Electronic behavior of micro-structured polymer foils immersed in electrolyte

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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 $2.0 \times 2.0 \ \mu m^2$ proton beam of 3 MeV. Subsequently, the foils were submitted to an etching procedure with NaOH, leading to microstructures of the order of 1000 μm^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.

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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 multipurpose 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,

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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 $2.0 \times 2.0\ \mu m^2$. 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 $2 \times 100\ \mu m^2$ 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, corresponding 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 PCSGU250 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 MΩ. 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.
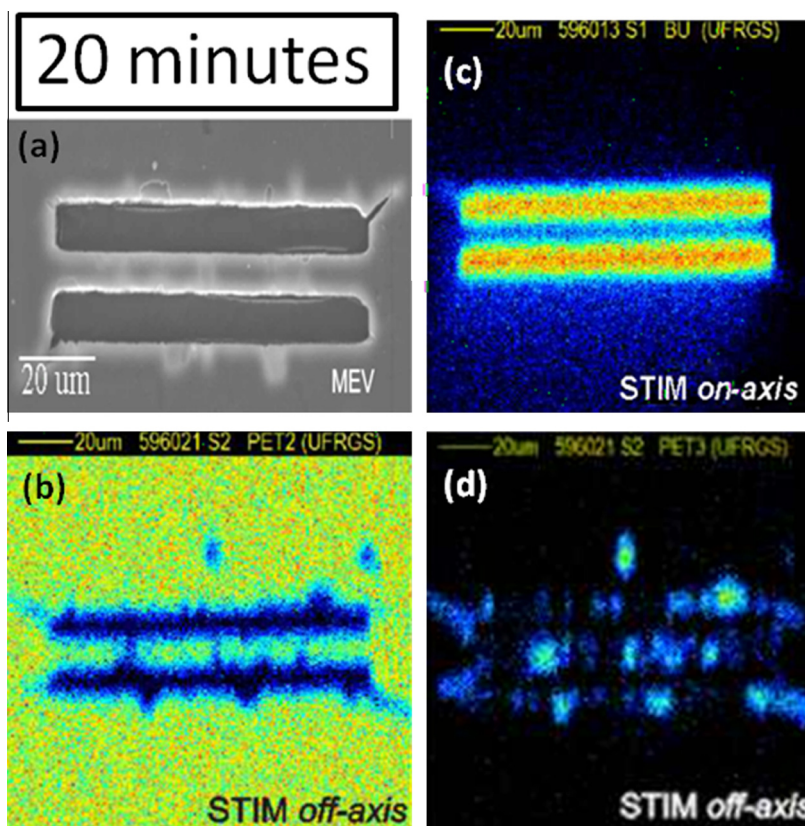

Fig. 1. SEM (a), on-axis STIM (c) and off-axis STIM (b, d) images obtained for the rectangular patterns after 20 min of etching. The PET foils were irradiated by 3.0 MeV protons and etched by a solution of 6 M NaOH. STIM measurements were carried out with 1.0 MeV protons impinging on the polymers. STIM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

3. Results and discussion

Despite the foils were already perforated after 5 min of etching, longitudinal and lateral bulk etching still continued, leading to rectangular structures with an area of approximately 1000 μm². Fig. 1 shows SEM and STIM images of the rectangular patterns obtained after proton irradiation and 20 min of etching. An interesting feature observed in the SEM image is the appearance of buried structures along the patterns. On- and off-axis STIM images reveal the same structures which resemble cavities generated by the etching procedure. Such cavities have been observed in morphological studies of similar channel-like structures [15]. These results indicate that a careful choice of parameters related to the irradiation and to the etching is of utmost importance as far as nearby structures are concerned. Depending on the distance between the structures, the etching procedure may create buried communicating channels connecting the structures, which may hamper their use in particular applications.

From the analysis of the STIM and SEM images, it was possible to obtain the thickness of the foils as a function of the etching time. These results are shown in Fig. 2. A linear fitting of the data yields the etching speed of the bulk polymer. Under the present parameters, this speed is $V_b = (0.10 \pm 0.01)\,\mu m\,min^{-1}$. This value is compatible to the etching speed of lateral portions (length and width) of these structures [15] and is much smaller than the etching speed of the region where ion tracks were formed. Therefore, as the etching time increases, the foil thickness decreases and, at the same time, the area of the holes increases. The combination of these two processes has an impact on the measurement of the currents as discussed below.

