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Novel ultrafiltration membranes from low-fouling copolymers for RO pretreatment applications

Ralf Krüger[a], Denis Vial[a], Davis Arifin[b], Martin Weber[c], Martin Heijnen[a,*]

[a]*Inge GmbH, Flurstrasse 27, Greifenberg 86926, Germany, email: mheijnen@inge.ag (M. Heijnen)*
[b]*BASF SE, G-EVG/MS-MA-R64-1, Ludwigshafen 67056, Germany*
[c]*BASF SE, GMV/W—B001, Ludwigshafen 67056, Germany*

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ABSTRACT

For a consistent and reliable ultrafiltration (UF) membrane operation, the membrane flux level has always been determined conservatively so that fouling rate is controllable, and therefore, chemical cleaning requirements are minimized. A better solution is to prevent the fouling to happen in the first place by modifying the surface properties of the membrane materials. This paper presents novel approaches to improve the fouling-propensity performance of existing UF membranes based on polyethersulfone. More hydrophilic membranes and anti-adhesive membranes were developed by using various novel copolymers as base membrane materials or as an additive in the spinning process. Incorporating these copolymers, improved Multibore® fibers were produced and validated in multiple pilot trials for various applications, namely surface and wastewater purification and seawater reverse osmosis pretreatment for desalination. The paper demonstrates that, for each application, a reduced fouling propensity performance was achieved, allowing the fibers to be operated at a substantially higher flux of up to 30%. This study underscores the importance of chemistry in obtaining low-fouling and high-performance UF membranes by modifying their surface properties.

Keywords: Copolymer; Fouling; Membrane modification; Ultrafiltration; Seawater

1. Introduction

Although human factors and climate change put intensive stress on world’s existing freshwater resources, there is enough water available for the whole global population especially when considering that originating from seawater. For many years, ultrafiltration (UF) is considered as the preferred technology for pretreating, in an economical way, challenging seawater before reverse osmosis membranes. Typically, fluxes in filtration are rather low or conservative in order to limit fouling. Different routes have been considered and reviewed to prevent the fouling of membranes [1,2]. Of special interest is the modification of the UF membrane surface by increasing the hydrophilicity of the membrane material. This can be achieved by the addition of copolymers

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*Corresponding author.

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containing hydrophilic moieties such as polyethylene oxide (PEO) [3,4]. Furthermore, the backbone of polyethersulfone (PESU) can be modified by sulfonation, leading to membranes with higher hydrophilicity [5,6]. Another approach discussed in the literature is based on groups having low interaction with organic molecules. This leads to antiadhesive properties that might also positively influence the fouling performance [7]. This paper describes the chemical modification of standard PESU membranes. It also presents results on membrane characterization and performances of small-scale modules operated on different types of water.

2. Methods and approach

The goal of this study is to evaluate and to select an improved membrane formulation able to limit or prevent the fouling tendency of all membranes when operated on challenging waters. The approach was to first test hundreds of formulations on very small flat-sheet membranes, then to perform short-term fouling tests on about 100 of the 500 original formulations using very small laboratory-scale modules. Then, three formulations are selected and evaluated in bigger modules. The best formulation is finally tested on full-scale modules running in parallel with modules containing standard membranes used as reference. Test steps are summarized in Fig. 1.

The synthesis of the hydrophilic PESU-polyethylene oxide (PESU-PEO) copolymers was performed according to procedures from literature [8]. Various PESU-PEO-copolymers, showing different hydrophilic–hydrophobic balance, were prepared based on commercially available Polyethylene oxides with molecular weights between 2,000 and 8,000 g/mol (Fig. 2). The composition and the molecular weights of the obtained copolymers are summarized in Table 1.

In addition, other variants of antiadhesive PSU-PEO-polysiloxane copolymers were prepared by coupling of HO-terminated polysulfone (HO-PSU-OH) with PEO-polysiloxane-PEO-products by means of an addition reaction. The composition of the antiadhesive PSU-PEO-polysiloxane-copolymers are given in Table 2.

The newly developed copolymers were mixed into a dope solution, and subsequently, flat-sheet membranes were prepared using a standardized process including film formation on a glass plate, precipitation in water and subsequent post-treatment with NaOCl solution. The PWP (pure water flux) and the molecular weight cutoff (MWCO) of the obtained membranes were characterized using a stirred pressure cell with a membrane surface of 35 cm^2. A pressure of 1 bar was applied and filtration of 300 ml of ultrapure water was done five times. The MWCO values were measured filtering a PEO/PEG-standard solution (1,000 ppm) at a pressure of 0.2 bar and comparing the gel permeation chromatography (GPC) traces of permeate and feed solution.

Based on these trials, qualified candidates for further spinning trials were chosen. Flat-sheet membranes were produced for trials to validate the surface composition of new membranes by X-ray photoelectron spectrometry (XPS), a technique used to assess the surface enrichment of the additive on the active side of the asymmetric membrane especially in the

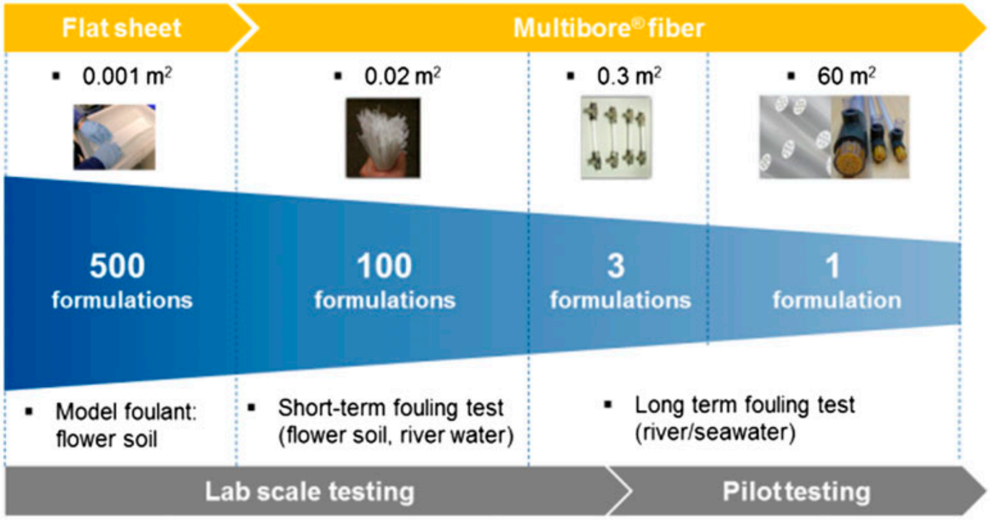


Fig. 1. Step-by-step membrane screening and validation approach.

