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The AFM and XPS Investigation of the Surface of Polyethylene Terephthalate Irradiated by High Energy Ions

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Specific features of the surface chemical structure of the nuclear membranes based on polyethylenetherephtalate are discussed. The AFM and XPS were used as the tools. A considerable quantity of hydroxyls and carboxyls was found to be present on the surface of the membranes. A combination of the AFM and chemical derivatization technique (CDT) were used to make an attempt of determining the local distribution of functional groups along the membrane surface.

1. Introduction

Various techniques have been used to study the structure of polymer-based nuclear membranes. The investigation of peculiarities of chemical structure of their surface by means of the AFM and XPS in combination with the chemical derivatization technique (CDT) will hopefully add some valuable information on their structure and allow a controlled modification of their characteristics. The focus of the paper presented was the investigation of peculiarities of physicochemical structure of the surface of polyethyleneterephthalate (PETP) based nuclear membranes by means of the AFM and XPS, as well as the evaluation of the potential application of the CDT in the AFM determination of the localization of different functionalaties on the membrane surface.

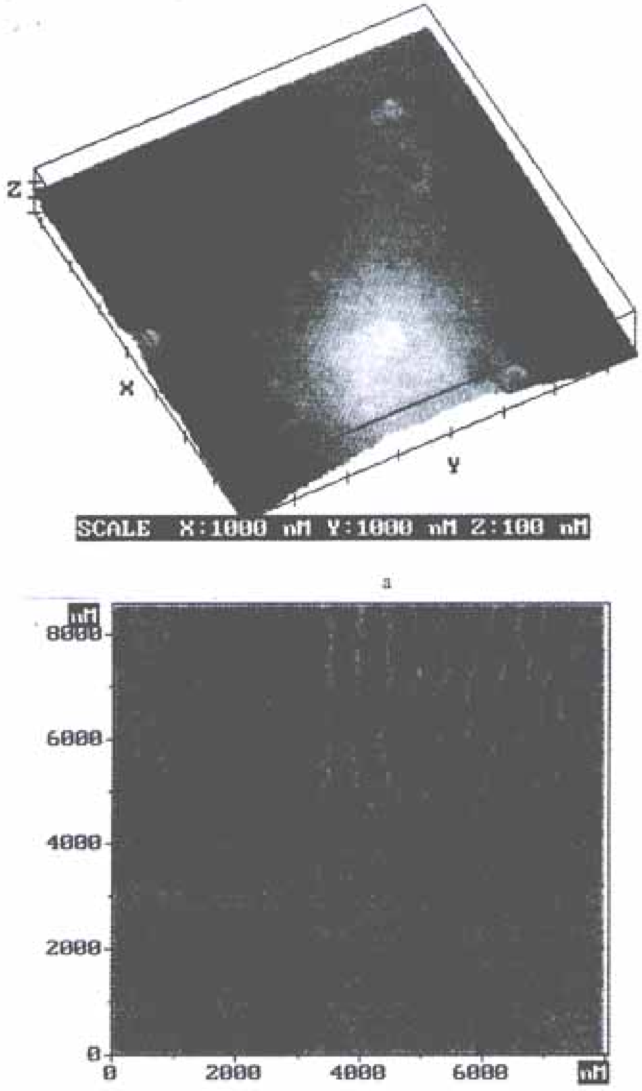
2. Experimental

The membranes were prepared by irradiation of the PETP film with Xe-ions.

The density of irradiation was $1 \cdot 10^8$ ion/cm^2. The surfaces of both the initial PETP film and the resulting membrane were investigated. The AFM images of the sample surfaces were measured at room temperature in air on the Solver P4 microscope (NT-MDT Corporation) in contact mode. The rectangular Si-cantilever (NT-MDT Corporation) 250 μ long with a force constant of the order of 0.10 N/m was used. The surface topography was judged from the roughness parameters, namely, the height amplitude S_y and t mean root square value S_q on different surface parts with the dimensions 2×2 μ. The relative hardness of the polymer sample surfaces was determined according to Ref. [1]. The ES2401 spectrometer was used for the XPS investigations [2]. For hydroxyl groups identification the CDT method was used [3]. Trifluoroacetic anhydride (TFAA) was used to label hydroxyl groups.

