Available online at www.sciencedirect.com

ELSEVIER

Polymer 47 (2006) 3464–3476

polymer

www.elsevier.com/locate/polymer

Study of the characteristics and the performance of self-made nanoporous polyethersulfone membranes

K. Boussu *, C. Vandecasteele, B. Van der Bruggen

Laboratory for Applied Physical Chemistry and Environmental Technology, Department of Chemical Engineering,
K.U. Leuven, W. de Croylaan 46, B-3001 Leuven, Belgium

Received 29 November 2005; received in revised form 14 March 2006; accepted 14 March 2006
Available online 5 April 2006

Abstract

Polyethersulfone (PES) membranes were prepared in this study by using the DIPS technique (diffusion induced phase separation) in view of a better insight into the performance of commercial polyethersulfone membranes and a verification for the limited information given by the manufacturer. During this process, a lot of conditions influence the final membrane structure. Beside the choice of the solvent (dimethylformamide (DMF) or *N*-methyl-pyrrolidone (NMP)), it was shown that the concentration of the polymer and the relative air humidity are the most crucial ones. Optimizing these factors led to reproducible membranes, which were characterized for hydrophobicity, roughness, surface charge and molecular weight cut-off (MWCO). The performance was studied by doing cross-flow filtration experiments with aqueous solutions of uncharged and charged component. Although the self-made membranes were characterized by a larger MWCO in comparison with commercial polyethersulfone nanofiltration membranes, the retention for the self-made membranes was almost equal to or even higher than the commercial membranes in the case of filtrating negatively, respectively, positively charged component. The high retention of the self-made membranes for positively charged component can be explained by adsorption experiments or by surface charge measurements before and after filtration.

Keywords: Nanoporous membranes; Polyethersulfone; Phase inversion

1. Introduction

Membrane processes in general, and nanofiltration in particular, are becoming more and more important in environmental technology. Nanofiltration (NF) membranes can remove multivalent ions as well as organic molecules with a molecular weight above 300 Da. Because of these properties, nanofiltration is nowadays applied in the treatment of wastewater in the textile industry [1–3] and in the production of drinking water [4–6]. However, the main drawback of the use of membranes in industry is the phenomenon of fouling, which is defined as a ‘process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its surfaces, at its pore openings, or within its pores’ [7]. As fouling is an interplay between the membrane and the feed components, it is important to have a good understanding of the performance of the membranes. However, information given by the membrane manufacturer is rather poorly, only the polymer type (polyethersulfone or polyamide in the case of NF) is often mentioned.

Therefore, the goal of this study was to prepare nanoporous polyethersulfone membranes and to compare the characteristics and the performance of these membranes with commercial NF membranes. This allows obtaining a better insight into the performance and fouling tendency of commercial membranes.

A common technique to prepare asymmetric polymeric membranes is the DIPS technique (diffusion induced phase separation) [8–12]. In this process, a thin layer of the polymer dissolved in an appropriate solvent is cast on a suitable support and phase separation is induced by a non-solvent. This phase inversion can be obtained in several ways [13], of which the immersion precipitation is the most efficient one. In this process, the phase inversion is induced by immersing the polymer solution film in a non-solvent bath. A diffusion driven exchange between solvent and non-solvent starts: the non-solvent diffuses into the polymer solution and the solvent diffuses into the non-solvent bath. Because of this diffusion

---

* Corresponding author. Tel.: +32 16 32 23 41; fax: +32 16 32 29 91.
E-mail address: katleen.boussu@cit.kuleuven.be (K. Boussu).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.03.048

process, the composition of the polymer solution changes and moves into the binodal region of the ternary phase diagram (composed of polymer, solvent and non-solvent). Hence, the polymer solution is separated into two phases: a polymer-rich phase and a polymer-poor phase. At a certain stage during phase demixing, the polymer-rich phase is solidified into a solid matrix, while the polymer-poor phase develops into the pores.

Both kinetics and thermodynamics play an important role during the process of membrane formation and are extensively studied in literature [14–21]. Changing the preparation factors during the process will have an influence on both kinetics and thermodynamics, resulting in a different membrane structure and a different membrane performance. For example, an increase in the polymer concentration leads to a lower porosity of the membrane and hence to a lower water flux [20,22,23]. To increase the water flux, pore-forming agents, such as polyvinylpyrrolidone [24,25], polyethylene glycol [26] or an acid [27–29] can be added to the polymer solution. When on the other hand a volatile component like aceton is added to the polymer solution, a denser top layer will develop, resulting in higher retentions [22]. Not only to the polymer solution, but also to the non-solvent bath, components like alcohols [17,19] or a solvent [20] can be added to change the membrane structure. Another influential preparation factor is the temperature of the non-solvent bath: increasing this temperature may either lead to an increase [27] or a decrease [30] of the water flux depending on the studied polymer system. The polyethersulfone system is also thought to be sensitive to the relative air humidity [21]. By changing all these preparation factors, an optimized membrane for a specific purpose can be obtained.

From this literature overview, it becomes clear that up to now studies concerning membrane formation are rather focused on the principle of the formation process and on the influence of some preparation factors on the membrane structure without considering the membrane performance. Because the formation process of the membrane is a complex phenomenon, most of the articles are limited to the influence of only one or two preparation factors on the thermodynamics and kinetics of the formation process. The study about the performance (if any) is mostly limited to a dead-end set-up in which only the pure water flux and the retention of one specific component are tested. A thorough testing of the membrane performance in a real-life cross-flow set-up is currently missing. Also a thorough characterization of the membrane surface properties, which are important to explain fouling phenomena, can hardly be found in literature.

Therefore, this study aims at giving a systematic and complete overview of the synthesis of nanoporous polyethersulfone membranes by the phase inversion technique, seen from the point of the membrane performance (instead of from the point of the formation process). In a first part of the study, several preparation factors were studied experimentally to find the optimal circumstances to obtain a nanoporous polyethersulfone membrane. Membranes without support layer were chosen in the first part for two reasons. Firstly, at least one difficult factor (the support layer) could be excluded in the beginning of the research. Secondly, these membranes without non-woven support layer could be tested in a dead-end set-up that allows testing the performance of the membranes in a shorter time with a smaller piece of membrane. The knowledge of this first part will be used in the second part of the study, in which membranes on a non-woven support layer were prepared. These membranes were then characterized and tested in detail for their performance in a cross-flow set-up. To have a reference, the results were compared with those of commercial nanofiltration membranes.

2. Materials and methods

2.1. Preparation of the membranes

Polyethersulfone from Solvay Belgium (PES Radel A-100) was used and dissolved in two different solvents (dimethylformamide (DMF) or *N*-methyl-pyrrolidone (NMP)) by heavy stirring during several days to obtain a homogeneous solution. A thin film of the polymer solution with a thickness of 150 μm was made on a support with a filmograph (K4340 Automatic Film Applicator, Elcometer) at a speed of 20 mm/s in an atmosphere with controlled relative air humidity. The support was either a glassy plate or a glassy plate with a non-woven support layer taped on it. The non-woven support layers FO2471 (PP/PE, air permeability at 2 mbar: 300 dm^3/m^2 s) and FO2413 (polyester, air permeability at 2 mbar: 150 dm^3/m^2 s) were obtained from Freudenberg, Germany. To prevent the polymer solution of intruding in the pores of these support layers, the support layer was wetted with the appropriate solvent prior to casting [31]. The casting thickness was also increased to 250 μm to obtain a defect-free membrane.

The casted polymer film was then immersed in a non-solvent bath of distilled water at 293 K (unless otherwise mentioned), in which the phase separation starts and the membrane is formed. The membrane was afterwards repeatedly washed with distilled water and wet stored. For each set of process parameters, three identical membrane sheets were made and tested to obtain a mean value of the flux and the retention (Section 2.3).