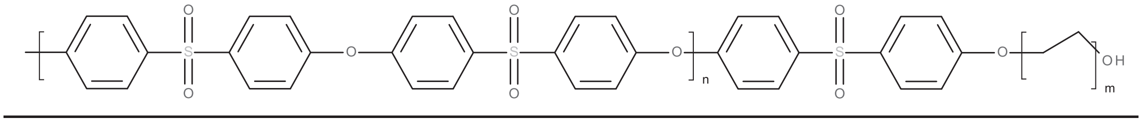


Fig. 2. Chemical structure of the PESU-PEO-copolymers.

Table 1
Chemical composition and properties of PESU-PEO-copolymers

Product	Mn PEO (g/mol)	PEO content (wt.%)	Mw/Mn (kD)	Tg (°C)	Contact angle (°)
PESU-PEO 2,000/11.5	2,000	11.5	77.2/22.1	156	66
PESU-PEO 2,000/18	2,000	18.0	69.9/24.0	129	62
PESU-PEO 4,000/20.4	4,000	20.4	92.5/23.2	108	–
PESU-PEO 6,000/26.2	6,000	26.2	57.7/15.7	71	–
PESU-PEO 8,000/34.8	8,000	34.8	67.3/17.4	9/152	20–25
PESU	–	–	60.2/17.0	226	75

Table 2
PSU-PEO-polysiloxane copolymers

Product	Mn PSU (g/mol)	PEO-polysiloxane content (wt.%)	Mw/Mn (kD)
PSU-PEO-polysiloxane 2,200/80–20	2,200	17.5	22.1/8.6
PSU-PEO-polysiloxane 2,200/66–34	2,200	23.3	18.6/4.5
PSU-PEO-polysiloxane 4,200/80–20	4,200	17.7	23.1/8.0

case of membranes with the PSU-PEO-polysiloxane-copolymer. For several samples, atomic force microscopy (AFM) was employed to characterize the adsorption and detachment performance of the membranes to specially treated tips.

The qualified candidates were mixed in a dope solution and subsequently hollow fibers were spun by means of the well-known nonsolvent-induced phase separation technique under a Multibore® membrane (patented fiber configuration of inge® combining seven individual capillaries in a highly robust fiber). After optimization of the spinning parameters, the properties of the new fibers were similar to those of reference Multibore® fibers in terms of mechanical strength, water permeability, and MWCO (Table 3).

Fouling propensities of the produced membranes have been quantified by a newly developed fouling and cleaning protocol. Organic components from a potting soil were leached out by mixing 1 kg of potting soil with 4 kg of a 0.25 N NaOH solution. This mixture was left for 12 h prior to filtering off the solids with a 100-micron bag filter. As the flower soil can be bought in bulk, the use of this extract enables reproducible results under controlled feed water conditions. It is estimated that this method leaches out approximately two-thirds of all the organic components in the soil.

Fouling experiments were conducted on different pilot units. First tests were performed on laboratory-scale pilot units equipped with modules containing either standard Multibore® fibers (used as reference)

Table 3
Characteristics of a PSU-PEO-polysiloxane compared to a reference Multibore®

Membrane	MWCO (kDa)	PWP (l/m^2 h bar)	Burst pressure (Bar)
Reference Multibore®	80–100	1,000-1,200	>12
PSU-PEO-Polysiloxane based	89	1,164	>12

or modified fibers, each module developing an active filtration surface of 0.02 m^2. Filtration parameters (flux and concentration of the organic extract) were chosen so that the transmembrane pressure (TMP) of a reference Multibore® membrane increases up to 0.8 bar within approximately 4 h. The total run time was chosen to be 20 h allowing one fouling measurement per day. Upon reaching the 0.8 bar TMP limit, the membranes were cleaned with NaOH (pH 12.3) followed by H_2SO_4 (pH 1.7). This cleaning regime typically removes more than 98% of all fouling.

Other piloting was conducted with small-scale automatic pilot units (Fig. 3) equipped with up to four modules (each 0.2–0.3 m^2 active filtration surface) able to run in parallel, each line being equipped with individual controls.

3. Results and discussion

Even though the rather high pH used for this extraction method is capable of causing some deterioration of some of the organics from the soil, the liquid chromatography–organic carbon detection (LC–OCD) component analysis of the mixture showed a good comparison with naturally occurring surface water such as the Windach River, southern part of Germany (Fig. 4).

CIRSEE's laboratories conducted similar testing in France with Seine river water also without adding coagulant. Fig. 5 shows the LC–OCD analysis of Seine river water taken at the same time as when the membrane testing was performed.

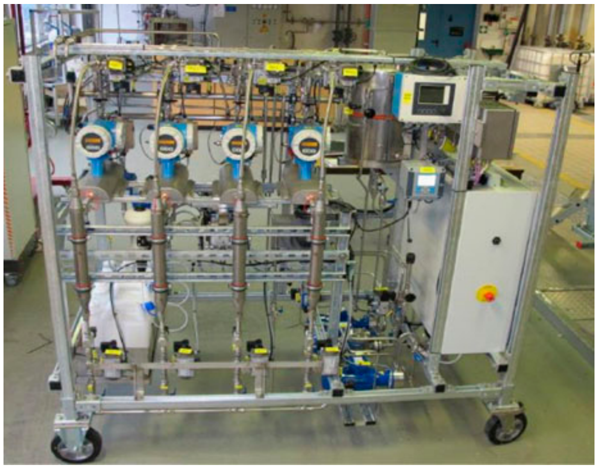


Fig. 3. Small-scale pilot unit.

