Journal of Membrane Science 399–400 (2012) 86–94

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

A new *in situ* method for the characterization of membranes in a wet state in the environmental scanning electron microscope

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ARTICLE INFO

Article history:
Received 24 November 2011
Received in revised form 24 January 2012
Accepted 26 January 2012
Available online 3 February 2012

Keywords:
Microfiltration membrane
Pore size distribution
Drying process
Environmental scanning electron microscope
In situ experiment

ABSTRACT

This work presents a new microscopic method for the characterization of microfiltration membranes. It allows the direct observation of the behavior of water at the membrane surface during wetting and drying. For this purpose, an environmental scanning electron microscope (ESEM) was equipped with a special cooling stage, enabling the investigation of wet samples inside the microscope chamber. The images recorded from the membrane surfaces provide information about the number and size distribution of dry and wet pores during the drying process. Additional information about the wetting and drying of the membrane interior was gained by simultaneously measuring the temperature of both membrane surfaces as a function of time. The basic mechanism is the strong influence of the evaporation of cooled water from the membrane interior on the membrane surface temperature. These temperature characteristics reflect the interior membrane structure. The correlation between the microscopic parameters, obtained from the observation of the wetting and drying of the surface pores and the temperature characteristic, a macroscopic parameter, enables a qualitative description of the membrane structure. This information also allows the liquid and gas transport inside the complex membrane structure to be studied. In the present work two different types of flat microfiltration membranes were investigated.

1. Introduction

Microfiltration is one of the most important processes in many industrial applications, for example in the beverage industry or waste water treatment as well as in pharmaceutical and medical applications. Membranes used in these applications should offer a well defined molecular weight cut off (MWCO), a high flow rate and low fouling tendency. As the membranes are often also used for filtration of aggressive substances, the used respective membrane material itself plays an important role. Especially membranes made from polyethersulfone (PES) are resistant to many aggressive substances even at high temperatures due to their glass transition temperature of 220 °C.

New designs of PES microfiltration membranes lead to an increase in filtration performance. Most of the recently developed microfiltration membranes offer a very asymmetric pore structure consisting of a thin separation layer and a broad backup or support layer. The separation layer inside the membrane is essentially responsible for the filtration process. The support layer is necessary for the mechanical stability and protects the separation layer from external damage. This asymmetric, so-called "hour glass" structure [1] can be tuned by varying the temperatures at the "roll side" and "air side" as well as the relative humidity at the "air side" during the production process. As a result, the position and thickness of the separation layer changes. Both the thin separation layer and the large-pored structures of the support layer, which strongly reduce fouling tendency and enable high permeability [1].

Scanning and transmission electron microscopy (SEM, TEM) play a major role in the characterization of this "hour glass" structure. The surfaces of the membranes [1] and their cross-section morphologies have already been studied in full detail in two dimensions (2D) [2]. But a complete description of the pore structure is only possible by reconstructing the membrane morphology in three dimensions (3D). 3D reconstruction enables a visualization of the pore network and the calculation of quantitative parameters like the mean pore diameter, the mean pore length, the average number of connected pores, the specific surface area and volume porosity [3]. Subsequently, both the reconstructed 3D model and the calculated parameters can be used as input for fluid simulations.

Such a static model does not, however, provide information about the nature of the membrane pore surfaces, *e.g.* whether they are hydrophilic or hydrophobic, or the interaction mechanisms between pore surfaces and fluid.

The focus of this work was thus on studying the dynamics of the system 'liquid (water)–solid (membrane matrix)–gaseous (water vapor)' during the wetting and drying process of the membrane. The membranes were mounted in an environmental scanning electron microscope (ESEM) and images of the membrane surfaces

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doi:10.1016/j.memsci.2012.01.031

were recorded during the drying process. As a consequence, the change in the number of dry pores and their size distribution as a function of time can be determined. The liquid transport inside the pores is influenced not only by the membrane structure, but also by environmental parameters (pressure and temperature), as well as the properties of the pore surfaces (hydrophobic of hydrophilic). As the contact angle of the liquid is determined by the membrane material, its measurement can give relevant information about membrane hydrophilicity [4]. As PES is a hydrophobic material, manufacturers use different additives for enhancing the hydrophilic properties. The quantity and composition of these additives have an influence on the contact angle. The hydrophilic properties of the pore surfaces are essential for proper filtration performance.

Hydrophobic as well as hydrophilic membranes under wet conditions were studied by de la Parra [5], who used an ESEM for the recording of images of the membrane surfaces during the wetting process. Hydrophobic membranes show water droplet formation at the surface. The droplet shape is in correlation with the hydrophobic level of the membrane material. As the hydrophobicity of the membrane surface increases, the shape of the droplet becomes more and more spherical. The images also show droplet formation at hydrophobic spots at the surface of an otherwise hydrophilic membrane surface. The potential of using an ESEM for localization of less hydrophilic areas was clearly shown. However, the results are more qualitative and do not provide a direct correlation between the membrane structure and the flow of water.