The viscosity of the polymer solutions was measured with a DSR (dynamic stress rheometer rheometrics) in a nitrogen atmosphere at 303 K.

To have a reference, commercial nanofiltration membranes with a top layer of (permanently hydrophilic) polyethersulfone were also studied. It concerns the membranes N30F and NFPES10 from Nadir, Germany. According to the manufacturer, the MWCO (molecular weight cut-of or the molecular weight of a component with 90% retention) of N30F and NFPES10 is, respectively, 400 and 1000 Da.

2.2. Characterization of the membranes

The MWCO of the membranes was determined by doing filtration experiments in the cross-flow set-up. The feed solution consisted of a mixture of polyethylene glycols (PEG) with different molecular weights (from 150 till

3000 g/mol) in a concentration of 1 g/l. Analysis of the concentration of PEG in feed and permeate was done with Gel Permeation Chromatography (Shodex OHpak SB-804 HQ). By fitting the obtained retention curve with the log-normal model [32], the MWCO can be calculated as the molecular weight of PEG with 90% retention.

The hydrophobicity of the membrane surface was analysed by contact angle measurements, performed with a Drop Shape Analysis System DSA 10 Mk2 (Krüss) in a three-phase system consisting of the membrane surface, air and water droplets of 2 μl. The sessile drop method was chosen. Each contact angle was measured 10–15 times and an average value was calculated. The contact angle of the wet, clean membrane was determined for all membranes.

Non-contact atomic force microscopy (AFM) was carried out with an AFM system Autoprobe M5 (VEECO). The cantilever was made out of Si with a spring constant of 3.2 N/m and a nominal tip apex radius of 10 nm. The roughness was measured on a scan area of 1 μm × 1 μm. After flattening the RMS (root-mean-squared roughness) was calculated. Each measurement was performed three times on two different areas to obtain a mean value of the RMS roughness. The standard deviation of the different measurements was lower than 10%.

The zeta potential of the membranes was determined by streaming potential measurements with a 0.01 M KCl solution, using the experimental set-up described in detail in [33]. The pH was set within the range between 3 and 10 by adding NaOH and HCl. The relative fault on the measured values was below 10%. Only around the neighbourhood of the iso-electric point (when the surface charge is very small), the relative faults increased up to 30%.

To visualize the membrane structure, SEM-images of the cross-section of the self-made membranes were made with a Philips Scanning Electron Microscope XL30 FEG with an accelerating voltage of 20 keV. To obtain a clear cross-section, the membranes were fractured after immersing in liquid nitrogen.

2.3. Performance of the membranes

The performance of the self-made membranes was tested in a dead-end or in a cross-flow set-up. The dead-end set-up was used for testing the membranes made without non-woven support layer, because these membranes lack the mechanical strength to withstand the shear velocity in cross-flow.

In the dead-end module (Sterlitech, USA), a static pressure of 8 bar is applied on a small vessel filled with the feed solution (300 ml). The temperature during dead-end filtration was equal to room temperature (293 K) during the whole experiment. To minimize concentration polarization, the feed solution is continuously stirred. At the bottom of the vessel a membrane with diameter 4.3 cm is placed. The permeate (which passes through the membrane) was collected in a graduated cylinder, as presented in Fig. 1(a). To test a membrane, the dead-end module was in a first step filled with distilled water and the pure water permeability was calculated according to formula (1).

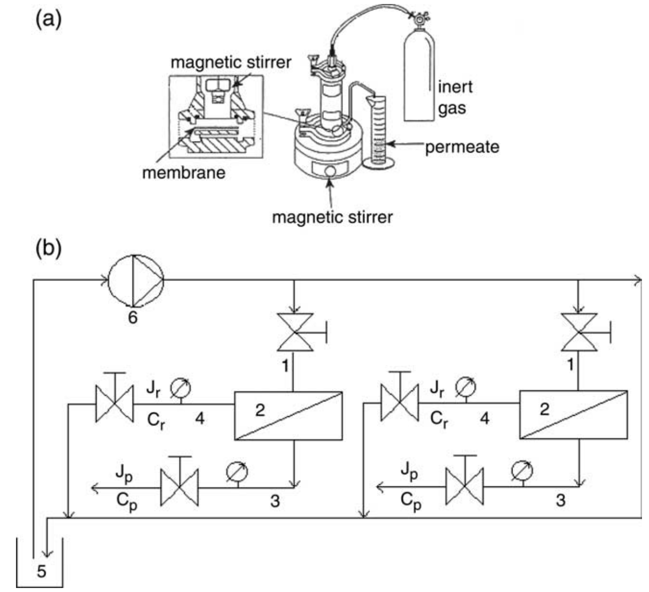


Fig. 1. The dead-end set-up (a) and the cross-flow set-up (b) used for testing the performance of the self-made membranes. [(1) feed, (2) filtration module, (3) permeate, (4) retentate, (5) feed vessel, (6) pomp]

$$\text{Water permeability} = \frac{\text{permeate volume (l)}}{\text{membrane area (m}^2) \times \text{time (h)} \times \text{pressure (bar)}} \quad (1)$$

In a second step, the retentions of an uncharged component (raffinose, $M_w = 504$ g/mol) and a negatively charged component (congo red, $M_w = 697$ g/mol) were studied. Therefore, an aqueous feed solution was made with a concentration of 2 mmol/l for raffinose or 0.02 mmol/l for congo red. The retention can be calculated with formula (2).

$$\text{Retention (\%)} = \left(1 - \frac{\text{concentration permeate}}{\text{concentration feed}}\right) \times 100 \quad (2)$$

In the cross-flow set-up (Amafilter, The Netherlands, Fig. 1(b)), membranes made on a non-woven support layer were tested. In the experiments the applied pressure was 8 bar and the temperature was maintained at 293 K by a cooling water circuit. Concentration polarization is minimized by using a feed velocity of 4.5 m/s. The feed volume is 10 l, while the membrane surface is 0.0059 m^2. Because only a small permeate volume is necessary for the analysis of the concentration and because permeate and retentate are recycled back to the feed vessel, the concentration of the feed solution hardly changes. In the cross-flow set-up, the membranes were also firstly tested for the pure water permeability. Afterwards the evolution of the permeate flux and the retention in function of time was followed when filtrating an aqueous solution of uncharged or charged components in a concentration of 0.2 mmol/l. To compare the flux decline between different membranes, relative fluxes (in %) were defined as the relation of the permeate flux to the pure water flux. Due to the small concentrations, osmotic pressure was negligible.

Table 1
Summary of the properties of the components used to test the performance of the self-made membranes

	M_w (g/mol)	Charge at neutral pH
Raffinose	504	0
Diphenylaminosulfonic acid	271	−
Methyl orange	327	−
Congo red	697	− −
Neutral red	289	+
Methylene blue	320	++
Janus green	511	+

The properties of the used components are summarized in Table 1; both negatively and positively charged components were selected. An UV 1601 spectrophotometer was used to analyse the concentration of all charged components, the concentration of raffinose was determined using a colourimetric method [34].

3. Results and discussion

3.1. Preparation of membranes without non-woven support

Membranes were made on a glassy plate without non-woven support to study the influence of different preparation factors to obtain the optimal circumstances for a nanoporous polyethersulfone membrane. The preparation factors include a non-solvent bath of distilled water at 293 K, a relative air humidity of 40% and no addition of components either to the non-solvent bath or to the polymer solution. As solvent, DMF or NMP was used. The influence of the polymer concentration and the relative air humidity were studied first. Then different components were added to the non-solvent bath and to the polymer solution. Of the non-solvent bath, not only the influence of the additives, but also the influence of the bath's temperature on the membrane performance was investigated.