3.1. Synthesis and characterization of PESU-PEO copolymers

High molecular weight PESU-PEO-copolymers with different composition are accessible by nucleophilic polycondensation. The amount of hydrophilic component in the investigated products lies between 11.5 and 34.8 wt.% (Table 1). In each case, the achieved molecular weights are in the region comparable to the standard PESU material used in this study, the Ultrason® E 3010.

Due to the known miscibility of PESU and PEO, most copolymers show only a single Tg and no indication for crystalline segments as already observed by Ting et al [8]. The thermograms displayed in Fig. 6 clearly show the significant decrease in the Tg of PESU with increasing amount of PEO in the copolymers due to the miscibility of the two components. The PESU-PEO 8,000/34.8-copolymer shows two Tg´s (not displayed) and also no sign of crystallinity. The reason for this unusual phase behavior is not clear yet. One can assume that it might be due to a phase separation into two phases with significantly different composition (PEO-rich and PESU-rich).

Considering the thermal requirements during potting and cleaning operations of such membranes, the main focus for the membrane screening tests lies on candidates having a Tg above 125°C. The molecular weight of particular copolymers can be easily tuned by the means of stoichiometric adjustment. The GPC-traces (Fig. 7) clearly show a molecular weight distribution for the copolymers comparable to the reference material Ultrason® E 3010. Applying HPLC-techniques, the absence of free polyethylene oxide blocks (<0.1 wt.%) could be proven. Due to the applied purification procedure, these compounds are completely removed.

In conclusion, the used synthetic procedure allows the synthesis of tailor-made copolymers by either changing the molecular weight of the PEO building block or the molar amount of the PEO building block used in the synthesis. By variation of the stoichiometric ratio between the monomers the molecular weight can be adjusted as well.

3.2. Synthesis and characterization of PSU-PEO-PSiloxane

PSU-PEO-polysiloxane-copolymers with various compositions and different PSU-block copolymer length (Table 2) were prepared as well. The molecular weights of the copolymers are controlled by the amount of Di-isocyanate used for the coupling reaction. For the copolymers employed in this study, diphenylmethane-4,4´-diisocyanate (MDI) was used as

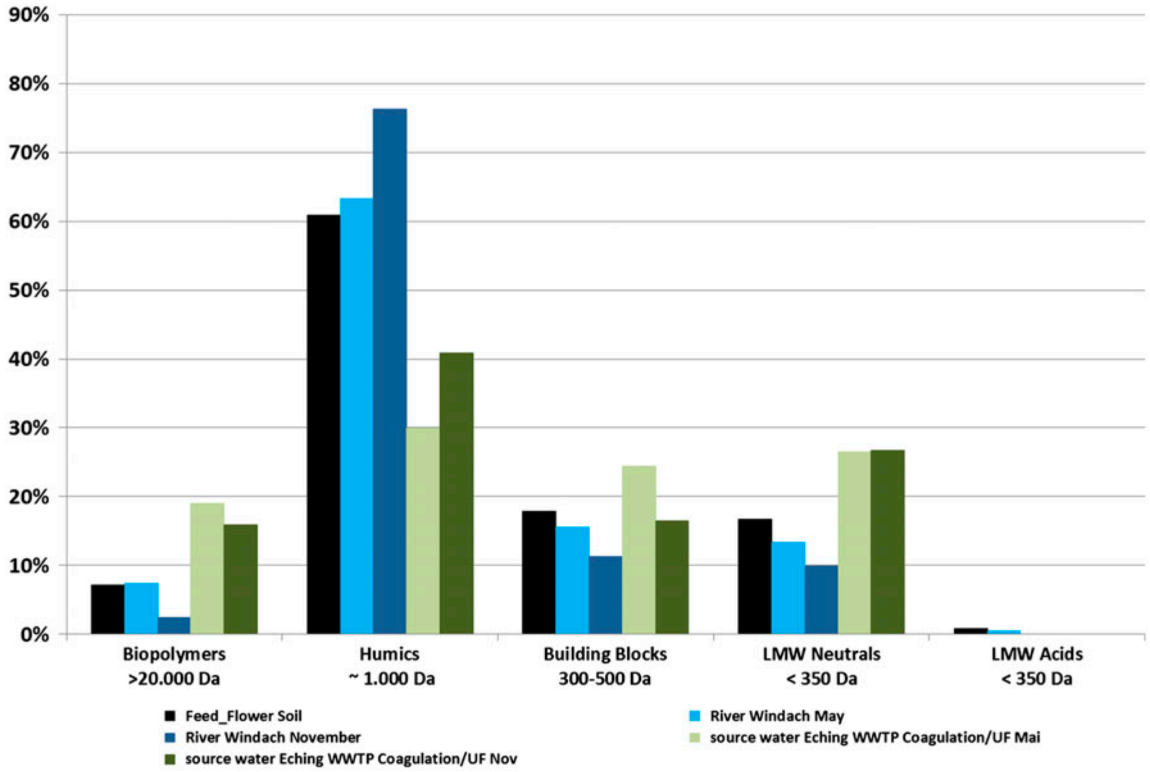


Fig. 4. LC-OCD analysis of flower soil extract in comparison with that of Windach river water.

