Oxidative Degradation Preparation of Porous Polymer Samples for SEM

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INTRODUCTION

Scanning electron microscopy is widely employed to determine the structural characteristics of different porous materials: sorbents, catalysts, microfiltration and ultrafiltration membranes, etc. Among microfiltration membranes, the so-called track-etch membranes are of special interest because of their unique morphology [1]. Track-etch membranes (TMs) are manufactured by irradiation of polymer films with high-energy ion beams and subsequent chemical etching. As a result, a system of through pores (parallel or nonparallel to one another) is formed in the film. Depending on the irradiation and etching conditions the pore channels can be shaped as cylinders, cones or other. Comprehensive information on the membrane structure can be obtained by analysis of the images of both the membrane surfaces and cross-sections. The latter is realized by preparation of fractures of the membrane samples [2-5].

The absence of strain in the fractured samples is an important requirement of this technique. Otherwise the fracture surface fails to represent the primary pore structure of the object. To avoid a residual strain, a sample is immersed in liquid nitrogen and broken. This procedure is a standard practice in SEM investigations of polymer morphology. However, even under such conditions most conventionally used polymers such as polyethylene terephthalate (PET) or polypropylene (PP) do not become brittle enough to break without strain. Under the action of an applied force, the polymer in a glassy state undergoes a forced elastic strain that does not disappear after removal of the stress. Ideally, the forced elastic strain tends to zero below the polymer brittleness point (fracture transition temperature) [6]. However, in actual practice this is hardly feasible even at liquid nitrogen temperature. A way to solve this problem is the use of costly equipment with the help of which a sample is cooled down to -260°C and fractured with a special device [7].

Analysis of published SEM data on TMs [2-5] shows that, in most cases, the freeze fractures made at the temperature of liquid nitrogen are of poor quality; the fracture surface has no visible strain only in the case of large pore diameters (>1µm) and high porosities (when the volume of pores is about 30% or so). The effect of strain increases with decreasing pore diameter: the fracture edges look like a fringe, and the walls between adjacent pores are stretched. As a result, pores in the membrane bulk look larger than the openings of pores at the surface of strain-free regions. Typical views of such freeze fractures are shown in Figs 1a and 1b.

This study was aimed at developing simple methods that would make it possible to prevent strain in polymer samples in the course of their preparation and obtain reliable information on the pore structure. We have applied the developed methods to track-etch membranes produced of different polymers.

MATERIALS AND METHODS

Samples of PET, PP and polycarbonate (PC) track-etch membranes were chosen for this study. The membranes were produced at the Flerov Laboratory of Nuclear Reactions (JINR, Dubna) [1]. Pre-treatment of the same samples was carried out by gamma-irradiation in air (137Cs source, dose rate of 0.5 Gy/s) or by photo-oxidation with ultraviolet light exposure (lamp emission peak at 310-320 nm, photon flux of 1017 cm-2 s-1). Thermo-oxidation of PP samples was performed in air at 120°C. The samples were fractured with two tweezers either in liquid nitrogen or in air at room temperature. The fractures were gold coated in a JFC-1100 ion sputter (1200 V, 10 mA, 2-3 min) and viewed using a JSM-840 scanning electron microscope in the secondary electron mode.

RESULTS AND DISCUSSION

We used gamma-irradiation, photo- or thermo-oxidation degradation to embrittle samples to be fractured. With proper selection of the conditions for the polymer degradation reaction,

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Type of pre-treatment</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Gamma-irradiation in air Exposure to ultraviolet light</td>
<td>Dose of 2-5 MGy, room temperature Photon flux $10^{17}$ cm$^{-2}$ s$^{-1}$, 10-20 h, 30-50°C</td>
</tr>
<tr>
<td>PC</td>
<td>Gamma-irradiation in air Exposure to ultraviolet light</td>
<td>Dose of 2-5 MGy, room temperature Photon flux $10^{17}$ cm$^{-2}$ s$^{-1}$, 20-40 h, 30-50°C</td>
</tr>
<tr>
<td>PP</td>
<td>Gamma-irradiation in air Exposure to ultraviolet light Heat treatment</td>
<td>Dose of 50-100 Kgy, room temperature Photon flux $10^{17}$ cm$^{-2}$ s$^{-1}$, 10-100 h, 30-50°C 120°C, 10-20 h</td>
</tr>
</tbody>
</table>

it was possible to substantially change the mechanical properties of the polymer, keeping sample morphology unaltered. Techniques based on both gamma-radiation and photo-oxidation degradation were suitable for PET. Its macromolecules contain aromatic rings that render the polymer radiation resistant [8]. The gamma-radiation absorbed dose of about 2 MGy halved the ultimate tensile strength of PET. The decrease in the ultimate strength was accompanied by a significant reduction in the ultimate strain of the sample [8].