The goal of changing all these preparation factors was to obtain a nanoporous polyethersulfone membrane. To verify if this criterion was fulfilled, the membrane performance (namely the pure water permeability and the retentions of congo red and raffinose) was studied. Because of the absence of a non-woven support, these membranes lack mechanical strength and could hence only be tested in the dead-end set-up. Using the dead-end set-up also has the advantage that the performance of the membranes could be tested in a shorter time with a smaller piece of membrane. If, by changing a preparation factor, the performance of the self-made membrane corresponded with the performance known for commercial nanofiltration membranes, it can be concluded that this preparation factor is favourable to obtain a nanoporous membrane. The pure water permeability for commercial nanofiltration membranes ranges between 1.5 and 15 l/m^2 /h/ bar. The retention of congo red (negatively charged component) is about 98% for all commercial nanofiltration membranes, while for raffinose (uncharged component) the retention differs strongly from membrane to membrane.

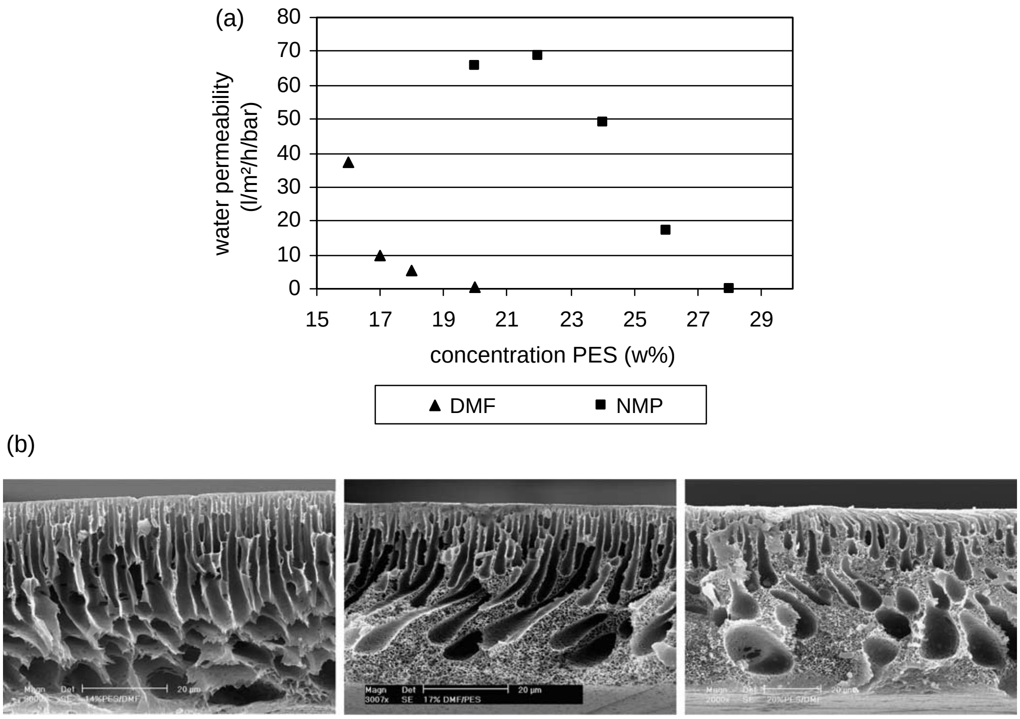
3.1.1. Influence of the polymer concentration

The influence of the polymer concentration on the water permeability for both DMF- and NMP-membranes is shown in Fig. 2(a). Fig. 2(a) shows that an increase in the polymer concentration corresponds to a decrease in the pure water permeability. This can be explained by the observed increase in the viscosity of the polymer solution. For example, in the case of NMP, the viscosity of a 26% polymer solution was 2.15 Pa. s, while a viscosity of 6.11 Pa. s was measured for a 30% polymer solution. This increase in viscosity hampers the diffusional exchange between solvent and non-solvent and leads to a higher polymer concentration at the interphase between polymer solution and non-solvent bath and hence to a lower porosity and a lower permeability of the membrane.

SEM-images of the cross-section of a DMF-membrane with different polymer concentrations are shown in Fig. 2(b). A comparison between these images indicates that a high polymer concentration indeed results in a less porous membrane with less fingerlike pores (called macrovoids). There is also an influence of the polymer concentration on the final thickness of the membrane. Starting from 150 μm casting thickness, the final thicknesses of the membranes made with a 14% PES/DMF and a 20% PES/DMF solution are, respectively, 50 and 60 μm. In both cases, a reduction in thickness is observed because the transport of non-solvent (distilled water) into the polymer solution (DMF/PES) is slower than the transport of the solvent (DMF) into the non-solvent (water). This phenomenon is related to the good miscibility of solvent and non-solvent and to the hydrophobic nature of the polymer if water is used as non-solvent. So, by increasing the polymer concentration and hence the viscosity, both the rate of the solvent into the non-solvent and the rate of the non-solvent into the polymer solution decrease, resulting in less contraction and hence in a thicker membrane. The same trend was observed for the NMP-membranes.

The polymer concentration has not only an influence on the permeability as shown in Fig. 2(a), but also on the retention of the membranes. For congo red, the retention increases from 91% (for 20% PES/NMP) to 99% (for 26% PES/NMP) and from 93% (for 16% PES/DMF) to 99% (for 17% PES/DMF). The retention of raffinose was in all cases very low (below 5%). From these data, it can be seen that there is a big difference between the retention of raffinose and the retention of congo red. This can be explained by the fact that raffinose is uncharged while congo red carries a negative charge. Because the membrane surface is also negatively charged at neutral pH (Section 3.2.2), congo red experiences a repulsion force, resulting in a high retention of this component.

This paragraph proves that there is a large influence of the polymer concentration on the membrane performance and structure. To study the influence of the other preparation factors, one polymer concentration was selected, namely 17% PES in case of DMF and 26% PES in case of NMP. These concentrations were chosen in such a way that a nanoporous structure was obtained: congo red was retained very well (99%)



(1) 14% PES/DMF [magnification: 3000x]

(2) 17% PES/DMF [magnification: 3000x]

(3) 20%PES/DMF [magnification: 2000x]

Fig. 2. Influence of the polymer concentration on (a) the pure water permeability measured in dead-end and (b) the membrane structure.

and the water permeability was still reasonable (10 l/m^2/ h/ bar for 17% PES/DMF and 19 l/m^2/ h/ bar for 26% PES/NMP).

3.1.2. *Influence of the relative air humidity*

To study the influence of the relative air humidity on the water permeability, 15 membranes were synthesized at relative humidities of, respectively, 30, 50, 70 and 90%. The results are given in Fig. 3 for a 17% PES/DMF membrane; the results for PES/NMP were similar. Fig. 3 shows that an increasing relative humidity gives rise to a larger variation on the measured water permeability or hence to a decreased reproducibility. This was not reported in literature before. Only Chaturvedi et al. [27] reported that exposure to higher humidity gives more porous membranes with higher water permeation rates for the system PES/DMF and PES/NMP. However, only two different humidities were tested (55 and 90%) and no standard deviations were given on the experimental water fluxes.

The relative humidity plays an important role to control the membrane performance, as during the casting of the polymer solution to a film, the composition of the casted film is varied by water vapour sorption. Water vapour sorption occurs rather than evaporation of the solvent, since DMF and NMP are highly hygroscopic and non-volatile solvents. Due to this water vapour sorption, phase separation occurs on some places on the membrane surface, prior to the phase separation that occurs when placing the casted film in the non-solvent bath of distilled water. The relative humidity can thus only have an influence on the top layer of the membrane surface, as the underlying layers of the membrane are only formed at the moment of immersion in the non-solvent. SEM-images of the cross-section of the membranes at low and high relative humidity were similar and can be compared with Fig. 2(b2). A change in the top layer of the membrane should have an influence on the observed retentions, but the effects were small: congo red is almost completely retained at all humidities, while the retention of raffinose is always very small (below 5%).

