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Influence of the strongly anisotropic cross-section morphology of a novel polyethersulfone microfiltration membrane on filtration performance

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Abstract

Polyethersulfone (PES) microfiltration membranes with remarkably improved filtration performance were recently developed. Subtle changes in the conditions of the phase separation process lead to a very pronounced anisotropic ("hour glass"-like) cross-section morphology of these novel membranes named DuraPES®. Furthermore, due to macromolecular additives, the membranes are permanently hydrophilic. The properties and performance of the DuraPES® membranes are compared to other membranes available on the market, such as AMC Accupor, Osmonics Micron PES, Pall Supor, Sartorius Sartopore, and Millipore Express. Parameters investigated are on the one hand focussed on membrane structure such as pore morphology (from SEM), volume porosity, trans-membrane pore size distribution, contact angles and wetting with water, and trans-membrane streaming potential. On the other hand, membrane performance is evaluated with respect to water permeability, the filtration of a protein solution and the correlated fouling, as well as other filtration tests with more complex feed solutions. Up to >10 times higher filtrate fluxes are observed for the DuraPES® membranes as compared to the other membranes having the same nominal pore size. However, such higher performance is only achieved with the macroporous surface upstream to the feed. The overall analysis of all data shows that the significant advantages of DuraPES® membranes resulted from their special surface and pore morphology.

Keywords: Polyethersulfone; Solvent-induced phase separation; Microfiltration membrane; Structure–performance relationship

1. Introduction

Microfiltration (MF) is a mature unit operation in (bio)chemical and environmental engineering, in biotechnology, life sciences and medicine as well as several other areas [1–3]. One major established application field for MF membranes is the clear filtration of aqueous streams, i.e. the removal of particulate and colloidal matter based on size. Emerging large markets such as the filtration of juices, wine or beer are especially attractive [4]. Improved membrane modules should have a longer service time at the specified performance. Prolonged service times can be achieved by increased membrane areas, improved flow conditions in the cartridge or a higher loading capacity of the membrane itself. Larger, i.e. more than incremental, improvements will typically be achieved only by the use of novel membranes.

In this paper, the membrane polymer polyethersulfone (PES) was chosen because this high performance material provides a high glass transition temperature (T_g ~220 °C), chemical stability against caustics, acids and other aggressive substances as well as high values of tensile strength and elongation at break. In comparison to other novel specialty polymers with similar or even better properties (for example, poly(etheretherketone) [5,6]), PES has become a kind of "standard" material for many membrane manufacturers, because it is reliably available in well-defined qualities and (almost) unlimited quantities. There is detailed knowledge about the formation of porous membranes via non-solvent-induced phase separation (NIPS) [7,8]. With respect to improved membrane properties, modifications of the pore structure and of the surface physico-chemistry had been addressed in several previous efforts. With a given polymer, in this case PES, such modifications can be achieved by additives to the casting solution and by changes in the conditions during the membrane formation process (NIPS) as well as by combinations thereof [9–13]. Another alternative is offered by surface

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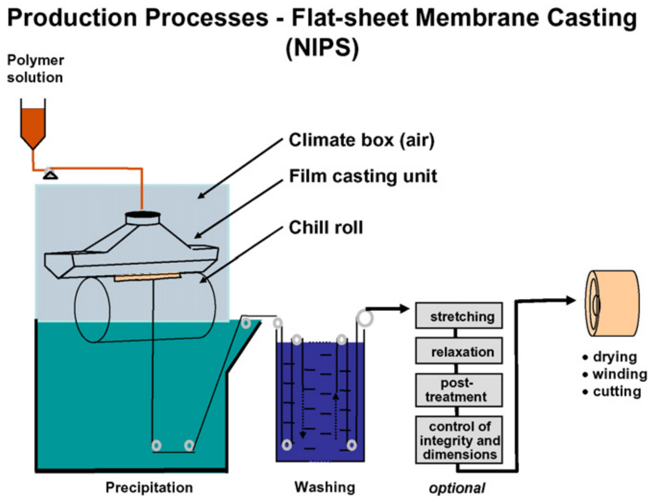
modifications of the membrane after preparation [14–16]. Many of those modifications had ultimately been motivated by the aim to reduce the membrane fouling [17–19].