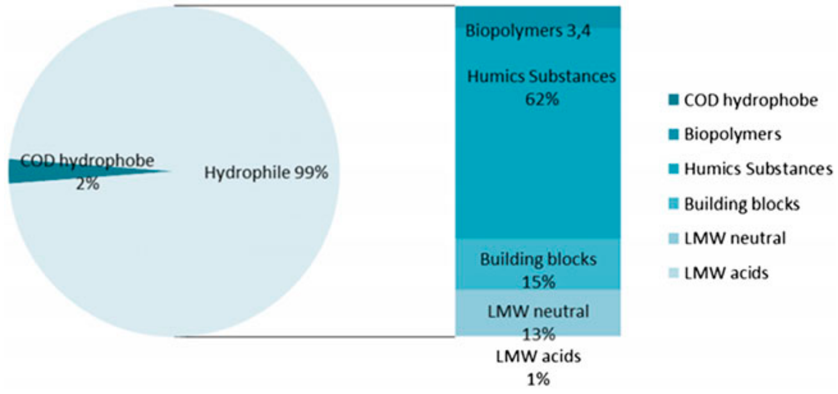


Fig. 5. LC-OCD analysis of Seine (Paris) river water.

coupling agent. The composition of the obtained copolymers was determined using proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) and elemental analysis (S, Si, N). As can be seen from Fig. 8, the different components of the PSU-PEO-polysiloxane-copolymer can be clearly identified and quantified by signal integration.

The stability of the PSU-PEO-polysiloxane copolymers against diluted acids (0.01 m H_2SO_4) and bases (0.01 m KOH) was tested and no significant change of the molecular weight was detected.

3.3. *Preparation and characterization of flat sheet membrane*

The dope formulation consists of PESU-based polymer, pore-forming agent PVP (polyvinylpyrrolidone) and organic solvent (NMP (N-methyl-2-pyrrolidone).

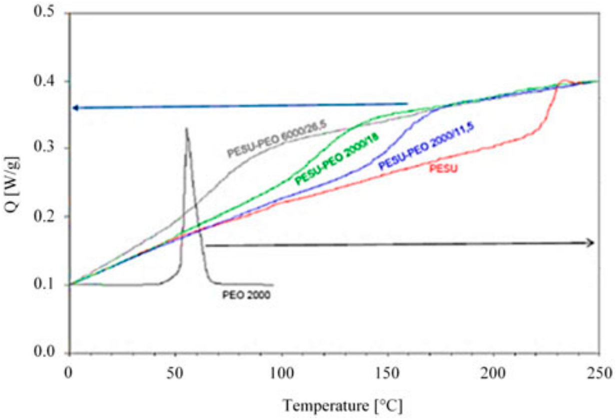


Fig. 6. DSC-traces of PESU, PEO and different PESU-PEO-copolymers, please note the different scale for the PEO.

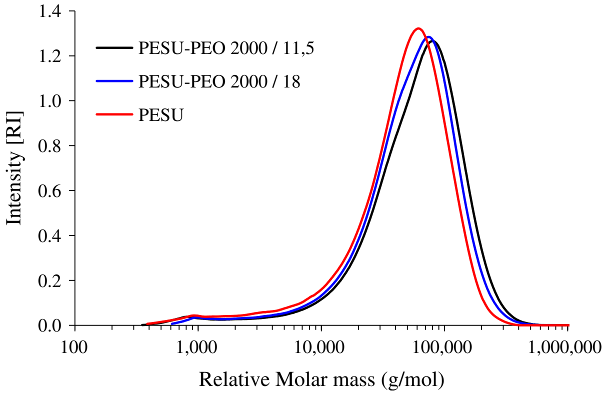


Fig. 7. GPC traces of PESU and different PESU-PEO copolymers.

Flat-sheet membranes (wet thickness 200 μm) were prepared by casting the dope solution on a glass plate and subsequent precipitation in water. After precipitation, the obtained membranes were subjected to a post-treatment procedure to reduce the amount of residual PVP in the membrane. The membranes were then thoroughly washed with water and stored in water. Table 4 summarizes the data obtained for the different membranes based on PESU-PEO-copolymers.

During the membrane preparation, the time to achieve precipitation increased with increasing part of the PEO in the copolymers. Hence, the copolymers with higher PEO content form membranes with significantly larger pores, as can be seen from the MWCO values obtained. In all cases, the permeability increased quite substantially compared to the reference sample.

For this reason, subsequent trials focused on the use of PESU-PEO copolymers with lower content of PEO (<20 wt.%). Furthermore, the polymer concentration of the dope solutions was increased to 15.6 wt.% (Table 5). Several different PESU-PEO copolymer concentrations were introduced to produce the flat-sheet membranes. The PESU-PEO copolymer with 11.5 wt.% PEO forms membranes with comparable properties as PESU. At higher PEO-content, again the MWCO-value of the membrane is much higher. Hence, for further trials, the PESU-PEO copolymer with 11.5 wt.% PEO was employed.

Similar screening trials were performed for the PSU-PEO-polysiloxane copolymers. Table 6 summarizes screening trials using flat-sheet membranes. The preparation of the membranes was done as previously described, in which the amount of the PESU polymer was kept constant at 15.6 wt.%. In first trials, the influence of the amount of PSU-PEO-polysiloxane was studied. Increasing the amount of additive from 0.4 to 1.2 wt.% in the dope solution leads a slight reduction in the permeability, while the MWCO values remain in the target area. Trials with different composition of the copolymer show no clear trends. The best results were obtained using a PSU-PEO-polysiloxane 4,200/80–20 copolymer, and hence, this material was prepared in larger quantities to prepare Multibore® hollow fibers.

Due to the known low surface energy of polydimethylsiloxane, it was expected that during the membrane formation these units might accumulate at the membrane surface as previously observed by Owen et al. [9]. Since the PSU blocks interact with the PESU of the membrane, the PSU-PEO-polysiloxane additives are permanently fixed to the membrane surface. To prove this, the concentration of silicon at the surface of the membranes was detected by XPS analysis. The bulk content of the membranes was analyzed by inductively coupled plasma mass spectrometry using 0.5 g samples of the membrane. A typical XPS-spectra for membrane 6 (M6) is shown in Fig. 9. The level of Si was determined to be 6.1 wt.% on the surface.