This paragraph proves that, to enhance the reproducibility, membranes should be made in an atmosphere with a relative humidity as low as possible. Because of the presence of a non-solvent bath of distilled water, there are restrictions on the minimal relative humidity. A relative humidity of 40% was achievable to reach in all experiments.

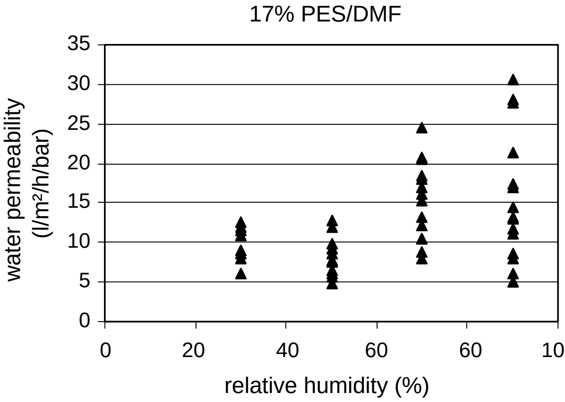


Fig. 3. Influence of the relative air humidity on the pure water permeability. Each point represents the water permeability of a membrane at a specific relative air humidity.

3.1.3. Influence of additives to the polymer solution

Different components were added to the polymer solution, such as aceton (a volatile additive) or distilled water (non-solvent). No pore-forming agents were added, because according to literature [24–28], these additives would dramatically enlarge the pores resulting in undesired low retentions of both congo red and raffinose.

The purpose of adding volatile components is to obtain smaller pores as these components evaporate during the casting of the polymer solution. Just as with the relative humidity, a volatile additive is thought to have only an influence on the top layer of the membrane. However, by adding up to 8% aceton, the permeability for the 17% PES/DMF membrane only slightly increased from 10 l/m^3/ h/ bar to 13 l/m^2/ h/ bar and there was also no effect on the observed retentions of congo red and raffinose. So, adding aceton to the polymer solution did not provide a large improvement in the membrane performance.

By adding water (non-solvent) to the polymer solution, the starting polymer solution (which is normally located in the stable region) moves closer to the unstable binodal region in the ternary phase diagram of the polymer system. By immersing this polymer solution in the non-solvent bath, only little water is needed for phase separation to occur. This results in the formation of a porous membrane with a thin top layer and hence with a high water permeability. This phenomenon was observed for the 17% PES/DMF system where the water permeability increases from 10 to 20 l/m^2/ h/ bar by adding up to 0.9% of distilled water. Because, however, the retention of congo red decreases from 99 to 94%, adding water to the polymer solution did not seem to ameliorate the membrane performance.

3.1.4. Influence of additives and temperature of the non-solvent bath

The influence of adding an alcohol to the non-solvent bath of distilled water was investigated for the DMF/PES and the NMP/PES system. Increasing the alcohol concentration (isopropanol or ethanol) in the distilled water bath from 0 to 40% causes a decrease in the water permeability for the 17% PES/DMF membrane from 10 l/m^2/ h/ bar to 4 l/m^2/ h/ bar. When the non-solvent bath consisted of pure isopropanol, the water flux was reduced to zero for both the DMF/PES and the NMP/PES system. Although the influence of adding alcohol to the non-solvent bath on the water permeability was remarkable, congo red was in all cases retained for 99% (except for the case of a pure alcohol bath, where no flux was measured and hence no permeate sample could be collected). This phenomenon can be explained by the fact that, if alcohols are used as non-solvent, the binodal region in the ternary phase diagram shrinks significantly [17]. This implicates that more non-solvent (alcohol) is needed to diffuse into the polymer solution before this solution reaches the binodal region and phase separation can occur. This results in the formation of a membrane with a dense top layer, which can explain the decrease of the water flux.

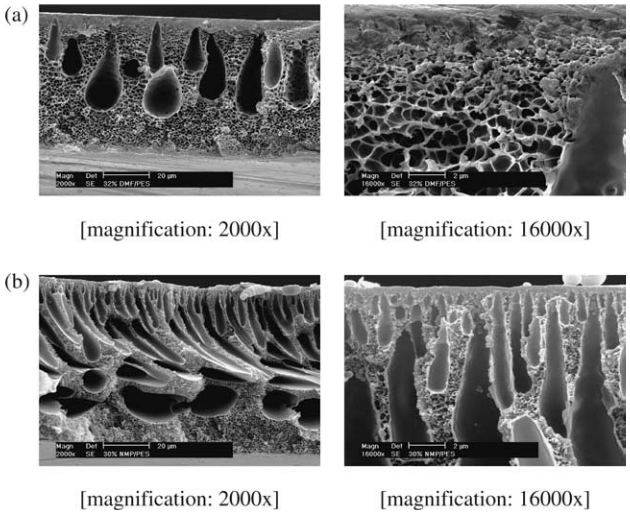
Table 2
Influence of the temperature of the non-solvent bath on the water permeability (l/m^2/ h/ bar) and on the retention of congo red (%)

Temperature (K)	17% PES/DMF		26% PES/NMP	
	Permeability	Retention congo red	Permeability	Retention congo red
285	13	99	24	99
293	10	99	19	99
320	3	94	1	92

A decrease of the water flux was also observed when increasing the temperature of the distilled water bath for both the DMF/PES and the NMP/PES system, as presented in Table 2. Increasing the bath temperature caused not only a decrease of the water permeability but also a slight decrease of the retention of congo red, also indicated in Table 2. This effect can be explained by considering the viscosity and the solubility of the polymer solution. When the bath temperature increases, the polymer solution will become less viscous, resulting in an increased diffusivity of the solvent through both the internal polymer phase as well as through the interface between the developing membrane and the non-solvent bath. This results in a faster concentration of the polymer in the film, giving a thicker dense layer and hence a smaller flux. Another effect, that plays an important role when increasing the bath temperature, is the increased solubility of the polymer in the solvent. Because of this, the polymer is kept in the solution state at a higher water concentration without phase separation, again generating a thicker dense film.

3.1.5. Influence of the solvent

Beside all these preparation factors, the solvent (DMF or NMP) also influences strongly the membrane performance. This effect, which was not yet reported in literature, was particularly observed for the water permeability (as presented in Fig. 2(a)). The explanation for this large difference in water permeability can be found in the membrane structure. Fig. 4



[magnification: 2000x] [magnification: 16000x]

[magnification: 2000x] [magnification: 16000x]

Fig. 4. SEM-images of (a) 32% PES/DMF and (b) 30% PES/NMP with a zoom on the top layer.

presents SEM-images of the cross-sections and of the top layers of a 32% PES/DMF and a 30% PES/NMP membrane.

From Fig. 4, it becomes clear that the NMP-membrane is thicker than the DMF-membrane (85 μm, respectively, 60 μm) and that the NMP-membrane has longer and smaller macrovoids in comparison with the DMF membrane. Also the thickness of the top layer differs for both membranes, as the NMP-membrane has a top layer of about 0.5 μm, whereas a top layer of about 3 μm is observed for the DMF-membrane. When studying SEM-images of membranes made with a lower polymer concentration, the same conclusions could be drawn.