3. Results and Discussion

Fig.1a depicts the image of a membrane surface which indicates the highly nonuniform topography of its surface. Fairly smooth areas ($S_y = 61$ nm, $S_q = 10$ nm) and areas with detailed topography ($S_y = 99$ nm, $S_q = 17$ nm) can be distinguished. It was found during determination of the surface layer hardness that indentation of the initial PETP-surface took place at a force 60 nN. As low as 15 nN was enough to cause indentations on the membrane indicating a decrease in the membrane surface layer hardness. This may be a consequence of radiolysis and ething processes used in the process of membrane preparation from PETP. It was found from the XPS analysis that a substantial quantity of polar functionalities – hydroxyl and carboxyl groups – are present on the membrane surface. An attempt was made to determine the presence and spatial localization of these groups on the investigated surfaces by means of the AFM, and the force–distance curves were measured with this purpose. The analysis of the results obtained demonstrated that for both the initial PETP and membrane the cantilever spring force was not enough to tear the probe off the sample surface which is an indication of a strong probe-sample interaction. Since the probe surface consists of polar molecules of silicon oxide, this interaction testifies the presence of polar functionalities on the initial PETP surface [4], which is in agreement with the XPS data. After derivatization of the surfaces of the investigated samples with TFAA, the hydroxyl groups present will be blocked by less polar fluorine-containing groups, resulting supposedly in a decrease of the probe-sample interaction force in the hydroxyl localization site, and in changes in force-distance curves. It has really become possible to measure the force-distance curves and to determine the magnitude of the tip detachment force practically for the whole surface under analysis excluding the protuberances.



a

b.

Figure 1.) AFM image of the membrane surface; b) AFM image of the surface of PETP after hardness test.

Along the perimeter of a pore, at 100 nm from its edge, the obtained force-distance curves were practically the same. The average detachment force was 13.5 nN. It has increased up to 18 nN with the distance from the pore (Fig.2).

4. Conclusions

Thus, we can conclude that each surface part is characterized by its own

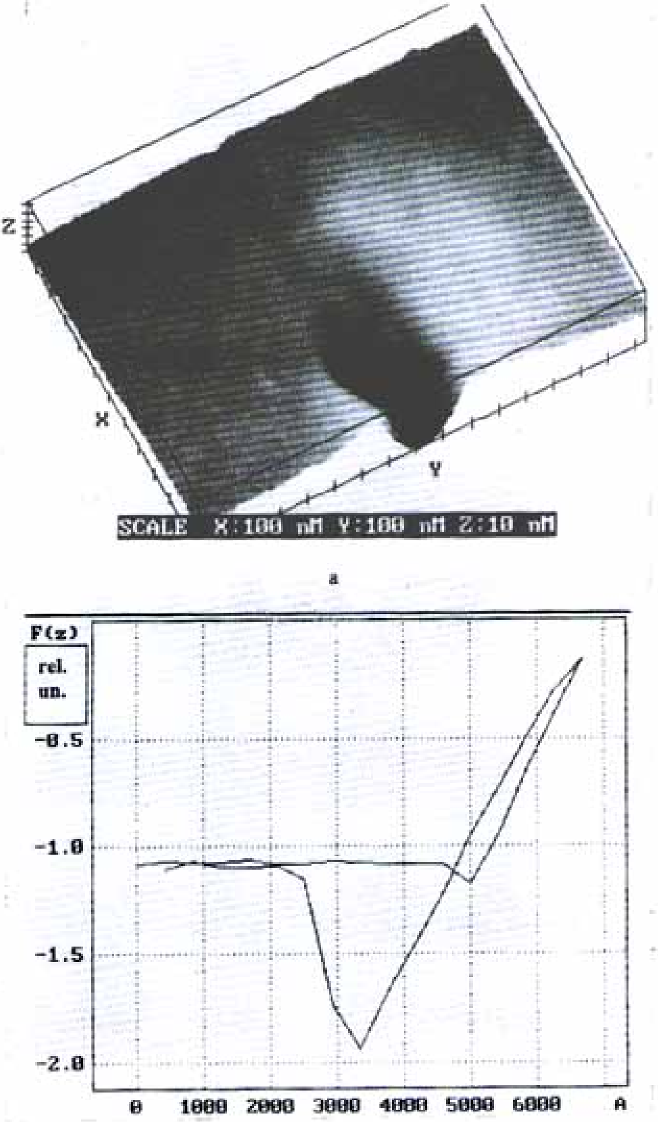


Figure 2.) AFM image of the pore on the membrane surface; b) force-distance curve near the pore after derivatization reaction with TFAA.

adhesive force, and hence, hydroxyls are distributed over the membrane surface non-uniformly. An increased concentration of these groups is observed near the pore edges while it drops with the distance from the pore. A high adhesive force near the protuberances may be indicative of the presence of polar functionalities of different chemical nature in these areas. Based on the experimental results, we hope to obtain a map demonstrating the distribution of the functionalities over the surface of the investigated samples.

Acknowledgements

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