The data obtained for two samples are shown in Fig. 10. In both cases, a significant enrichment of the siloxane units at the membrane surface could be detected. The value obtained for the bulk sample is 15–20% lower as expected, indicating a slight loss of the additive either during membrane preparation or post-treatment. A significant enrichment of the Siloxane units at the membrane surface could be detected by these measurements.

Furthermore, the surface of the membranes containing the PSU-PEO-polysiloxane additives was investigated by AFM technique. As shown in Fig. 11, the addition of the PSU-PEO-polysiloxane additive

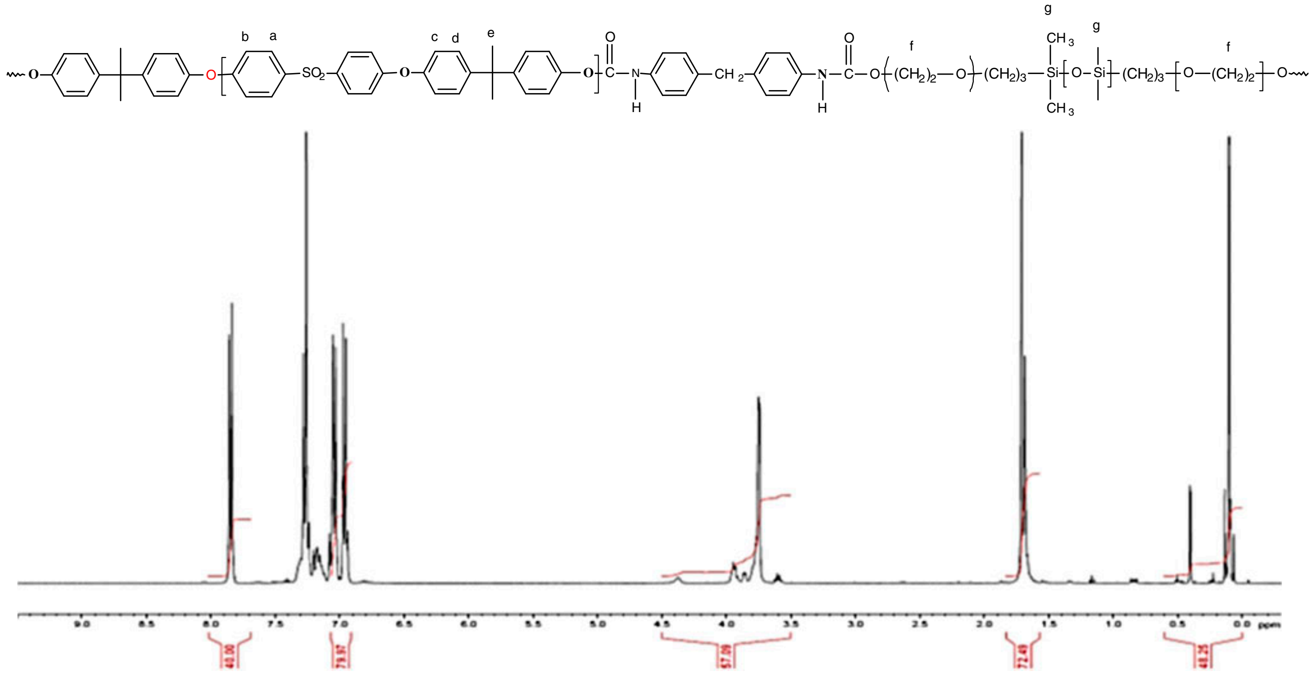


Fig. 8. ^{1}H-NMR-spectra of PSU-PEO-polysiloxane 2,200/80–20 (in $CDCl_3$, no TMS).

leads to new structural features at the membrane surface. Circular dots of 0.2–0.8 μm in diameter are visible in the AFM image of membrane three, containing 0.8 wt.% of PSU-PEO-PSiloxane 2,200/80–20. Further, measurements are necessary to clearly understand the origin of the circular objects that appear at the surface of the membrane containing the additive.

Since the polysiloxane-PEO-block and the PSU-block are chemically linked to each other, the additive is fixed to the membrane surface by the strong interactions of the PESU-matrix and the PSU-blocks as well as by entanglements between the PEO-units and PESU, due to the miscibility of both polymers [10].

The membranes were further analyzed by means of scanning electron microscopy (SEM) where the outer skin, the inner filtration layer as well as the overall foam structure of the produced membranes could be visualized. Some of the obtained images depicting the inner layer as well as the overall

Table 4
Properties of UF flat-sheet membranes prepared from PESU-PEO copolymers (14%)

Product	PWP (kg/m^2 h bar)	MWCO (kD)
PESU	950	87
PESU-PEO 2,000/11.5	1,600	250
PESU-PEO 2,000/18.0	1,900	>500
PESU-PEO 4,000/20.4	1,700	>500
PESU-PEO 6,000/26.2	1,650	>500

Table 5
Properties of UF flat-sheet membranes prepared from PESU-PEO copolymers (15.6%)

Product	PWP (kg/m^2 h bar)	MWCO (kD)
PESU	1,300	99
PESU-PEO 2,000/11.5	1,230	165
PESU-PEO 2,000/18.0	1,470	>500

Table 6
Properties of UF flat-sheet membranes based on PESU with PSU-PEO-polysiloxane additives

Product (membrane no.)	PWP (kg/m^2 h bar)	MWCO (kD)
M1 PESU	1,200	86
M2 PESU/PSU-PEO-polysiloxane 2,200/80–20 (0.4%)	1,070	84
M3 PESU/PSU-PEO-polysiloxane 2,200/80–20 (0.8%)	1,020	81
M4 PESU/PSU-PEO-polysiloxane 2,200/80–20 (1.2%)	900	79
M5 PESU/PSU-PEO-polysiloxane 2,200/66–34 (0.8%)	950	78
M6 PESU/PSU-PEO-polysiloxane 4,200/80–20 (0.8%)	1,040	76