From this SEM-study, it becomes clear that the DMF-membranes are characterized by a thicker top layer than the NMP-membranes. Because the water flux is inversely proportional with the thickness of a membrane (Hagen–Poiseuille) and because the sublayer of the DMF- and the NMP-membranes is very porous with many macrovoids, the main resistance for the water flux is located in the top layer. So, the thicker the top layer, the more resistance and the lower the water flux, which was observed for the DMF-membranes.

The presence of the thicker top layer in DMF-membranes can be explained by thermodynamics and kinetics. By performing viscosity measurements, it became clear that the DMF-solution is less viscous than the NMP-solution (4.81 Pa.s for 32% PES/DMF versus 6.11 Pa.s for 30% PES/NMP). This lower viscosity of the PES/DMF solution increases the diffusivity of DMF versus NMP through both the polymer solution as well as through the interface between the developing membrane and the non-solvent bath. DMF also has a higher enthalpy of solution in water than NMP as can be seen from DMF's solubility parameter (12.1 versus 11.3 $(\mathrm{cal/cc})^{0.5}$ for NMP). The transport of DMF into water will hence be faster than the transport of NMP into water, while the uptake of water into both polymer solutions will be more similar. So, DMF will have a higher gradient into the water phase than NMP. This will result in a faster concentration of the polymer in the DMF/PES-film, giving a thicker dense top layer.

Another explanation for the thicker top layer of the DMF-membranes could be that DMF is a better solvent for polyethersulfone than NMP. This implicates that the polymer in the DMF/PES system is kept in the solution state at a higher water concentration, generating a thicker dense film.

3.2. Preparation of membranes on a non-woven support

In the first part of this study, it was proven that the polymer concentration and the relative humidity are the most important preparation factors to obtain a membrane with a good performance. The choice of the solvent also plays an important role in the formation of the membrane. This knowledge is used in the study of polyethersulfone membranes on a non-woven support. This permits to study the performance of the membranes in a more realistic way.

Two different support layers (FO2413 and FO2471) and two different solvents (DMF and NMP) were used. This implies that four different types of membranes were made. As non-solvent, a distilled water bath at 293 K was used. No components were added to the non-solvent bath or to the polymer solution. During casting of the polymer solution, the relative air humidity was 40%. After synthesis, the membranes were characterized and tested for their performance in the cross-flow set-up.

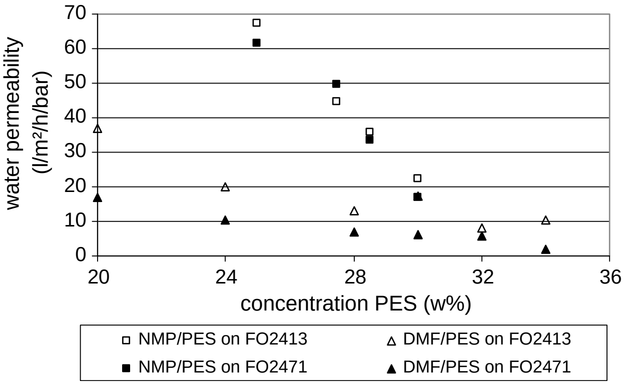


Fig. 5. Influence of the polymer concentration on the water permeability, measured in cross-flow.

3.2.1. Influence of the polymer concentration

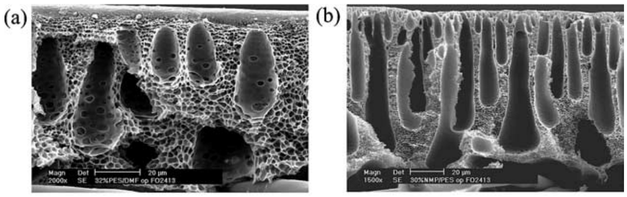
Fig. 5 shows the influence of the polymer concentration on the water permeability for the four different membranes. Just as it was the case without non-woven support layer (Section 3.1.1), the water permeability decreases with increasing polymer concentration. Beside the polymer concentration, the non-woven support layer used is also important, as the more porous non-woven support FO2413 gives rise to a higher water permeability than the denser support FO2471. This effect is also reported by Barth et al. [22].

To characterize and to test the performance of the membranes, an optimal polymer concentration should be selected, so that a reasonable water flux is combined with a good retention of an uncharged component (raffinose). In the experiments, it was observed that the retention of raffinose increases with increasing polymer concentration. So, a highest possible polymer concentration would be advantageous for the retention, but disadvantageous for the water permeability. There are also practical limitations, as a very high polymer concentration would result in a very viscous solution. This hampers the defect-free casting of the solution on the support layer.

The optimal concentrations were determined as 32% PES for DMF and 30% PES for NMP. The membranes made of these concentrations will be studied in the rest of the article and will be referred to as: D13 and D71 (for a 32% PES/DMF solution cast on FO2413, respectively, FO2471) versus N13 and N71 (for a 30% PES/NMP solution cast on FO2413, respectively, FO2471). The water permeability of these membranes was determined as 17.0 and 22.2 $\mathrm{l/m^2/h/bar}$ for N71, respectively, N13, while D71 and D13 have a water permeability of, respectively, 4.7 and 9.4 $\mathrm{l/m^2/h/bar}$. The retention of raffinose was almost equal for all membranes and was about 27% (as described in more details in Section 3.2.3).

A comparison between the membranes without support layer (Section 3.1) and with non-woven support layer (this paragraph) indicates that the latter ones have higher water permeabilities and also higher retentions of uncharged components. Such a comparison has not yet been described in literature. The good retention of raffinose can be explained by the higher polymer concentrations used for making membranes on the support layer. The difference in water permeability cannot be explained by a difference in temperature, as the experiments were performed at 293 K in both the cross-flow and the dead-end set-up. However, the difference in water permeability can be related to the way the membranes are placed in the non-solvent bath. When casting on a non-woven support, this support is taped on a glassy plate and the casting solution is then applied as a wet film. By immersing the solution in non-solvent, phase separation occurs and propagates from the top surface of the wet film into the film bulk, forming an integrally skinned dense layer on the top surface of the remaining porous structure. On the other hand, when the wet film is cast directly on the glassy plate and then immersed in the non-solvent bath, the membrane may rapidly lift of the glassy plate with a considerable amount of solvent remaining in the membrane. With non-solvent (or distilled water in this case) on both sides of the developing membrane, a solvent gradient on the backside of the membrane is also established. A dense layer will hence be formed on the backside as well as on the topside of the asymmetric membrane, resulting in a lower water flux. This mechanism can be supported by comparing the SEM-images of membranes made from a 32% PES/DMF or a 30% PES/NMP solution on a glassy plate (Fig. 4) or on a non-woven support layer (Fig. 6). A comparison between Figs. 4 and 6 seems to indicate that the backside of the membranes made on a glassy plate is less porous than the backside of the membranes made on a non-woven support. In the latter case, the macrovoids run all through the polyethersulfone layer towards the non-woven support layer.

Fig. 6 also shows again the difference in membrane structure when using DMF or NMP as solvent. The influence of the solvent, when making a membrane on a non-woven support layer, is however, twofold. Firstly, there is the influence of the solvent when the solvent is used to dissolve the polymer, which can be clearly seen in Fig. 6. Secondly, when making a membrane on a support layer, the solvent is also used to wet the non-woven support layer prior to casting, so that intruding of the polymer solution in the pores of the support layer is prevented. Mostly, the same solvent as the one used to dissolve the polymer, is used. When different solvents are applied, the water permeability will be influenced. For instance, when wetting the support layer with DMF prior to casting a NMP/PES solution, the water permeability decreases for N71 from 17.0 to 11.2 l/m^2/h/bar and for N13 from 22.2 to 10.2 l/m^2/h/bar. In contrary, when casting a DMF/PES solution on a support layer wetted with NMP, the water permeability increases from 4.7 to 6.3 l/m^2/h/bar for D71 and from 9.4 to 10.7 l/m^2/h/bar for D13. Apparently, using DMF as solvent either to dissolve the polymer or to wet the support layer has a disadvantageous effect on the water permeability. Using NMP as solvent, however, seems to have an advantageous effect on the water flux. This is an interesting subject, which has not yet been studied in literature.



