Filtration Membranes, Water and the ESEM

A Thermodynamic Study and In Situ Characterization

Great progress in the filtration performance of microfiltration membranes has been achieved in the past few years. As a consequence the structures of the respective membranes have become more and more intricate. New microscopic characterization methods are therefore necessary to reveal the membrane structure in full detail. The environmental scanning electron microscope (ESEM) has the potential for also studying microfiltration membranes in their wet state. The dynamics of the wetting and drying of the membrane surface can be imaged at sub-µm resolution. Simultaneous temperature measurements at both membrane surfaces, macroscopic parameters, provide information about the progress of these processes in the membrane interior, thus complementing the microscopic results gained from the images.

Introduction

The ESEM is a versatile tool, which besides imaging the membrane surface, also enables three dimensional (3D) analysis of the inner membrane structure. For this purpose a slice and view tool can be mounted into the microscope chamber. The interior membrane structure can also be imaged by cutting thin slices off the membrane in an automated manner and subsequently recording the residual blockface. This provides detailed information on membrane morphology such as pore connectivity and specific surface area [1].

But the filtration performance of membranes is also strongly influenced by other parameters, e.g. the chemical properties of the pore surface. This requires the dynamic behavior of the membrane to be investigated during the wetting and drying process, which can also be done in the ESEM [2].

In addition to the conventional high vacuum (HV) mode, this instrument offers a pressure range between 0.1 and 20 torr [3]. In this study water vapor was used as chamber gas. ESEM analysis of the wetting and drying process of the membrane surface requires chamber pressures above and below the dew point. To enable work at sufficiently low pressures, the experimental setup needs to be cooled. A special cooling stage designed for the investigation of flat membranes was developed. The membrane is fixed between two cooling clamps, which are cooled to
a temperature of 4°C (fig. 1). As the chamber pressure exceeds the dew point (6 torr), water starts condensing at the cooling clamps, consequently wetting the membrane. By reducing the pressure below the dew point the membrane begins to dry. The temperatures of both surfaces of the membrane were measured using two micro thermocouples (Type T, COCO-001 from Omega, Newport) [fig. 1, insert a]. The number and size of dry and wet pores can be determined by simultaneous imaging of the membrane surface.

**Materials**

The investigation was carried out on poly-ethersulfone (PES) membranes, widely used in waste water treatment, the beverage industry and many areas of bio-technology due to their resistance to many aggressive substances.

One must be aware, however, that organic materials are especially prone to irradiation damage. This is even more critical when additionally water is present, because electron irradiation of water creates many highly mobile free radicals, which too can attack the organic material [4]. But for PES membranes irradiation damage was observed only at very high magnifications.

The new generation of microfiltration membranes offers a very asymmetric pore structure. Figure 2 shows the cross-section of a Dura PES 450 membrane (Membrana Wuppertal, Germany). The bright areas represent the membrane matrix; the dark areas represent the pores. The membrane consists of the separation layer and a backup layer. The separation layer consists of small pores and is responsible for the filtration process, whereas the backup layer should provide mechanical stability and protect the separation layer from outside damage. The wide pore structure of the backup layer offers high penetration and a great "loading volume", which results in low fouling tendency. This special structure provides optimal flow rates due to the thin separation layer, necessary for many filtration applications [5].

The asymmetric pore structure is provided by a specially controlled production process. The roll side of the membrane often has much larger pores than the air side. The flow of the liquid inside the membrane is determined by the separation layer, due to the small size of its pores and their correspondingly high capillary forces. The ESEM, however, can only image the membrane surface, because the penetration depth of the electrons at the energies used is only a few µm. However,
the temperature characteristics recorded at the membrane surfaces during the wetting and drying process give additional information about both the interior structure of the membrane and the distribution of the water inside the membrane.

**Image Processing**

Pores filled with water appear brighter than the dry pores in the SEM images. In the dry pores the primary electrons penetrate deep into the membrane and the detector becomes shadowed. Figure 3 shows a sequence of images of the membrane surface (air side) during the drying process. In figure 3a the membrane surface is completely wetted. No dry pores are visible and the membrane surface appears dark, nearly no contrast differences are visible - an indication of a homogenous water film covering the surface. In figure 3b the drying process has already started, brightness differences and some of the big pores are already appearing. In figures 3c and 3d an increasing number of pores have run dry.

Thresholding can be used for image segmentation. All image pixels with a grey value below a specified threshold are regarded as belonging to a pore, while the others represent the membrane material. Thus the number and size of the pores can be determined [6]. The diagram in figure 4 shows the results of such an evaluation of a series of images of the drying process (analyzed area: 140 µm x 120 µm). The number of dry pores and their mean pore size are plotted as a function of time. Large pores dry first as a consequence of the capillary forces at the beginning of the drying process. At the end of the drying process the smaller pores also dry up and so the mean size of the dry pores decreases. Due to the large number of small pores, a steep increase in the characteristic occurs as soon as they start drying up.

**Temperature Characteristics and Membrane Structure**

A dry looking membrane surface does not imply that it is also free from water inside. The electron microscope images can only give information about the water distribution at the surface. As the water inside the membrane evaporates during the drying process via the surface pores, however, measuring the membrane surface temperature can give additional information about the water content inside the membrane structure. This is due to the fact that the clamps holding the membrane are cooled down to a temperature of 4°C. As the membrane itself has extremely poor heat conductivity, its temperature is mainly controlled by the temperature of the water inside. As soon as this is completely evaporated, a steep increase in the temperature can be observed, and the dry membrane reaches the temperature of the surrounding gas.

Figure 5 shows the temperature characteristics recorded at both membrane
surfaces during the wetting and drying processes. At the beginning of the experiment the temperatures decrease, but the membrane surface looks dry (no image, time period 1). This is an indication of the wetting of the separation layer. The temperatures reach a constant value once the membrane surface has become wet (time period 2, fig. 3a). The drying process is initiated by reducing the chamber pressure from 6.5 torr to 4.5 torr. This pressure change causes an expansion of the chamber gas, entailing a drop in its temperature, as is also visible in the diagram. Afterwards the temperatures at the two membrane surfaces begin to increase, but with different slopes, due to the asymmetric membrane structure (time period 3, figs. 3b-d). Although the membrane surface already looks dry, the temperatures at the membrane surfaces have not yet reached the initial value. The final strong increase in temperature indicates the drying of the inner membrane separation layer (period 4). Thus the temperature characteristics reflect the interior membrane structure.

Summary and Outlook

The ESEM is a very useful tool, which allows the 3D reconstruction of complex porous materials and also enables in situ investigations of these structures in a wet environment. Simultaneously, it also provides the opportunity to record microscopic (number and size of the dry and wet pores) and macroscopic parameters (surface temperature characteristics). These parameters reflect both the surface and the interior structure of the porous material, and also provide information about the behavior of these structures in a wet environment. The investigation of a greater number of membranes with different porosity is necessary to gain a deeper insight into the potential of the method and to be able to fully exploit its possibilities.

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References


Contact
Dipl. Ing. Herbert Reingruber
Dr. Armin Zankel
Dr. Peter Pölt
University of Technology Graz
Institute for Electron Microscopy and Fine Structure Research
Graz, Austria
www.felmi-zfe.at

Contact

Techn. Univers. Graz
Steyrergasse 17
8010 Graz
Austria
Phone: +43 316 873 8335