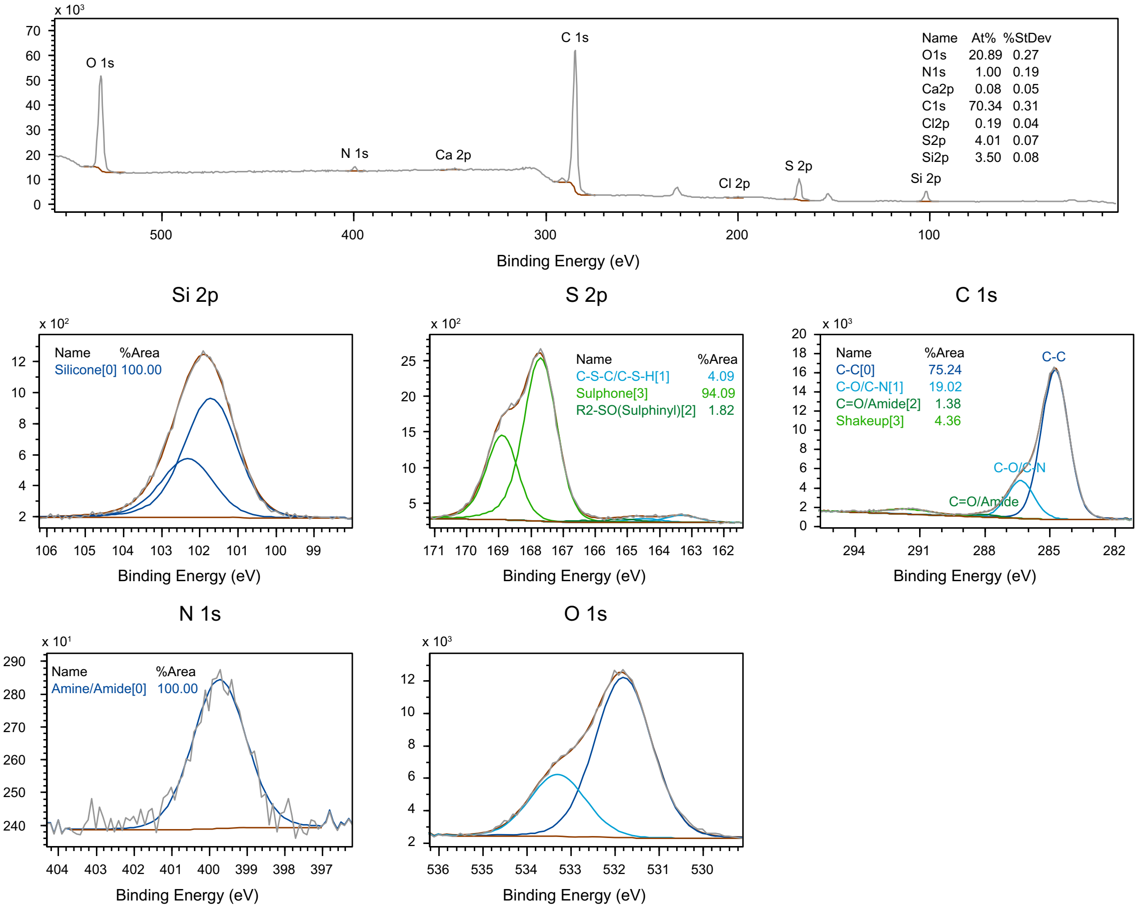


Fig. 9. XPS-spectrum of membrane M6.

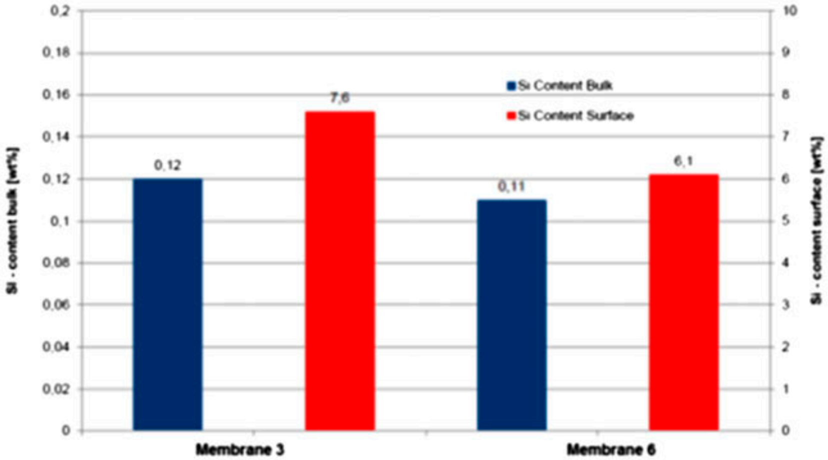
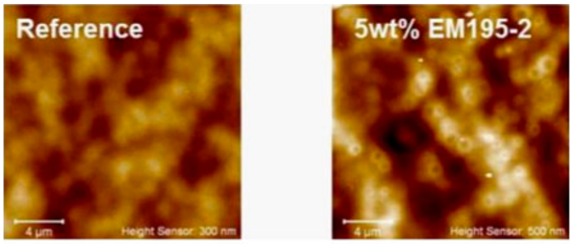
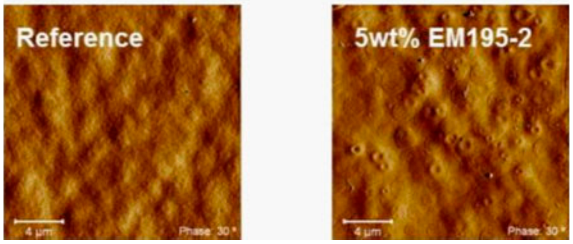


Fig. 10. Si-concentrations at the surface and the bulk for membrane samples M3 (PESU/PSU-PEO-PSiloxane 2,200/80–20 (0.8%)) and M6 (PESU/PSU-PEO-PSiloxane 4,200/80–20 (0.8%)).