[magnification: 2000x] [magnification: 1500x]

Fig. 6. SEM-images of the cross-sections of the polyethersulfone layer of (a) D13 and (b) N13.

3.2.2. Characterization of the membranes

Table 3 summarizes the characteristics of the four self-made membranes on a non-woven support layer. The characteristics of two commercial polyethersulfone nanofiltration membranes are also added to Table 3 for reference.

To test the reproducibility, 15 different membrane samples were prepared and tested for the water permeability. The obtained standard deviations on the water permeability (given in Table 3) were comparable to the commercial membranes, which indicates that the self-made membranes are reproducible.

Contact angle measurements were performed to study the hydrophobicity of the membrane surfaces. A larger contact angle implicates a more hydrophobic surface. Table 3 shows that the commercial membrane N30F has the most hydrophobic membrane surface, while the hydrophobicity of the other membranes is comparable.

The roughness of the membrane surface, measured in non-contact mode AFM on a scan area of 1 μm × 1 μm, is visualized in Fig. 7 for D13 and N13. As can be seen from Table 3, the roughness values are similar for all membranes. NFPES10 has the smoothest membrane surface.

From the behaviour of the zeta potential in function of the pH, it becomes clear that all polyethersulfone membranes are largely negatively charged at high pH and that this negative charge diminishes when the pH decreases. The iso-electric point, defined as the pH for which the net charge of the membrane is equal to zero, is located around 3 for all membranes. This behaviour of the charge in function of the pH can be explained by the presence of sulfonic acid groups (–SO$_3^-$) on the surface. These sulfonic groups are strongly acidic and are completely dissociated over nearly the entire pH-range.

The fact that the hydrophobicity, the surface charge and the roughness are almost similar for the self-made and the commercial membranes indicates that the top layer of all membranes is composed of the same polymer. However, there is a difference between the self-made and the commercial membranes as can be seen in the molecular weight cut-off.

Table 3
Characteristics of the self-made membranes and commercial polyethersulfone nanofiltration membranes

	N71	N13	D71	D13	NFPES10	N30F
Water permeability ($l/m^2/h/bar$)	17.0 (± 3.4)	22.2 (±3.1)	4.7 (±1.4)	9.4 (±2.6)	15.4 (±2.8)	3.8 (± 0.8)
MWCO (Da)	2200	2100	2000	1900	1200	700
Contact angle (°)	67	67	73	73	72	88
Roughness (Å)	19	22	26	29	13	25
Zeta potential (mV)						
pH 4	−7	−4	−3	−2	−2	−5
pH 7	−12	−10	−13	−8	−12	−15
pH 10	−17	−14	−13	−12	−15	−18

The MWCO or the molecular weight of polyethylene glycol with 90% retention, is larger for the self-made membranes and is about 2000 Da. Probably, the commercial membranes are post-treated after synthesis through which the MWCO of these membranes is smaller.

3.2.3. Testing of the performance of the membranes

The performance of the self-made membranes was tested in a cross-flow set-up, by filtrating a feed solution of uncharged and charged components during 2 h. To have a reference, the same experiments were repeated for the commercial membranes. The results of the retention and the relative flux after 2 h filtration for both the self-made and the commercial membranes are summarized in Table 4.

3.2.3.1. Evaluation of the retention. Table 4(a) shows a difference in retention of the self-made membranes, depending on the charge of the component. The uncharged component raffinose has the lowest retention, which is due to the absence of charge interactions between the component and the membrane surface. The larger MWCO of the self-made membranes in comparison with the commercial membranes causes the retention of raffinose to be lower for the self-made membranes.

However, when the components carry a negative charge, the retention increases considerably, even for very small components like diphenylaminosulfonic acid ($M_w = 271$ g/mol) or methyl orange ($M_w = 327$ g/mol). Strong repulsion forces between the negatively charged membrane and the negatively charged component can explain this phenomenon. These repulsion forces are even so strong that the retention of the self-made membranes is only a little lower than the commercial membranes, in spite of the larger MWCO of the former ones. For congo red, a large negative component ($M_w = 697$ g/mol), the same retention was observed for the different membranes after 2 h filtration.

However, this was not the case during the whole duration of the filtration experiment. The retention of congo red by the commercial membrane N30F was only 70% after 15 min of filtration and reaches a stable value (of 100%) only after 1 h. In contrast, the retention of the self-made membranes was already stable from the beginning of the experiment. Also for diphenylaminosulfonic acid, a very low retention of 30 and 50% was observed for, respectively, N30F and NFPES10 during the first hour of filtration. This phenomenon was not only observed for negatively charged components, but also for positively charged components like janus green. Unlike the stable retention of the self-made membranes, janus green was only retained for 40 and 80% by, respectively, N30F and NFPES10 in the beginning of the filtration experiment. Only after 90 min, a stable value of the retention (95%) was observed.

Another remarkable phenomenon is that janus green, even after reaching a stable retention, is less retained by the commercial membranes than by the self-made membranes. Five percent of janus green is passed through the commercial membranes, while D71 and D13 let pass only 1 or 2% of janus green. For N71 and N13 a retention of 96% or a passage of 4% of janus green was measured. This discrepancy between the commercial and the self-made membranes gets even larger when filtrating small positively charged components like

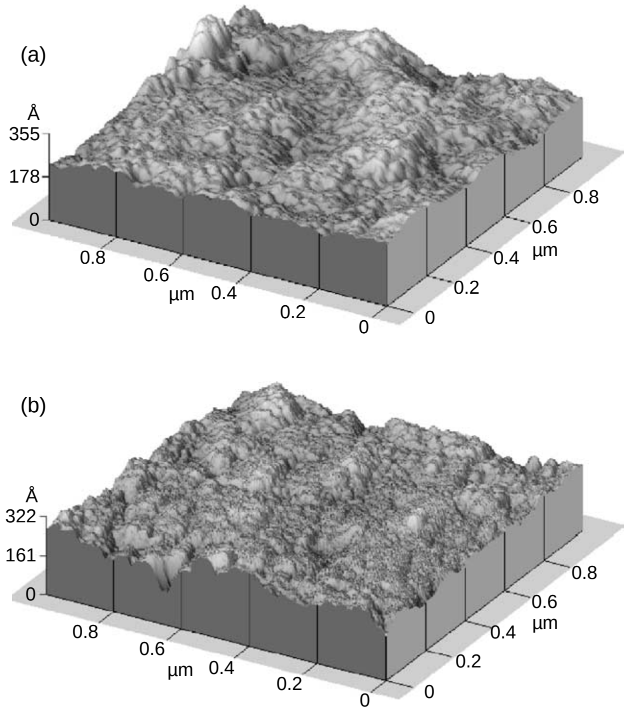


Fig. 7. Non-contact AFM images of (a) D13 and (b) N13.

Table 4
Retention (a) and relative flux (b) after 2 h of filtration in cross-flow

	N71	N13	D71	D13	NFPES10	N30F
(a)						
Raffinose	22	28	33	26	58	75
Diphenylamino-sulfonic acid	84	82	75	74	87	93
Methyl orange	55	55	72	69	76	88
Congo red	100	100	99	99	100	99
Neutral red	72	75	55	76	50	61
Methylene blue	79	80	80	79	32	35
Janus green	96	96	99	98	95	95
(b)						
Raffinose	70	86	58	71	63	42
Diphenylamino-sulfonic acid	69	72	79	81	53	29
Methyl orange	70	53	59	7	59	34
Congo red	36	85	32	75	55	43
Neutral red	56	54	63	11	49	17
Methylene blue	52	52	84	63	60	57
Janus green	55	52	83	60	53	46

neutral red ($M_w = 289$ g/mol) or methylene blue ($M_w = 320$ g/mol). Especially for methylene blue, a component with a double positive charge, this effect is remarkable: methylene blue is retained only for 32 or 35% by the commercial membranes, while retentions up to 80% were measured for the self-made membranes.