The current amplitudes and phase shifts between the electrodes measured with the electrolyte (NaCl) and with pristine PET foils immersed in the electrolyte are shown in Fig. 3. From the phase shift φ between the applied voltage and the current response it is possible to identify different regimes: purely capacitive ($\varphi = -\pi/2$); both capacitive and resistive ($-\pi/2 \leqslant \varphi \leqslant 0$); purely resistive ($\varphi = 0$); and inductive or memristive ($\varphi > 0$). The results of the current and phase shifts measured with the electrolyte only are practically constant over a wide range of frequencies from 100 Hz up to 1 MHz. As shown in Fig. 3b the phase shifts confirms that the electrolyte presents basically a capacitive behavior. Indeed, the NaCl solution is abundant in ionic species and therefore
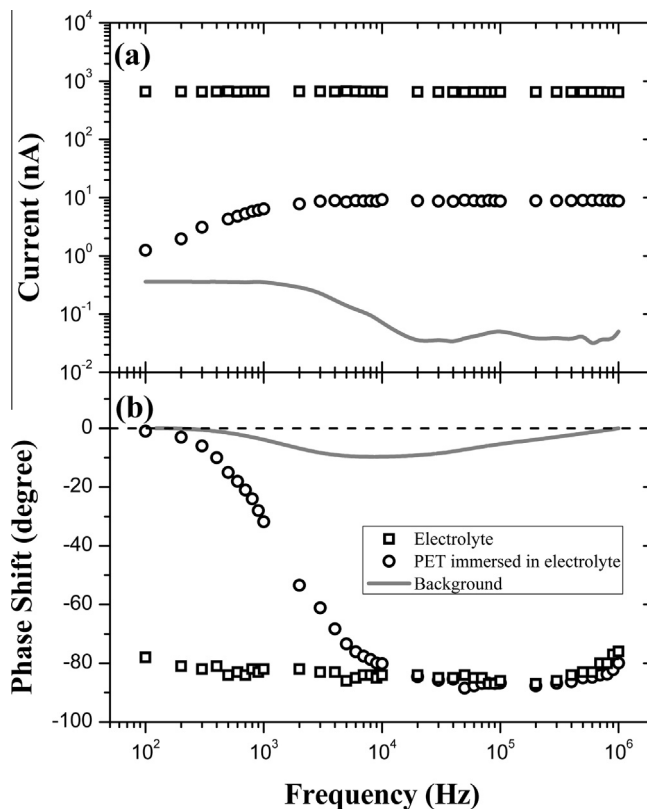
Fig. 3. Current (a) and phase shift (b) as a function of the frequency for the electrolyte (open squares) and pristine PET foil immersed in the electrolyte (open circles). The electrolyte consists of 5 M NaCl. The gray line stands for the instrumental background measured over the entire frequency range.

its response to the external electric field is sufficiently fast even at higher frequencies.

The currents measured for pristine foils soaked in electrolyte (Fig. 3a) show a slight increase between 100 Hz and 1 kHz, reaching about 10 nA at 10 kHz and stabilizing at this value up to 1 MHz. Therefore, this result reveals that the impedance of PET foils immersed in electrolyte is of the order of 1 GΩ. In order to understand the reasons of such relatively low impedances, PIXE experiments were carried out with 2.0 MeV protons to check the composition of the pristine foils. The results show that the foils contain considerable amounts of Ca and traces of Ti and Fe. These impurities, together with the diffusion of water into the polymer that makes these ions dissociate and with the ions from the electrolyte, might be responsible for the observed PET conductivity above 1 kHz.

The phase shifts for the pristine PET foils shown in Fig. 3b indicate an increasing capacitive behavior as the frequency increases from 100 Hz up to 10 kHz, where it reaches and keeps an almost pure capacitive behavior up to 1 MHz. For higher frequencies, the capacitive component tends to decrease since the polarization of the polymer decreases for very rapid changes in the electric field. This overall behavior was observed for irradiated and etched PET foils as well. Fig. 4 shows the average of the phase shifts measured for the irradiated and etched PET foils. This result indicates that despite the influence of the decreasing thickness of the foil and the increasing area of the structures as a function of the etching time, the resistive behavior at low frequencies and the capacitive behavior at higher frequencies are preserved.

The currents were measured for different frequencies ranging from 100 Hz up to 1 MHz and the results are shown in Fig. 5. The relatively small uncertainty (represented here by the standard
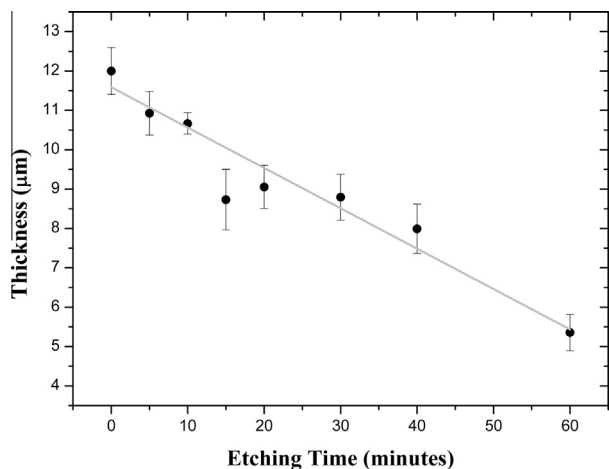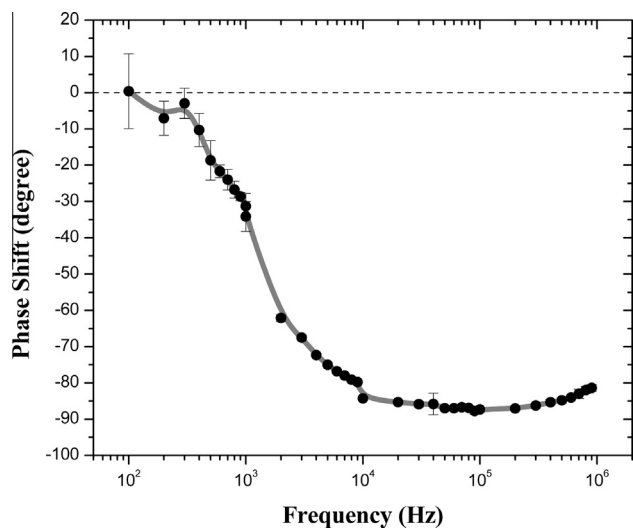

