



Electronic behavior of micro-structured polymer foils immersed in electrolyte

C.T. Souza^{a,b}, E.M. Stori^{a,b}, D. Fink^{b,c,d}, V. Vacík^d, V. Švorčík^d, R.M. Papaléo^e, L. Amaral^{a,b}, J.F. Dias^{a,b,*}

^a Programa de Pós-Graduação em Ciência dos Materiais, Universidade Federal do Rio Grande do Sul, CP 15051, CEP 91501-970, Porto Alegre, RS, Brazil

^b Instituto de Física, Universidade Federal do Rio Grande do Sul, CP 15051, CEP 91501-970, Porto Alegre, RS, Brazil

^c Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, P.O. Box 55-534, 09340 México, DF, México

^d Nuclear Physics Institute, 25068 Řež, Czech Republic

^e Pontifícia Universidade Católica do Rio Grande do Sul, Av. Ipiranga 6681, CEP 90619-900, Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:

Received 25 July 2012

Received in revised form 20 November 2012

Available online 29 December 2012

Keywords:

Polymers

Proton beam writing

Etching

Electrical properties

ABSTRACT

The presence of impurities in polymers makes them electroactive. When immersed in electrolytes, polymers can incorporate additional ions, thus changing their electronic properties. The aim of the present work is to characterize the electronic behavior of polymers with microstructures obtained from proton irradiation and etching. To that end, polyethylene terephthalate foils were irradiated with a $2.0 \times 2.0 \mu\text{m}^2$ proton beam of 3 MeV. Subsequently, the foils were submitted to an etching procedure with NaOH, leading to microstructures of the order of $1000 \mu\text{m}^2$. Finally, the polymers were immersed in a solution of NaCl and submitted to an AC voltage from a function generator. The results show that the etching procedure after proton irradiation leads to buried structures in the polymers. Pristine and microstructured foils show an Ohmic behavior for frequencies below 1 kHz and a capacitive behavior above this frequency up to 1 MHz. This behavior is independent of the foil thickness and the area of the structures.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

It is well known that contaminants like inorganic elements in polymers improve their ability to conduct electric current. Once the polymer is immersed in an electrolyte, the dissociation of the electrolyte into ions triggers a diffusion process and a strong interaction between the inorganic impurities and the electrolyte takes place [1]. As a result, a migration of ions into and through the polymer is established under the influence of the electrochemical potential, thus turning the polymer electroactive. Electroactive polymers have attracted considerable interest due to their multi-purpose applications as fuel cell membranes, biosensors, neural interfaces and organic electronics [2,3].

Among several techniques to study the interaction between a polymer and an electrolyte, the electrical conductivity method [1] provides a straightforward way to characterize such interaction. Under the presence of an alternating electric field, ions start migrating through the system composed by the electrolyte and the polymer. This ionic transport is dependent on several parameters like the intensity and frequency of the applied electric field and the radiation-induced bond rearrangements in the polymer.

Depending on the frequency, the system may exhibit a resistive, capacitive, inductive or even memristive [4] behavior.

The mobility of ions at the polymer – electrolyte interface and the ion uptake mechanism by the polymer are dependent on several parameters including the polymeric surface and the Nernst diffusion layer [5] which, in general, act as a barrier to ionic transport and delay the diffusion mechanism of ions into the polymer. In order to facilitate the diffusion, the polymer can be irradiated by swift ions, which changes the mechanical and electrical properties of both surface and bulk layers. These changes depend on several parameters including the chemical formula of the polymer, the atomic number, the energy and the fluence of the ions employed in the irradiation [6]. At low fluences, the changes observed in the irradiated polymer are essentially caused by bond scissions which often lead to surface roughening, severe chemical damage and enhancement of the electric conductivity and the adsorption of solvents. On the other hand, effects due to cross-linkings and carbonization usually prevail at higher fluences, improving resistance to solvent attack and making the polymeric surface harder and brittle [7,8].

The passage of charges and chemical species through polymers can also be altered and controlled by pore opening with focused ion beams or with single energetic ions, using the etched ion track method [6,9]. This subject has gained new impetus in recent years thanks to a wide range of applications of track-etched membranes functionalized by e.g. surface grafting techniques in medicine,

* Corresponding author at: Instituto de Física, Universidade Federal do Rio Grande do Sul, CP 15051, CEP 91501-970, Porto Alegre, RS, Brazil. Tel.: +55 51 33087248; fax: +55 51 33087286.

E-mail address: jfdias@if.ufrgs.br (J.F. Dias).

biology and biotechnology [6,10–13]. For instance, by using porous membranes grafted with hydrogels, it is possible to achieve gating properties which allow the controlled passage of substances through the membranes. Recently, we have started the development of sensors based on membranes produced by a combination of ion tracks and proton beam writing [14]. The design of such sensors is based on the construction of shallow depressions on thin polymer foils where the cells remain in their relaxed state and from where signals can be sent through responsive channels [14].

In this work we present preliminary results on the morphological and electrical characterization of polymer foils structured by proton beam writing (without any coatings on the walls) soaked in electrolytes. This is the first important step of the sensor development that will allow, in the near future, a clear assessment of the response function of the functionalized system under different stimuli.