We exposed PET and PC TMs to gamma rays up to different doses in the MGy range. At the absorbed doses of 5 MGy the samples became so brittle that good fractures could be made even at room temperature. These techniques are illustrated by the electron micrographs presented in Figs 2 and 3. One can see that the partitions between pores broke without any strain. The fractures of polymer samples with track-etch pores looked like similar objects made of inorganic glass [9]. As compared to Figs 1a and 1b, the internal pore structure was revealed much better. Figure 2 clearly shows that pores in the PET membrane sample are straight, long cylinders crossing the film at different angles. The pore diameter was practically constant throughout the membrane thickness. In contrast, the internal structure features were obscured in the case of the conventional freeze fracture presented in Fig 1b. Embrittlement of the samples using gamma-irradiation was also effective for polypropylene TMs. The relevant dose for polypropylene TMs was much lower (~50 kGy) in accordance with a much lower resistance of the polymer to ionising radiation [8]. It should be taken into account that the radiation resistance and the rate of post-radiation oxidation of PP strongly depended on the presence of stabilizing additives, in particular, antioxidants. To promote the process of sample degradation in the gamma-radiation field, the antioxidant should first be removed from the polymer matrix using extraction by a solvent (e.g. chloroform) at room temperature. After a few hours of extraction, the sample was allowed to air dry to remove the solvent. In this case, the track membranes, produced from isotactic polypropylene, kept their sizes unaltered and exhibited no changes in the parameters of the pore structure.

Figure 4 shows the results for another version of the method designed for PET, obtained with photo-oxidation degradation. PET is quite resistant to ultraviolet light. However,
Absorption of ultraviolet radiation with wavelengths \( \lambda > 320 \text{ nm} \) was hardly absorbed by PET molecules and, hence, failed to initiate degradation. That is why we irradiated PET-TM samples with lamps having their emission spectrum peak at wavelengths of 310-320 nm, i.e. around the absorption edge. For degradation to be more homogeneous in depth, both surfaces of the specimen were exposed. At a photon flux density of \( 10^{17} \text{ cm}^{-2} \text{ s}^{-1} \), the time required for ultraviolet irradiation of the samples was 20 h. After such preparation, the sample was easily broken with tweezers at room temperature. A PET membrane sample with cigar-shaped pores, produced by a special etching technique [10], is shown in Fig 4. Observation of the brittle fracture surface clearly revealed that the porosity changed substantially with the membrane thickness. The pore diameter was larger in the depth of the film and decreased towards both surfaces. Analysis of the membrane cross-section made it possible to estimate the pore diameter as a function of the distance from the film surface and to evaluate the total bulk porosity (which, in this case, agreed with the porosity value obtained with gravimetric analysis). This is an example of an object where investigation of the surface yielded totally inadequate information on its internal structure. However, examination of properly prepared fractures allowed us to reveal the morphological features of this type of membrane.

Photo-oxidation degradation was also efficient in the preparation of PP TMs samples. Absorption of ultraviolet radiation with wavelengths \( \lambda < 310-320 \text{ nm} \) by a matrix of PP TMs was much weaker as compared with PET; therefore, the mechanical properties of the polymer were altered uniformly with the sample depth. On the other hand, a longer exposure was needed to achieve a brittle fracture. The third method we mentioned above, which is based on thermo-oxidation degradation, was suitable for PP TMs. An optimal procedure we have chosen from measurement runs performed under varying conditions was treatment at 120°C for 10-20 h. A higher temperature cannot be recommended because the PP specimen may shrink. The image of the fracture surface obtained this way is presented in Fig 5. We emphasize that the process of degradation due to thermal oxidation also depended on the stabilizing additives, their type, and concentration in the polymer. In this connection, the time of thermal processing needed to embrittle the sample should be selected individually for each type of PP film. A characteristic difference in the shape of the pore channels in PC and PP is easily seen in Figs 3 and 5. In the former case, the pore channels were cylindrical, while, in the latter case, the pores were tapered along the direction from the surface to the film centre. This difference was determined by the high (up to several thousand) track to bulk etch rate ratio in PC, whereas, in PP this quantity was two orders of magnitude lower.

In conclusion, the recommended conditions for the pre-treatments of porous polymers are summarised in the Table. The developed methods are a simple and easily accessible tool for the preparation of specimens for SEM investigation. The principle of the methods can be extended to other polymers and to materials other than track-etch types of membranes.

REFERENCES


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