Exploiting the electrical conductivity of poly-acid doped polyaniline membranes with enhanced durability for organic solvent nanofiltration

Adem Sarihan[1,2,3], Salman Shahid[1,2], Junjie Shen[1,2], Ida Amura[1,2], Darrell Alec Patterson[1,2], Emma Anna Carolina Emanuelsson [2,*]

[1] Centre for Advanced Separations Engineering, University of Bath, Bath, United Kingdom, BA2 7AY.

[2] Department of Chemical Engineering, University of Bath, Bath, United Kingdom, BA2 7AY.

[3] Bilecik Vocational School, Bilecik Seyh Edebali University, Bilecik, Turkey, 11230

Submitted to

Journal of Membrane Science

*Corresponding author: E.A.Emanuelsson-Patterson@bath.ac.uk

Abstract

We have developed stable organic solvent nanofiltration (OSN) membranes that are electrically conductive. These membranes overcome key issues with current tuneable membranes: molecular weight cut off (MWCO) limited to the UF-range and lack of filtration stability. Polyaniline (PANI) was in-situ doped by poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) using chemical oxidative polymerisation that leads to formation of interpolymer complex. The PANI-PAMPSA membranes were prepared by phase inversion method and the pore sizes were shrunk by annealing the membranes at temperatures lower than the crosslinking temperature. The membranes were systematically evaluated using visual and chemical analysis and in-filtration experiments. The developed membranes were solvent stable, reusable, had a denser structure and lower MWCO and there was no thermal crosslinking as seen by IR. The solvent permeance obtained were: 0.46, 0.60 and 0.74 $Lm^{-2}h^{-1}bar^{-1}$ for acetone, 2-propanol and methanol respectively, with MWCO below 300 Da and 266 Da for methanol. For the tuneability investigation, when applying an electrical potential (20 V) in a custom-made cross-flow membrane cell, an increase in MWCO and permeance (10.4% and 55.6%, respectively) was observed. These results show that this simple in-situ doping method with heat treatment can produce promising and stable PANI membranes, for OSN processes in different solvents, with the distinctive feature of in-situ performance control by applying external electrical potential.

Key words: Polyaniline, Organic solvent nanofiltration, Electrical tuneable membranes, Heat treatment

1. Introduction

Organic solvent nanofiltration (OSN), also known as solvent resistant nanofiltration [1] can separate materials with molecular weight between 200-1000 Da present in organic solvents [2, 3, 4, 5]. It has several advantages in comparison to conventional temperature based methods, including low energy consumption and ease to integrate in existing processes [2, 3, 5, 6]. OSN has the potential to become the best available technology among the separation techniques in organic media [4] for a wide range of processes related to, e.g. food [7-9], fine chemical [10, 11], pharmaceutical [12, 13] and petrochemical industries [14, 15]. The main limitations with existing OSN membranes are limited solvent and filtration stability and fouling. Membranes that change the permeance and MWCO during filtration (tuneable membranes) could change

their transport properties and allow for in-situ self-cleaning/fouling removal, therefore changing the pore size during filtration has the potential to overcome fouling. To the best knowledge of the authors, there are no OSN membranes that have tuneable properties.

To achieve tuneability, materials are prepared to respond to external stimuli, such as pH [16, 17], ionic strength [18], temperature [19], light [20], electricity [21] etc. Among these, electrical tuneability offer the advantage that it can easily and quickly be applied to the membrane [22]. To obtain electrical tuneability, the material must be able to undergo an electrical change. Polyaniline (PANI) is a widely used polymer [23-28] that become conductive through acid doping [21, 29]. Small acid dopants, like HCl, do leach out during filtration [30] and therefore change the performance characteristics, including loss of electrical conductivity [31] and make the membranes brittle [22]. Our research group has recently shown that polymeric acids, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA), can overcome the above disadvantages, possibly due to steric effects and the strong interaction between the acidic group of the polymeric acids and the PANI. Although the membranes were conductive and tuneable, the MWCO was in the UF-range and they had low filtration stability [31].

Heat treatment is one of the simplest and cheapest post-treatment processes to both (i) shrink the pores to obtain nanofiltration (NF) MWCO [32] and (ii) to improve filtration stability [27, 32, 33] as there is no need for chemicals like solvents and cross-linkers etc. However, the thermal crosslinking occurs on the imine nitrogen of PANI [33, 34] which act as carriers of the electric charge [35], reducing or losing the conductivity [32]. In addition, heat treatment also result in significant reductions in permeance, with no permeance for certain solvents [33]. To date, the crosslinking of PANI has been performed at comparatively high temperatures because the thermal transition of the PANI occurs at 180 °C [24, 27, 34, 36 - 39]. We hypothesise, in difference, that we can shrink the membrane pores at a lower temperature and thus achieve NF membranes with conductivity properties, without having thermal crosslinking. This would reduce the energy consumption and fine-tune the porosity of the membranes. We also hypothesise, that these membranes will have improved solvent stability due to producing denser and more compact membranes, further widening the application in OSN.