Fig. 2. Thickness of the PET foils as a function of the etching time. Each data point represents several measurements obtained from the analysis of the STIM and SEM images. The uncertainties stand for the variance of the data. The gray line is the result of a linear fitting to the data.

Fig. 4. Phase shift as a function of the frequency for irradiated and subsequently etched PET foils. Each data point represents the average results obtained from the foils etched during 5, 10, 15, 30, 40 and 60 min. The uncertainties represent the variance of the data. The gray line was drawn to guide the eye.
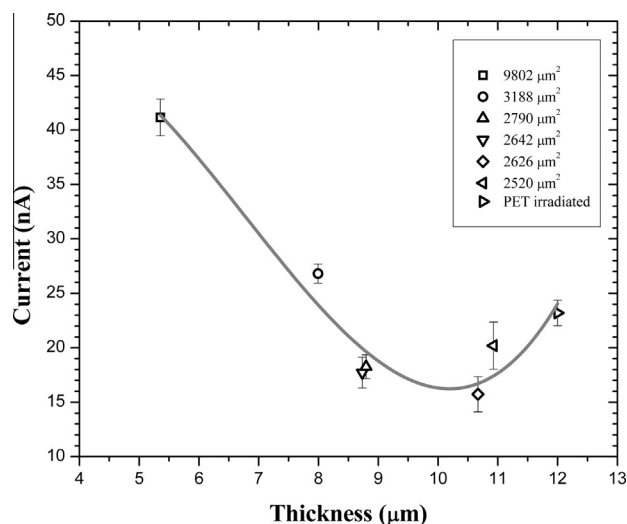

Fig. 5. Current as a function of the thickness of the foils. The data correspond to different etching times shown in Fig. 2 except that at 20 min due to experimental problems. The point at 12 µm was irradiated but not etched. Each data point represents the average results obtained from the measurements carried out at 100 Hz, 1, 10, 100 and 1000 kHz. The uncertainties stand for the variance of the data. The sum of the individual areas of the structures are marked for each corresponding foil thickness. The gray line is to guide the eye.

deviation) of the data means that the current does not change appreciably for different frequencies. However, the magnitude of the current does change from foil to foil. The general trend indicates that upon the first contact of the electrolyte solution with the foil, the transmitted currents decrease. This is usually understood as the result of the polymer's swelling upon water uptake. For thicknesses around 10 µm, corresponding to etching times longer than 15 min, the transmitted currents through the foils start to increase, indicating the effects of the degradation of the polymer. After about 20 min of etching, the transmitted currents increase in a linear fashion with further etching time. This can be interpreted as the result of both the lateral widening of the microstructure and the reduction of the foil thickness by the etching procedure.

4. Conclusions

In this work, 12 µm thick PET foils were irradiated with 3 MeV protons and subsequently submitted to a chemical attack. Due to the relatively high fluences employed in the present experiments, 5 min of exposure of the foils to the etchant (6 M NaOH) was sufficient to corrode the structures throughout, leading to holes with an approximate area of 1000 µm^2.

The morphological results show that hidden cavities are produced during the etching procedure. Such cavities may pose severe problems when nearby structures are constructed since they can establish undesirable connections among the structures, which may affect its primary purpose. Therefore, when structures in polymers are obtained through proton beam writing and subsequent etching, the distance among the structures and the irradiation and etching parameters must be carefully chosen in order to obtain the desired functionality.

In general, a resistive behavior was observed for all foils (pristine and irradiated) studied in this work for frequencies between 100 Hz and 1 kHz. Above this frequency, the resistive component gives room to a strong capacitive behavior that persists up to higher frequencies. However, at frequencies close to 1 MHz, the capacitive component appears to decrease. This effect is related to the response of the polymer's polarization due to the very rapid changes of the electric field. This overall picture appears to be independent of the thickness of the foils and of the area of the etched structures.

The thickness of the foils decreases linearly with the etching time. On the other hand, the current measured through the foils increases almost linearly for decreasing foil thicknesses. This effect results from the overlapping of two factors, namely the decrease of the foil thickness and the increase of the area of the holes. Under the present experimental parameters, the sudden rise of the current takes place for foils with thicknesses below about 9 µm. Finally, different frequencies have little impact on the measurement of the current measured through the foils as a function of the thickness.

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