2. Experimental procedure

For the experiments, we used polyethylene terephthalate (PET, Melinex[®], Mylar[®]) foils with a nominal thickness of 12 μm . The foils were exposed to 3 MeV protons with typical beam sizes of $2.0 \times 2.0 \mu\text{m}^2$. In this work, we opted for the writing of two nearby patterns resembling channels in order to complement morphological studies carried out with similar structures [15]. To that end, two rectangular patterns of about $2 \times 100 \mu\text{m}^2$ were generated with the Oxford triplet scanning microprobe system. The experiments were carried out with typical currents of about 20 pA. The accumulated charge was fixed at 65 nC for all experiments, corre-

sponding to a total dose of about 6×10^{15} ions cm^{-2} . The choice of the proton energy was based on the performance of the focusing system, while the ion dose was chosen based on the etching time required to corrode the irradiated area.

After irradiation, the foils were immersed in a 6 M NaOH solution at 60 °C for times ranging from 5 to 60 min. The thickness of the foils after etching was measured with on- and off-axis STIM (Scanning Transmission Ion Microscopy) and SEM (Scanning Electron Microscopy).

For the electrical measurements, the foils were mounted in a small stainless steel vessel which accommodates two Teflon[®] compartments. Each compartment has a length of 3 cm and an inner radius of 3 mm, thus representing a cross sectional area of about 28 mm². The Teflon compartments are open at one end and thus can be pressed against each other, forming a hermetically continuous compartment 6 cm long containing the electrolyte solution. Alternatively, the compartments can be separated by a polymer foil, thus leading to two 3 cm long compartments hermetically sealed from each other by the polymer. These compartments are filled with 5 M NaCl solution, which constitutes the electrolyte. The compartments are connected by platinum electrodes to a Velleman PC5GU250 function generator and oscilloscope unit. In this way, the polymer's response upon application of an AC voltage with frequencies between 1 mHz and 1 MHz and voltages between 0.1 and 10 V (peak-to-peak) could be recorded. The built-in resistance in the probe tip of the oscilloscope used for the measurement of the current was either 1 or 10 M Ω . The present measurements were restricted to the measurement of Bode plots, i.e. of the complex currents as a function of the frequency with a sinusoidal AC voltage input of 5 V (peak-to-peak) and frequencies between 100 Hz and 1 MHz.

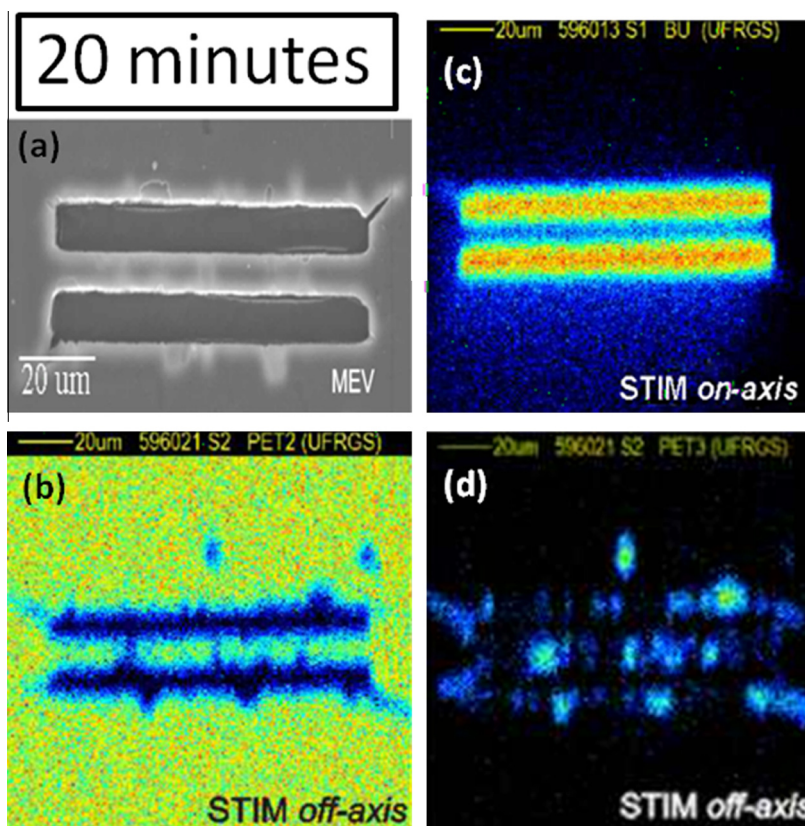


Fig. 1. SEM (a), on-axis STIM (c) and off-axis STIM (b, d) images obtained for the rectangular patterns after 20 min of etching. The PET foils were irradiated by 3.0 MeV protons and etched by a solution of 6 M NaOH. STIM measurements were carried out with 1.0 MeV protons impinging on the polymers. STIM images were obtained by selecting distinct energy regions in the energy loss spectrum [15].

Download English Version:

<https://daneshyari.com/en/article/8042650>

Download Persian Version:

<https://daneshyari.com/article/8042650>

[Daneshyari.com](https://daneshyari.com)