This remarkably higher retention of positively charged components by the self-made membranes can be explained in two different ways. A first way is by considering the adsorbed amount on the membrane surface. To that purpose, adsorption experiments were performed by using the set-up, described in detail in [35] and summarized in Table 5. Table 5 indicates that methylene blue is more adsorbed by the commercial membranes NFPES10 and N30F than by the self-made membranes, while janus green adsorbs almost equally on all polyethersulfone membranes. Because of the higher adsorption of methylene blue on the commercial membranes, these membranes will become saturated, which results in a breakthrough effect [36] and hence in a lower retention of this component by the commercial membranes. As no specific difference in adsorption of janus green between the commercial and the self-made membranes is observed, the breakthrough effect and hence the retention will be similar for all membranes. In spite of this breakthrough effect, the retention of janus green is larger than the retention of methylene blue by the commercial membranes, due to the larger size of janus green in comparison with methylene blue.

A second way to explain the high retention of positively charged components on self-made membranes is by studying the surface charge of the membranes, before and after the membrane has been in contact with the feed solution [37]. Therefore, surface charge measurements were performed for the pure membrane and for the same membrane after being immersed during 2 h (i.e. the duration of a cross-flow experiment) in a feed solution of methylene blue or janus green. For janus green, the surface charge of the membrane after 15 min immersion was also measured. The data are presented in Fig. 8 for D13 and N30F; the results were similar for the other membranes. Because the filtration experiments were performed at near neutral pH (pH 6), the following reasoning will be limited to this pH. Fig. 8(a) shows that for methylene blue, no difference in surface charge is observed between the pure and the immersed membrane. This effect is seen both for the commercial and the self-made membranes, in spite of the different amounts of adsorption of methylene blue on these membranes (Table 5). Starting from Fig. 8(a), the lower retention of methylene blue by the commercial membranes could be explained by the large negative surface charge. Between the positively charged component and the negatively charged surface an electrostatic attraction force will act, resulting in an increased concentration of the component in the membrane and hence in a lower retention. Because the self-made membranes are not so negatively charged as the commercial membranes, the attraction force between component and surface is smaller and hence a larger retention of methylene blue is obtained. For janus green (Fig. 8(b)), the surface charge of the commercial membrane N30F did not change during the first 15 min. Only after 2 h the membrane surface became less negatively charged, probably due to adsorption of janus green. Although the same amount of adsorption was observed for the self-made and the commercial membranes (Table 5), no decrease in the surface charge of the

Table 5
Adsorbed amount (in mmol/m^2) of methylene blue and janus green on the self-made and the commercial membranes

	Methylene blue	Janus green
D13	0.2	6.1
N13	0.5	4.9
NFPES10	3.7	8.0
N30F	2.8	5.7

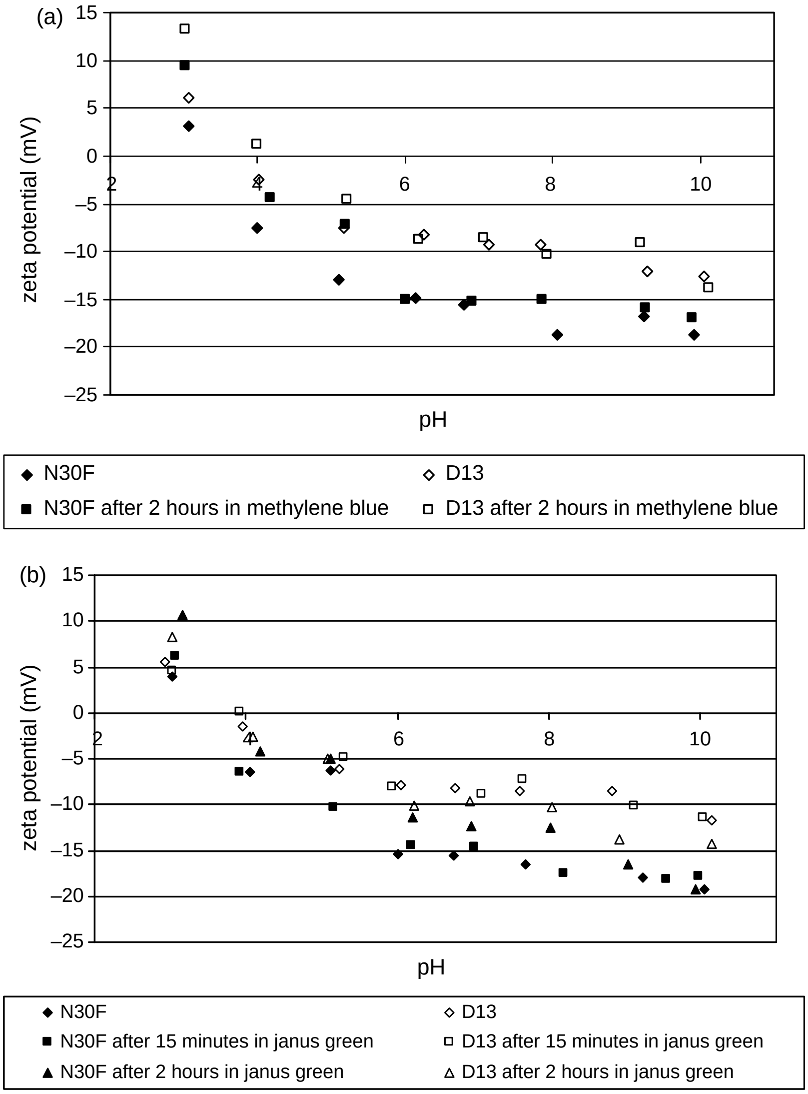


Fig. 8. Zeta potential in function of the pH for D13 and N30F, before and after immersing in (a) methylene blue and in (b) janus green.

self-made membrane D13 was observed. The surface charge of D13 remained almost the same after 15 min immersion and even became a little more negatively charged after 2 h immersion. The latter is probably due to inaccuracies during measuring. From the observations given in Fig. 8(b), two conclusions can be drawn. The first conclusion is that the time dependency of the surface charge corresponds to the time dependency of the retention of janus green. As mentioned previously, low retentions of janus green for the commercial membranes were observed during the beginning of the filtration because the membrane surface is then still very negatively charged. Only after 2 h, when the surface has become less negative, the electrostatic attraction force between component and surface diminishes resulting in a higher retention. Unlike the commercial membranes, the self-made membranes had a stable high retention from the beginning of the filtration, which is in agreement with the fact that almost the same surface charge was observed before and after immersing these membranes in a solution of janus green. A second conclusion that can be drawn from Fig. 8(b), is that the surface charge of both the commercial and the self-made membranes is almost equal after immersion during 2 h in janus green. This could explain the similar retention of janus green for these membranes.

From this description of the influence of the component's charge on the retention, it becomes clear that the self-made membranes have the highest retention for charged components, independently of the sign of the charge. In contrast, the retention for the commercial membranes is dependent on the sign of the component's charge as the lowest retention was observed for small positively charged components. Beside the influence of the component's charge, there is also an influence of the molecular weight as larger components are better retained. The only exception to this is methyl orange, which shows a too small retention for his molecular weight for all membranes.