Therefore the aim of this study is to prepare novel, electrically tuneable and stable OSN membranes with PAMPSA as a dopant for PANI by using heat treatment at temperatures lower

than the crosslinking temperature (110-130°C and 1-15h), to tighten the pores without crosslinking. The physical, chemical and electrical properties of the membranes will be evaluated using SEM, AFM, FTIR, dynamic contact angle goniometry and four-point probe conductivity techniques. Solvent stability and swelling degrees of the heat treated membranes will be investigated in a range of solvents with different polarity and compared to untreated membranes. Rejection studies, MWCO determinations and electrically tuneability properties will be performed using dead-end and cross-flow filtration techniques.

2. Experimental

2.1. Materials

Aniline, Poly (2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, ammonium persulfate (APS),4-methyl piperidine (4MP), N-methyl-2-pyrrolidone (NMP) were obtained from Sigma-Aldrich, UK and used to synthesize the PANI-PAMPSA as monomer, dopant chemical oxidant, gel inhibitor and solvent for membrane casting solution, respectively. HPLC grade toluene, n-hexane, acetone, isopropanol and methanol were supplied by Fisher Scientific and used as solvents, UK. Tripropylene glycol and poly(propylene) glycols (PPGs, MW = 400, 725 and 1000 g mol^{-1}), were purchased from Alfa Aesar and used for MWCO determination of prepared membranes. The non-woven polyethylene/polypropylene (PE/PP) mixture membrane support layer (Novatexx 2431) was supplied by Freudenberg Filter, Germany. Deionized (DI) water was produced by an ELGA deioniser from PURELAB Option, USA.

2.2. Synthesis of PANI-PAMPSA polymer

PANI-PAMPSA powder was synthesized by oxidative polymerization of aniline in PAMPSA. 0.2 mol of aniline and 0.05 mol of PAMPSA was used to prepare a solution in water (Solution 1). 0.2 mol of APS was dissolved in a second water bottle (Solution 2). Solution 2 was slowly added into the aniline solution by a peristaltic pump at a speed of 20 mL h^{-1}, temperature was15 °C, t for 24 h for complete polymerization. The obtained PANI-PAMPSA was filtered and washed firstly with DI water 3 times and then with acetone 3 times until the pH of the filtrate became neutral to remove the PANI oligomers and then dried in a vacuum oven at 65 °C for 24 h. Finally, the powder was grinded in mortar and a dark green product was obtained. The chemical structure of the PANI-PAMPSA can be seen in Figure1.

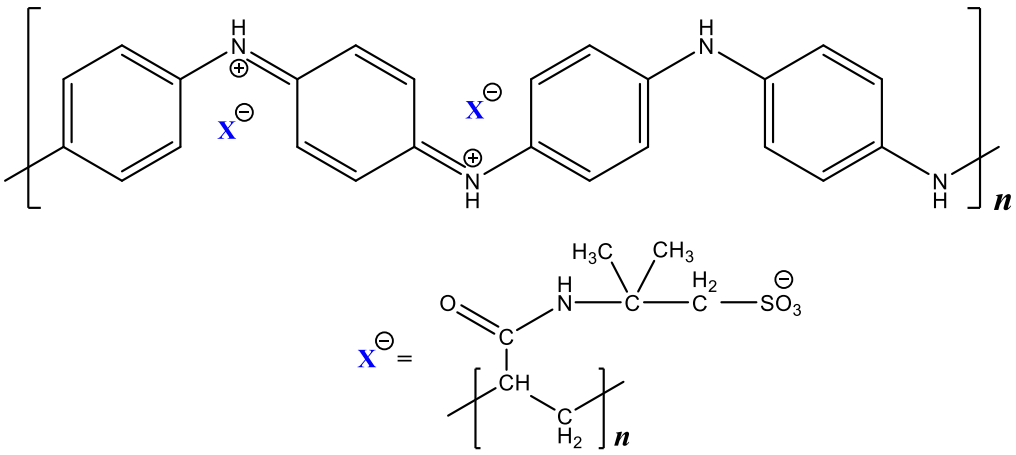


Figure 1. Chemical structure of the PANI-PAMPSA polymer (in Figure, X^- = PAMPSA).