Wang et al. give additionally quantitative data of the swelling behavior of fibers inside a cellulose based Sartobind® cation exchange membrane during water uptake and release in the gas phase. The membrane was not studied under complete wet conditions; however it was shown that small fibers inside the macropores show significant volume change [6].

Jenkins and Donald [7] use a special sample holder for the investigation of cellulose fibers. The water swelling behavior of the fibers was documented by series of images. To get accurate and repeatable data of the swelling behavior, nearly each sample shape (fibers, flat or particles) needs a special "adapted" holder. But contrary to cellulose membranes at polymer membranes a swelling behavior is not to be expected. For the polyethersulfone membranes investigated notable swelling could not be observed.

As porous solid materials show characteristic drying rate curves, the drying behavior of membranes should also give information about the interior porous structure [8]. Staude and Passlack use drying rate curves for characterizing different types of membranes [9]. The change in membrane weight during the drying process was measured by a precise balance to obtain characteristic drying rate curves, which are influenced by both the membrane structure and the membrane material. The direct observation of the membrane surface during the drying process and the simultaneous measurement of membrane weight were not implemented in our actual microscope setup. Instead of the change in membrane weight, we recorded the change in temperature at both membrane surfaces during the wetting and drying of the membrane with cooled water.

It is vital for the investigations that the dry membrane has a much higher temperature than the cooled water. These temperature–time characteristics provide information about the successive wetting and drying of membrane layers with different pore size distributions and thus about the membrane structure, especially for asymmetric membranes. This is mainly due to the dependence of the capillary force on the pore diameter. Thus small pores will dry more slowly than large ones. As soon as the surface of the membrane is dry, it starts warming up, even if inner membrane layers still contain cooled water. This and other effects entail characteristic features in the temperature–time characteristic, which reflect the membrane structure. The advantage of this method over

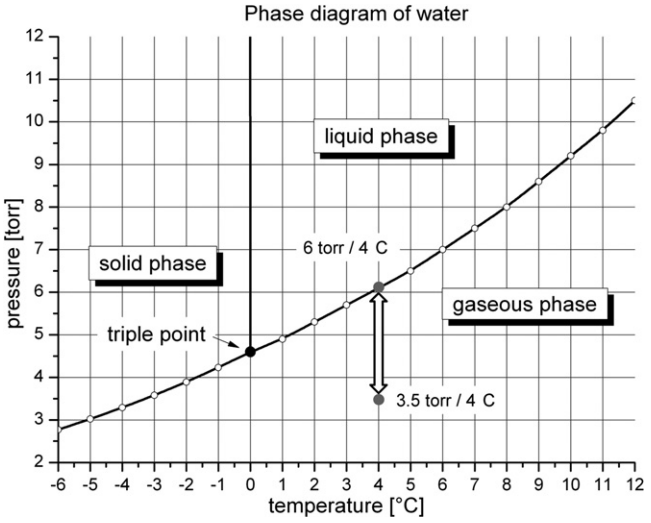

Fig. 1. Phase diagram of water (data points from [6]). The pressure and temperature values used in the experiment are marked.

3D reconstructions is the much larger volume investigated (membrane volume around 15 mm × 5 mm × 0.15 mm). It provides the additional opportunity to study the interaction between pore surface and water. Changes in the properties of the pore surfaces or membrane fouling may result in changes in the temperature characteristic.

If the membrane properties change substantially during operation these characteristics could thus help to find the cause for that change. The correlation of microscopic parameters, obtained by direct observation of the membrane surface, and the temperature, a macroscopic parameter, can provide maximum information about both the membrane structure and the interaction between membrane and water.

2. Materials and methods

The ESEM analysis provides detailed information about the membrane structure in the dry [3] as well in the wet states. Contrary to the conventional high vacuum (HV) mode, this instrument can also be operated in the ESEM mode [10], where the pressure in the specimen chamber can be varied between 0.1 and 20 Torr. This enables the investigation of wet specimens or even liquids (Fig. 1). In this study water vapor is used as the chamber gas. The wetting and drying process can be controlled by changing the pressure between values above (wetting) and below (drying) the dew point (Fig. 1). The sample must be cooled to be able to restrict the wetting to the specimen. Because of the poor heat conductivity of the membrane material, the cooled dry membrane and the cooled water have different temperatures. By recording successive images of the membrane surface, the number, size and size distribution of dry pores as a function of time can be determined. As the cooled water inside the membrane evaporates via the surface pores during the drying process, measuring the membrane surface temperature can give additional information about the water content inside the membrane. At the already dry surfaces a typical temperature rise can be observed, depending on the membrane structure. A correlation between the temperature curves and the results gained from the surface images can thus help in the interpretation of features of the temperature characteristic.

In the present study membranes of the type MicroPES® and DuraPES® (Membrana Wuppertal, Germany) were investigated. These membranes are characterized by a very asymmetric pore structure and consist of a relatively thin separation layer and a