3.2.3.2. Evaluation of the relative flux. Table 4(b) shows the relative fluxes after 2 h of filtration for different feed solutions. Because the relative flux is defined as the relation of the permeate flux to the pure water flux, the relative flux is a measure for the degree of fouling: a small relative flux corresponds with a lot of fouling. The fouling degree of all membranes for all feed solutions is almost comparable with some exceptions. For example, raffinose and diphenylaminosulfonic acid have smaller relative fluxes for the commercial membranes in comparison with the self-made membranes. However, the small relative flux of diphenylaminosulfonic acid for the commercial membranes was not observed during the whole duration of the filtration experiment: only after 1 h the permeate flux decreased considerably. This means that during the first hour of filtration, diphenylaminosulfonic acid is characterized by a small retention (Section 3.2.3.1) and a large permeate flux. After 1 h, however, the situation is changed and a high retention combined with a small permeate flux is observed for the commercial membranes. This phenomenon can be explained by the fact that a lot of fouling seems to occur during the filtration. This fouling blocks the pores more and more, finally resulting in less passage of component (high retention) and solvent (low permeate flux).

Very small permeate fluxes are also observed when filtrating methyl orange or neutral red with D13 or N30F. Especially for D13, specific interactions between these components and the membrane caused the flux through the membrane to decrease by 90%. Of the tested positively charged components, neutral red is the only one, which results in severe fouling on some membranes. This implicates that the good retention of the positively charged components by the self-made membranes does not result in more fouling, as the degree of fouling is comparable for the self-made and the commercial membranes. The D71 membrane even showed the least fouling for methylene blue and janus green in comparison with the other membranes.

4. Conclusions

In this study, nanoporous polyethersulfone membranes were prepared using the phase inversion technique. To combine a high retention of a reference component (congo red) with a reasonable water permeability, it was proven that the concentration of the polymer is an important preparation factor to control. The relative air humidity during casting should also be as low as possible to improve the reproducibility.

Beside these two preparation factors, it was shown that the membrane structure and hence the membrane performance are largely dependent on the solvent as NMP-membranes have a higher water permeability than DMF-membranes. Only giving information about the polymer type, as the manufacturers of commercial membranes do, is hence not sufficient to understand and to explain membrane fouling.

In the second part of the study, membranes on a non-woven support were characterized and tested for their performance in a cross-flow set-up. Although these self-made membranes were characterized by a larger molecular weight cut-off in comparison with commercial polyethersulfone nanofiltration membranes, the retention of charged components was remarkably high. This was especially observed for small positively charged components, which was explained by the less adsorption on the self-made membranes or by the small negative surface charge of these membranes. Although the retention is high, the degree of fouling for the self-made membranes is comparable with the commercial membranes, which in combination with the higher pure water permeability, leads to higher permeate fluxes. The fact that there is more and more pure permeate flux, makes the self-made membranes interesting when filtrating aqueous solutions of charged components.

Acknowledgements

Katleen Boussu is grateful to IWT-Vlaanderen (Institute for the Promotion of Innovation by Science and Technology in Flanders) for providing a fellowship. The authors also wish to thank Prof. C. Linder from the Ben-Gurion University of the Negev (Israel) for the useful discussions. Prof. Van der Meeren (Ghent University), Prof. Van Haesendonck (K.U.Leuven) and Prof. Delcour (K.U.Leuven) are also thanked for providing, respectively, the zeta potential set-up, the AFM set-up and the GPC set-up.

References

[1] De Florio L, Giordano A, Mattioli D. Desalination 2005;181(1–3): 283–92.
[2] Cornelis G, Boussu K, Van der Bruggen B, Devreese I, Vandecasteele C. Ind Eng Chem Res 2005;44(20):7652–8.
[3] Tang C, Chen V. Desalination 2002;143(1):11–20.
[4] Schafer AI, Fane AG, Waite TD. Desalination 2000;131(1–3):215–24.
[5] Escobar IC, Randall AA, Hong SK. J Water Sup Res Technol Aqua 2002; 51(2):67–76.
[6] Matilainen A, Liikanen R, Nystrom M. Environ Technol 2004;25(3): 283–91.
[7] Koros W, Ma Y, Shimidzu T. J Membr Sci 1996;120(2):149–59.
[8] McHugh AJ, Miller DC. J Membr Sci 1995;105:121–36.
[9] Kim IC, Yoon HG, Lee KH. J Appl Polym Sci 2002;84(6):1300–7.
[10] Kastelan-Kunst L, Dananic V, Kunst B, Kosutic K. J Membr Sci 1996; 109:223–30.
[11] Lin DJ, Chang CL, Chen TC, Cheng LP. Desalination 2002;145:25–9.
[12] Zhang SH, Jian XG, Dai Y. J Membr Sci 2005;246(2):121–6.
[13] van de Witte P, Dijkstra PJ, van den Berg JWA, Feijen J. J Membr Sci 1996;117:1–31.
[14] Tkacik G, Zeman L. J Membr Sci 1987;31:273–88.
[15] Barton BF, Reeve JL, McHugh AJ. J Polym Sci, Part B: Polym Phys 1997; 35:569–85.
[16] Barth C, Wolf BA. Polym Phys 2000;41:8587–96.
[17] Swinyard BT, Barrie JA. Br Polym J 1988;20:317–21.
[18] Kim JY, Lee HK, Kim SC. Korean J Chem Eng 2000;17(5):564–9.
[19] Han MJ, Bhattacharyya D. Chem Eng Commun 1994;128:197–209.
[20] Baik KJ, Kim JY, Lee JS, Kim SC, Lee HK. Korea Polym J 2001;9(5): 285–91.
[21] Han MJ, Bummer PM, Jay M. Polymer 1995;36(24):4711–4.
[22] Barth C, Gonçalves MC, Pires ATN, Roeder J, Wolf BA. J Membr Sci 2000;169:287–99.
[23] Mosqueda-Jiminez DB, Narbaitz RM, Matsuura T. Sep Purif Technol 2004;37:51–67.

[24] Marchese J, Ponce M, Ochoa NA, Pradanos P, Palacio L, Hernandez A. J Membr Sci 2003;211:1–11.
[25] Han MJ, Nam ST. J Membr Sci 2002;202:55–61.
[26] Kim JH, Lee KH. J Membr Sci 1998;138:153–63.
[27] Chaturvedi BK, Ghosh AK, Ramachandhran V, Trivedi MK, Hanra MS, Misra BM. Desalination 2001;133:31–40.
[28] Han MJ. Desalination 1999;121:31–9.
[29] Linder C, Kedem O. J Membr Sci 2001;181:39–56.
[30] Spricigo CB, Petrus JCC, Machado RAF, Sarmento LAV, Bolzan A. J Membr Sci 2002;205:273–8.
[31] Tsai FJ, Kang D, Anand M. Sep Sci Technol 1995;30(7–9):1639–52.
[32] Van der Bruggen B, Schaep J, Wilms D, Vandecasteele C. Sep Sci Technol 2000;35(2):169–82.
[33] Boussu K, Van der Bruggen B, Volodin A, Van Haesendonck C, Delcour JA, Van der Meeren P, et al. Accepted for publication in Desalination.
[34] Dubois M, Gilles KA, Hamilton K, Rebers PA. Anal Chem 1956;28(3): 350.
[35] Braeken L, Boussu K, Van der Bruggen B, Vandecasteele C. Chemphyschem 2005;6:1606–12.
[36] Braeken L, Ramaekers R, Zhang Y, Maes G, Van der Bruggen B, Vandecasteele C. J Membr Sci 2005;252(1–2):195–203.
[37] Susanto H, Ulbricht M. J Membr Sci 2005;266(1–2):132–42.