2.3. Preparation and heat treatment of PANI-PAMPSA membranes

The PANI-PAMPSA membranes were prepared using non solvent induced phase inversion process [40, 41]. For the preparation of membrane casting solution, firstly NMP (solvent) and 4-MP (gel inhibitor) and stirred for 5 minutes than appropriate amount of PANI-PAMPSA powder was added to solution slowly to get a 20% (w/w) PANI-PAMPSA. Then the mixture is stirred 24h to obtain a homogeneous solution. After 24h, the solution was left at least two hours at room temperature and put it in vacuum oven at 40 °C for 30 minutes to remove all the bubbles/air traps in it. The solution was then casted on the polyethylene/polypropylene (PE-PP) backing layer to make a 200 µm thick film using an adjustable casting knife (4340 Automatic Film Applicator, Elcometer, UK) and then the film was immediately fully immersed into a coagulation bath containing DI water. The phase inversion occurred in the coagulation bath forming the membrane. The obtained membranes was left in pure water to wait until test or treatment.

To shrink/tighten the pores and to get dense structure to obtain nanofiltration range membranes, the prepared membranes were heat treated as different temperatures and times (see Table 1). Overall the heat treatment that applied in this study were between 1-3 hours (only for 110 °C it was tested for 15h to check the longer time heat treatment effect on membrane).

Table 1. Heat treatment conditions of PANI-PAMSA membranes

Temperature (°C)	Time (h)
110	1
110	2
110	15
120	1
120	2
120	3
130	1

For the heat treatment process, the membranes were cut to suitable size disks for dead-end cell (14.6 cm^2) and the disks were placed between two glass plates to prevent curling. The heat treatment was performed in a vacuum oven (Thermo Scientific, VT 6025). After heat treatment, membranes were placed in water until filtration tests.

2.4. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Fourier transform infrared (FT-IR) spectrometer with an attenuated total reflectance (ATR) cell (Spectrum 100, PerkinElmer, USA) was used to determine the chemical compositions of the untreated and heat treated PANI-PAMPSA membranes. A background scan was run prior to sample testing and spectra were recorded from 4000 to 650 cm^{-1} but it was focussed especially 2000-1000 cm^{-1}.

2.5. Scanning electron microscopy (SEM) and Atomic force microscopy (AFM) analysis

The morphological properties of the membranes were investigated by a scanning electron microscopy (SEM) (JSM-6480LV, JEOL, Japan). The samples were prepared by breaking them in liquid nitrogen to obtain a smooth cross-section and then mounted on the SEM stubs by conductive double-sided tape and dried overnight. The samples were coated with gold under argon flow to reduce sample charging under the electron beam. Then the surface and cross-section images were recorded in different magnification ranges.

Atomic force microscopy (AFM) were used to investigate the membrane roughness structure. AFM images were taken by using Veeco multimode Nanoscope III microscopy. Besides the AFM images of the membranes, mean roughness (Ra) that is the arithmetic average of the absolute values of the roughness profile ordinates and root mean square roughness (Rq) that is the root mean square average of the roughness profile ordinates were used to examine the roughness.

2.6. Dynamic contact angle analysis

The dynamic contact angle analysis were performed by use of a contact angle goniometer (Contact Angle System OCA 15Pro, Dataphysics, Germany). The membrane sample was placed on an analytical platform a small drop of water (2μL) was placed onto the membrane surface. A video camera was used to record images of the water drop. The programme software was used to calculate the effective contact angle change on the membrane surface. The dynamic contact angle analysis were repeated at least three times for all tested membranes.

2.7. Swelling and stability tests

For the swelling tests, the untreated and heat treated PANI-PAMPSA membranes were cut into small samples (2cm × 2cm) and dried in a vacuum oven. The mass of the dried membranes were determined and the membranes put into the solvents in a sealed flask at 25 °C for 1 h. The swollen membranes were taken from the solvent and quickly dried with a filter paper to remove solvent from the external surface. The mass of the swollen membranes was then determined. The mass swelling degree (Q_m) was calculated by using equation 1:

$$Q_m = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (1)$$

Where m_{wet} and m_{dry} is the mass of the wet and dry membranes, respectively.

The stability of the PANI-PAMPSA membranes in the solvents were determined by immersing the membrane sample in the solvents for one week using the same conditions as the swelling test. The mass change of the dry membrane before and after soaking in the solvent indicated whether the membrane did dissolve in the certain solvent or not. Membrane stability (%S) was calculated by using equation 2:

$$\%S = \frac{W_1 - W_2}{W_1}\ x\ 100 \quad (2)$$

Where W_1 and W_2 are the dry weights of the membrane before and after soaking in the solvent for one week

Water, Methanol, 2-propanol, acetone, toluene and hexane were chosen as different polarity solvents to investigate the swelling and stability properties. The swelling and stability test was

repeated three times for each membrane. In addition, to investigate the stability during filtration, a 24 hour (8 hour per solvent) filtration stability tests was performed using 2-propanol, methanol and acetone under 20 bar pressure for the 120 °C 3h heat treated membrane.

