3D reconstruction & *in situ* characterization of microfiltration membranes in the ESEM

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Introduction

Microfiltration membranes made of polymeric mateials are used in a great variety of applications such as waste water treatment, filtration of colloids and particles in the beverage industry etc.

The increase in the complexity of the structure of these membranes requires also more and more sophisticated characterization methods [1]. Two recently developed methods based on electron microscopy will be presented:

➔ 3D reconstruction by use of automated serial sectioning and imaging in the environmental scanning electron microscope (ESEM). Quantitative determination of many membrane parameters is possible, but the volume investigated is very small.

➔ Investigation of the wetting and drying of membranes in the ESEM. Apart from a (more qualitative) characterization of the membrane structure this method enables also to study the interaction between the membrane and water. The volume investigated is much bigger than in case of 3D reconstruction.

PES microfiltration membranes

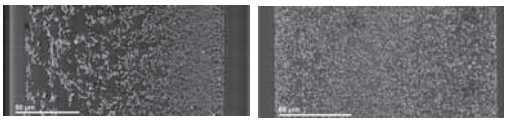


Fig. 1. SEM images (BSE) of the cross sections of the polyethersulfone (PES) membranes Membrana DuraPES®450 (left) and Sartorius 15406 (right).

➔ Images of the cross sections of membranes recorded by scanning electron microscopy provide quick and rough information about the asymmetry of the structure and the pore size distribution.

3D reconstruction

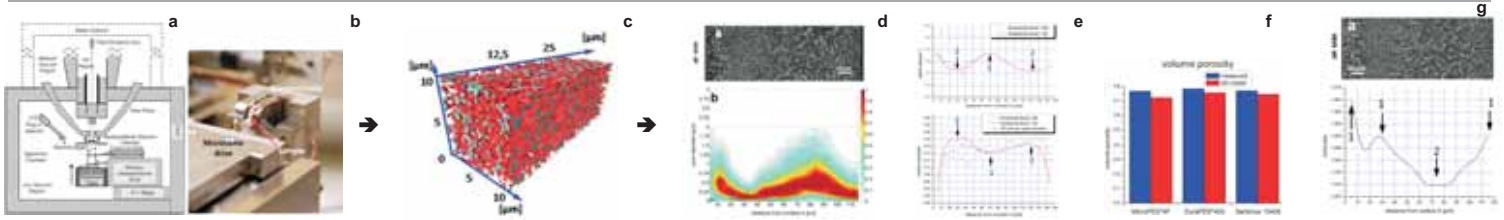


Fig. 2. a: Schematic of the ultramicrotome (Gatan 3View™) mounted in the specimen chamber of the ESEM; b: Image of a part of the microtome; c: 3D reconstruction of the separation layer of the membrane DuraPES®450 (see also Fig. 1); d: pore diameter distribution along the cross section of the membrane MicroPES®4F; e: specific surface area and volume porosity along the cross section of the membrane Sartorius 15406; the dependence of the results on the threshold value chosen for image segmentation is shown; the volume porosity is also compared to the porous area fraction calculated from a 2D image; f: comparison of the calculated volume porosities wth the measured values; g: change of the tortuosity along the cross section of the membrane MicroPES®4F. For the 3D reconstructions and the calculation of the parameters the software AVIZO® Fire was used.

➔ Automated serial sectioning and imaging of the block face (maximum area ~ 0.5 x 0.5 µm², slice thickness: 50 nm) makes recording of the image stacks for the 3D reconstruction less tedious and time-consuming [2]. Also all the images are already aligned and thus a realignment is not necessary. The membrane was embedded in resin. The contrast difference between resin and membrane in the SEM images is due to the sulfur in the PES membranes.

➔ A great variety of parameters characterizing the membrane structure can be calculated from the 3D reconstruction (see Fig. 2). Fig. 2f demonstrates that calclualted values are in good agreement with measured ones. But from the 3D reconstruction also local variations of the structure can be calculated [3].

Investigation of wetting and drying of membranes in the ESEM

From a 3D reconstruction quantitative parameters characterizing the membrane structure can be calculated. But no information about the chemical nature of the pore walls (hydrophilic, hydrophobic) and generally the interaction of water with the membrane is provided. Such information can be gained by the investigation of the wetting and drying of cooled membranes in the ESEM (Quanta 600 FEG, FEI).

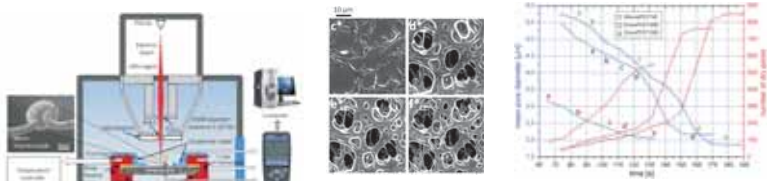


Fig. 3. From left to right: Schematic of the experimental setup; Membrane DuraPES®600 during different stages of the drying process; the mean pore size and the number of dry pores as a function of drying time.

Whereas the membrane surface can be directly observed in the microscope, the temperature measurement serves as a probe for the membrane interior. The vital point is the poor heat conductivity of the membrane material itself. Thus the temperature at different layers of the membrane is dependent on their water content [4].

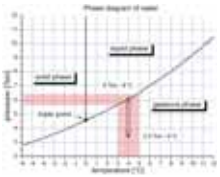
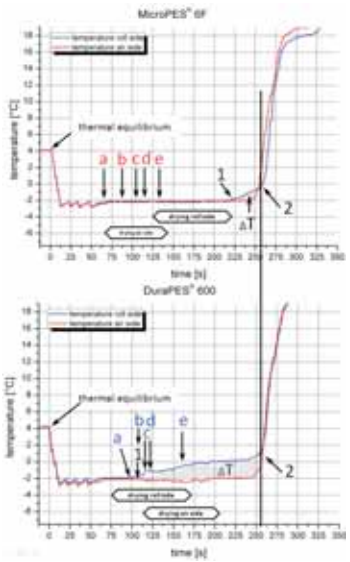


Fig. 4. Phase diagram of water.

The membrane is fixed between copper clamps, which are cooled to 4°C. The variation of the pressure in the specimen chamber of the microscope enables the control of the wetting and drying of the membrane. First water condenses at the cooled copper clamps, subsequently it penetrates the membrane due to the capillary forces.



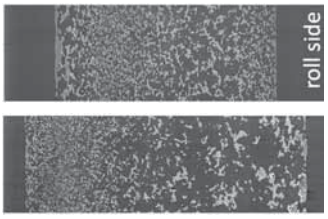


Fig. 5. Left: the temperature at both membrane surfaces of the cooled membranes (4°C) as a function of the drying time for the membranes MicroPES®6F and DuraPES®600. The bars show the time during which the drying of the respective membrane surface happend as observed in the microscope (see Fig. 3). Both, the surface temperatures and the drying of the membrane surface are recorded simultaneously.
Right: SEM images (BSE) of the cross sections of the membranes MicroPES®6F (top) and DuraPES®600 (bottom).

Conclusions

➔ 3D reconstruction of membranes is substantially simplified by automated serial sectioning and imaging. Besides the determination of the global parameters also their local variations along the cross section can be calculated. But the volume investigated is very small.

➔ Investigation of the wetting and drying of membranes in the ESEM provides information about both the membrane structure and the interaction of water with the membrane. A change in the properties of the pore walls or membrane fowling should cause a change in the respective temperature curves. The volume is big enough to get statistically relevant results.

References

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