Topography (High: bright–Low: dark)



Phase (Hard: bright –Soft: dark)

Fig. 11. AFM-images (topography, phase) of membrane one (PESU) and membrane three (PESU/PSU-PEO-PSiloxane 2,200/80–20 (0.8%)).

structure of the membrane are shown in Fig. 12 and can be compared to SEM picture of a Multibore® reference membrane (Fig. 13).

3.4. Multibore® membrane fiber quick screening with artificial foulant and Seine river water

The potential for synthesizing various new polymers either as base membrane material, or as an additive in the membrane spinning process is vast. As the spinning process also introduces a large number of variables, it is clear that not all membranes can be tested in long-term pilot studies. In order to shortlist a few lead candidates (LC) for further piloting, many of the novel membranes were potted in mini-modules and tested with the fouling procedure as explained in the experimental section. The TMP variation of two different membranes (LC1 made of PESU-PEO and LC2 made of PSU-PEO-polysiloxane) have been compared while filtering an extract of flower soil at a flux of 75–150 L/h m^2 under identical backwash (BW) flow rate of 300 L/h m^2 but under different concentration of the extract in the feed solution. At a flux of 150 L/h m^2, the concentration of the extract in the feed solution corresponds to 1/10 of the concentration at a flux of 75 L/h m^2.

From these tests (Fig. 14), it can be concluded that the TMP increase at a flux of 75 L/h m^2 is very similar for both types of membranes. However, under the higher flux of 150 L/h m^2, one can note that the TMP increase rate for the LC2 membrane is significantly lower than the one of the standard membrane resulting in a lower fouling rate of the membrane B. One can assume that the improvement is mainly due to the modified structure of the membrane allowing an increased efficiency of the BW process. In dead-end filtration, all foulants that are (partially) retained by the membrane will have to move to the membrane surface with which they interact in a variety of ways. As the LC2 membrane presents a 'nonstick' type of surface, the potential foulants have less grip on the membrane's surface, and a backwash is able to loosen these materials from the membrane in a much more efficient way. The result is that the LC2 membrane can be run under higher fluxes, without causing more permanent types of fouling.

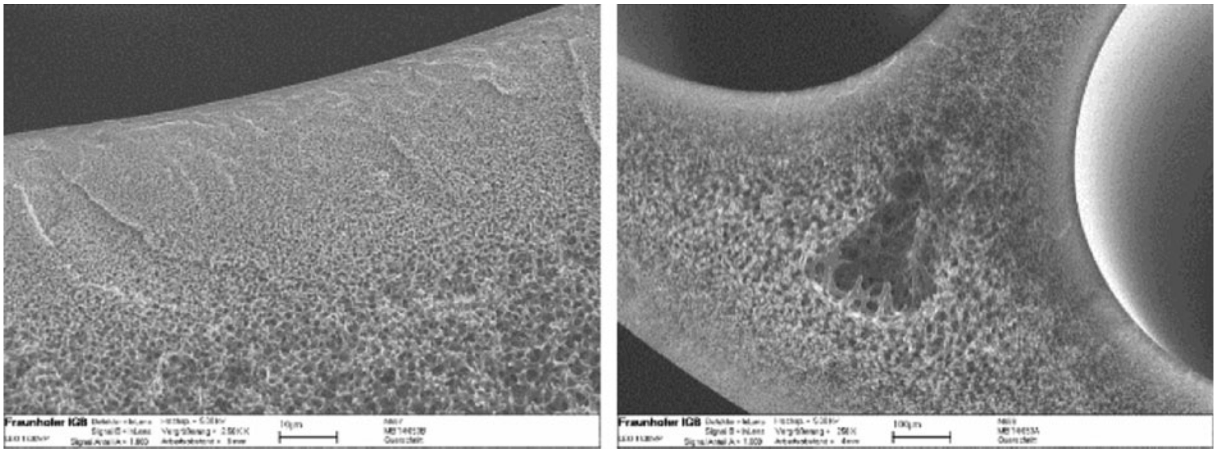


Fig. 12. SEM pictures of a membrane produced with PSU-PEO-Polysiloxane as an additive left: Inner skin—Right: Area between the outer wall and two capillaries.

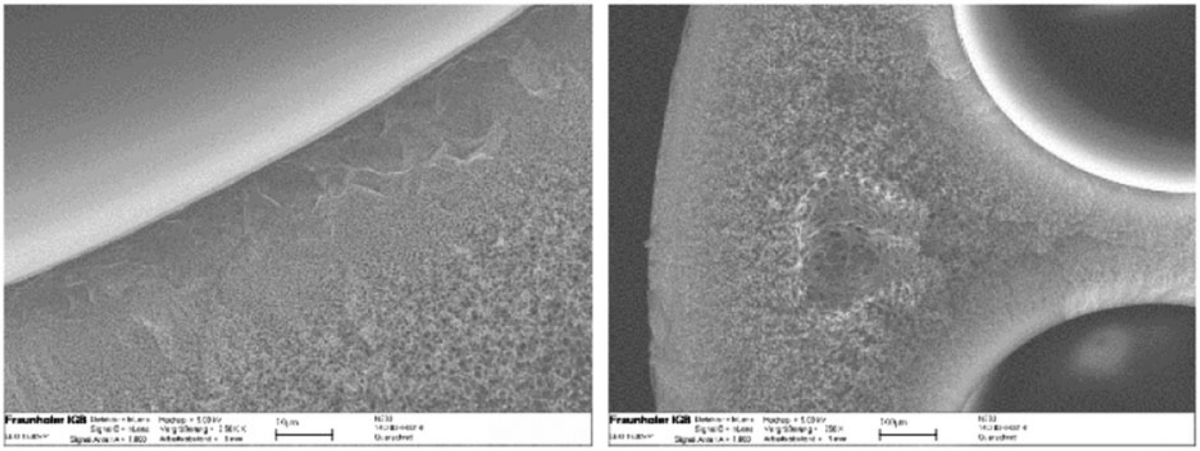


Fig. 13. SEM pictures of a Multibore® reference membrane left: Inner skin—Right: Area between the outer wall and two capillaries.

