paper reports on the etching mechanism of PVDF in order to find the key factors able to produce track membranes with pore diameter of nanometer dimensions.

Several authors have tested several oxidant solutions to produce visible tracks in PVDF foils irradiated with swift heavy ions [1,6]. Most of chemical solutions failed to produce damage, with the exception of permanganate solution in alkaline media. There are several reports on manufacturing of fluoropolymer track membranes; however, most of them deal with the production of filters of micron-size pore dimension [1,7–9]. The production of nanometer-scale pores using a relative simple condition was described by Komaki et al. [10,11]. Pore diameters in the range of 20–80 nm were reported using a highly concentrated sodium hydroxide solution (9–10 mol L^{-1}) at high temperature (85 °C). They irradiated 10 μm thick β-PVDF foils by swift heavy ion beams ($^{58}Ni^{10+}$, $^{63}Cu^{11+}$ and $^{35}Cl^{9+}$ ions with a kinetic energy in the 1–6 MeV per nucleon-MeV/amu-range). However, long etching times (15–50 h) were necessary to make holes through the irradiated films. This feature in addition to the high etching temperature can irreversibly destroy some interesting distinctive properties of the bi-axially stretched PVDF such as the piezoelectricity [8].

The potential technological applications of this membrane encourage us to study suitable etching conditions to produce nanometer-scale pores. Additionally, spectroscopic studies are performed to gain better understanding of the etching mechanism of heavy ion-irradiated PVDF.

2. Materials and methods

The following chemicals were purchased from Sigma-Aldrich: potassium metabisulphite ($K_2S_2O_5$), tetrabutylammonium bromide (TBAm). Potassium permanganate ($KMnO_4$) and potassium hydroxide (KOH, technical grade) are purchased from Prolabo. All chemicals were used as received. Hydrophobic β-PVDF films (Atochem, 25 μm thick) were Soxhlet-extracted in toluene and dried at 50 °C under vacuum prior to irradiation.

The β-PVDF foils were irradiated with a heavy ion beam of Sn (2.85 MeV per nucleon-MeV/amu, fluence range 9.5×10^8 to 9.5×10^9 cm^{-2}) *in vacuum* provided by the GANIL accelerator (Caen, France) and stored at −20 °C. Small pieces of irradiated PVDF were exposed to several etching conditions by soaking them in a beaker containing a fresh saturated $KMnO_4$ solution (0.25 mol L^{-1} prepared in 9 mol L^{-1} KOH). During the etching process all samples developed a brownish precipitate of MnO_2. Cleaning of the precipitate was performed by immersion of films in a $K_2S_2O_5$ saturated solution during 15 min.

Functional groups were analyzed by FT-IR using a Nicolet Magna-IR™ 750 spectrometer equipped with a DTGS detector. To analyze the first micrometers of the film, spectra were recorded in an Attenuated Total Reflection mode (ATR) using a diamond-crystal with single reflection. Spectra were collected by cumulating 32 scans at a resolution of 2 cm^{-1}.

A UNICAM model UV 300 spectrophotometer was used to record UV–vis spectra.

The pore diameter on the PVDF surface was determined from scanning electron microscope