The objective of this work was to investigate systematically the structure and filtration performance of commercial MF membranes made from PES, having the same pore size specification but different pore morphology and wetting properties. The new DuraPES® membranes are prepared under industrial manufacturing conditions using a modification in the NIPS process which should facilitate the formation of a very pronounced anisotropic cross-section pore structure. Its results will be presented. In addition, this membrane is permanently hydrophilic, due to specifically selected polymeric additives. In the main part of the paper, the resulting structure, properties and performance of the novel DuraPES® membranes are compared to five other PES MF membranes available on the market. It will be demonstrated that the significantly improved performance of the DuraPES® membranes derives from the special surface and pore morphology of this membrane.

2. Experimental

2.1. Membranes

DuraPES® membranes were prepared via the NIPS process using a casting solution containing PES, sulfonated PES (SPES), poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG) in a mixture of caprolactam and butyrolactone as solvent. An overview of the facility used for membrane manufacturing is given in Scheme 1. The conditions on both outer surfaces of the casted film are most important for adjusting the pore morphology of the membrane; different temperatures had been set by cooling the roll used as support and heating the atmosphere in contact with the film before precipitation. More details about the process can be found in ref. [20]. The impact of process parameters will be presented in Section 3. Lots of DuraPES® membranes with nominal pore diameters of 0.2 and 0.4 μm from routine manufacturing were used throughout the study. In order to compare the pore morphology, a sample of another PES membrane (MicroPES® 2F) prepared on the same facility under different conditions (smaller temperature gradient as for DuraPES®), but having also a nominal pore diameter of 0.2 μm, was used as well.



Scheme 1. Overview on membrane manufacturing facility.

Table 1
Overview on all MF membranes used in this study

Code	Manufacturer	Membrane type	Nominal pore diameter (μm)
MD	Membrana	DuraPES® 200	0.2
MD4		DuraPES® 450	0.45
MM	Membrana	MicroPES® 2F	0.2
A	AMC	Accupor-200	0.2
ME	Millipore	Express® SHF “hydrophilic”[a]	0.22
O	Osmonics	Micron-PES	0.22
P	Pall	Supor[a]	0.2
S	Sartorius	Sartopore 0.2[a]	0.2
S4		Sartopore 0.45[b]	0.45

[a] Membranes were taken from respective cartridges (Express, Supor and Sartopore).

[b] Pre-filter from the same cartridge (“Sartopore 2”).

An overview of all membranes investigated in this study, is given in Table 1. Because all the other membranes are also commercial materials, detailed information about their preparation is not available to the public. However, in all cases the general procedure will be based on the NIPS process as well.

2.2. Membrane structure characterization

Pore morphology was investigated by using scanning electron microscopy (SEM Philips type XL20). Samples were positioned on an aluminium specimen holder and afterwards sputtered with gold. Sputtering was done at a pressure of minimum 0.05 mbar, a current of 30–40 mA and for 10–20 s. The sputtered specimen holder was transferred to the SEM, and the acceleration voltage was chosen according to the sample’s requirements and the magnification desired.

Volume porosity was measured by water uptake. Four samples (15.2 cm^2) of each membrane type were weighed, then wetted with and equilibrated in water (50 mL, 16 h; at 25 °C), after removing the adhering water using tissue paper weighed again, and finally dried (at 50 °C, 16 h). The volume porosity was estimated based on the average values of the water uptake relative to the membrane material (final weight), using the densities of water (1.00 g/cm^3) and PES (1.37 g/cm^3 [21]). The relative uncertainty of this method was 5%.

Trans-membrane pore size distribution was measured by the combined gas flow/pore dewetting method [22]. The Permporometer Model CFP-34RTG8A-6-L4 (Porous Materials, Inc., USA) and the software CapWin Version 6.71.35 (PMI) were used. The test gas was nitrogen and wetting fluid was 1,1,2,3,3,3-hexafluoropropene (Galwick; PMI), having a surface tension of 15.9 dyn/cm. Here, the “dry-up/wet-up” method was applied, i.e. first the gas flow through the dry membrane sample and then the flow through this membrane sample filled with the wetting fluid was measured, both in upward direction. At least