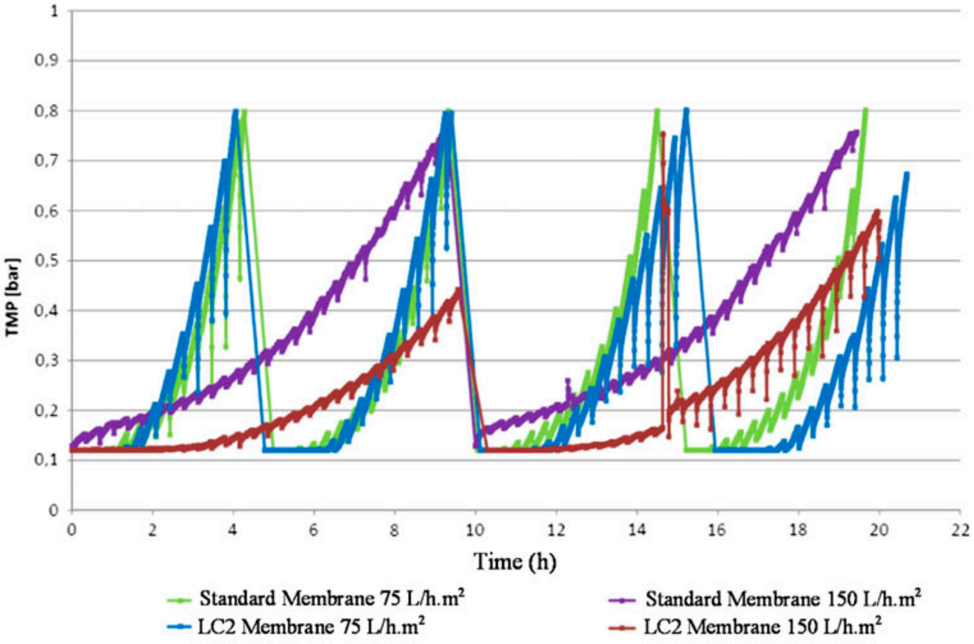


Fig. 14. Result from quick screening of Multibore® fibers with earth soil extract.

Trials conducted by CIRSEE aimed to predict the benefits of three of the leading low-fouling candidates on various types of water. Ten different types of water were available, either directly or imported from various sites in refrigerated containers. As the LC's are mainly able to limit the amount of organic fouling, the actual level of benefit of these novel membranes will be dependent on the fouling nature of the water in question.

Fig. 15 shows some of the results generated when filtering the Seine river water. A one-day trial, on consecutive days, was carried out on three different membranes. During the trial period, the Seine river was untreated and no coagulation was performed upstream the membranes. The operating flux was chosen so that in the short-time frame, significant fouling (mainly from NOM) was to be expected.

From the results, we can see that for this type of water the LC1 showed virtually the same fouling behavior as the reference/standard membrane. The LC2 module showed, however, again a delay in this initial fouling.

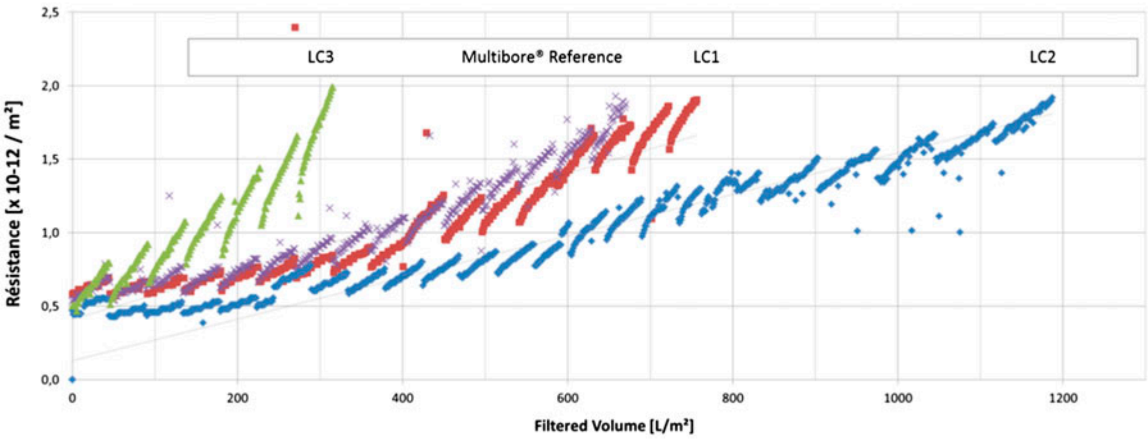


Fig. 15. Result from quick screening of Multibore® fibers with Seine river water.

One can conclude that modifications made in the formulation of the LC2 membrane results in a significantly lower fouling tendency.

4. Conclusions

With the established and structured qualification procedure, we were able to screen hundreds of polymeric formulations and finally focus on the most promising LC at later stages. At this stage of the study, lead candidate two (LC2) is the most promising one showing a significantly improved resistance to fouling due to the new formulation made of PSU-PEO-polysiloxane. This will provide a crucial advantage as, in the later piloting stage, the on-site trials with actual feed water required longer validation time and consequently only limited numbers of LC can be evaluated in a given time frame.

Novel approaches of polymer modification through chemistry will result in next-generation UF Multibore® fibers. These fibers will show improved antifouling properties as compared to their commercially available counterparts in various laboratory and on-site pilot studies. The reduced fouling propensity has ultimately allowed these new fibers to be operated at higher flux rates and with lower chemical usage as compared to their counterparts.

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