2.8. Nanofiltration tests and MWCO determinations

The filtration tests of untreated and heat treated membranes were performed by using a stirred high pressure stainless steel dead-end filtration cell (HP 4750, Sterlitech, USA). The pressure applied was dependent on the membrane structure, for untreated PANI-PAMPSA membrane 1 bar was used. However, for the heat treated ones, 20 bar was required to obtain appropriate permeance. The membranes were firstly preconditioned with solvents until obtaining a constant permeance. Then rejection studies were performed with feed solutions using different molecular weight of PPGs in the solvents (methanol, 2-propanol and acetone were chosen for the nanofiltration tests). The MWCO of membrane is the MW of the solute molecule that gives a 90% rejection [42]. Detailed information about the MWCO determination method used in this study is described elsewhere [43]. The analysis of the PPG solution feed and permeate were performed with high-performance liquid chromatography (HPLC) equipped with evaporative light scattering detector (ELSD) (1260 Infinity, Agilent Technologies, USA). Permeance and rejection results were calculated with equations 3 and 4, respectively.

$$\mathrm{P} = \frac{V}{A\,t\,p} \tag{3}$$

$$\mathrm{R}(\%) = \left(1 - \frac{Cp}{Cf}\right) x100 \tag{4}$$

Where *V, A, t, p*, *Cp* and *Cf* refers to volume (L), membrane effective area (m^2), time (h), pressure, permeate concentration and feed concentration, respectively.

2.9. Conductivity, cross-flow filtration and tuneability studies

The electrical conductivity of untreated and heat treated membranes were measured using a four-point multi height probe (RM3000, Jandel Engineering Limited, UK) at room temperature. The electrical conductivity was calculated as the reciprocal of electrical resistivity. Sheet resistivity (ρ) is calculated by using Equation 5.

$$\rho = 4.532\ x\ Vx\ \frac{t}{I} \tag{5}$$

Where ρ is resistivity, V is the measured electrical potential, I is the provided electrical current, and t is the membrane thickness. Conductivities the inverse of resistivity (1/ρ).

The tuneability studies of the PANI-PAMPSA nanofiltration membranes were performed with a custom-made electrically connected cross-flow filtration setup [22]. In a typical experiment, PANI-PAMPSA membrane was placed in the cross-flow membrane cell and 1.5 L of PPG feed solution in solvent was used in the reservoir tank. Permeates were collected at a constant pressure of 20 bar and the flow rate was adjusted to 0.8 L min^{-1} during the experiment. Different electrical potentials (0, 5, 10 and 20 V) were applied for the testing of the electrical tuneability of membranes. Then the MWCOs and permeances of the membranes were determined for the different potential applying filtrations. Methanol was chosen for cross-flow tuneability studies as solvent because the exact MWCO value of the membrane can be determined in this solvent.

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Figure 2 shows the FTIR spectra of the untreated and the 120°C 3h heat treated PANI-PAMPSA membrane (as a representative heat-treated membrane). The orange columns represent peak widths. The absorption bands at approximately 1225-1113 and 1040 cm^{-1} correspond to the asymmetric and symmetric stretching of $–SO_2–$ in the PAMPSA, respectively [44, 45]. The peak at 1166 cm^{-1} could be assigned to the vibrational band of the nitrogen quinone on the PANI [44, 46]. At 1298 cm^{-1}, the C-N stretch of a secondary aromatic amine from the PANI was observed and the characteristic absorption peaks at 1595 cm^{-1} and 1498 cm^{-1} could be assigned to the stretches of the quinone and benzene ring from PANI, respectively [44]. The C=O stretch band in the PAMPSA is shown near to 1660 cm^{-1} [52]. Finally, the methyl groups of PAMPSA give rise to absorption bands at1450 and 1385 cm^{-1} [45]. Confirming that the obtained polymer is PANI-PAMPSA. In addition, there is no significant difference between the two FTIR spectra showing that there is no chemically difference (crosslinking etc.) between the two membranes. If crosslinking had occurred, the secondary amine band would be much smaller due to the formation of tertiary amines [27] and the width of the peaks would have increased because of the increased interaction of the vibrational modes due to physical chain crosslinking [47]. In summary, the heat treatment did not cause any crosslinking, but caused some physical changes that was also observed in other

characterization results like SEM, AFM etc. See the supplementary materials (Fig S3) for the infrared spectra of the other heat treated membranes.

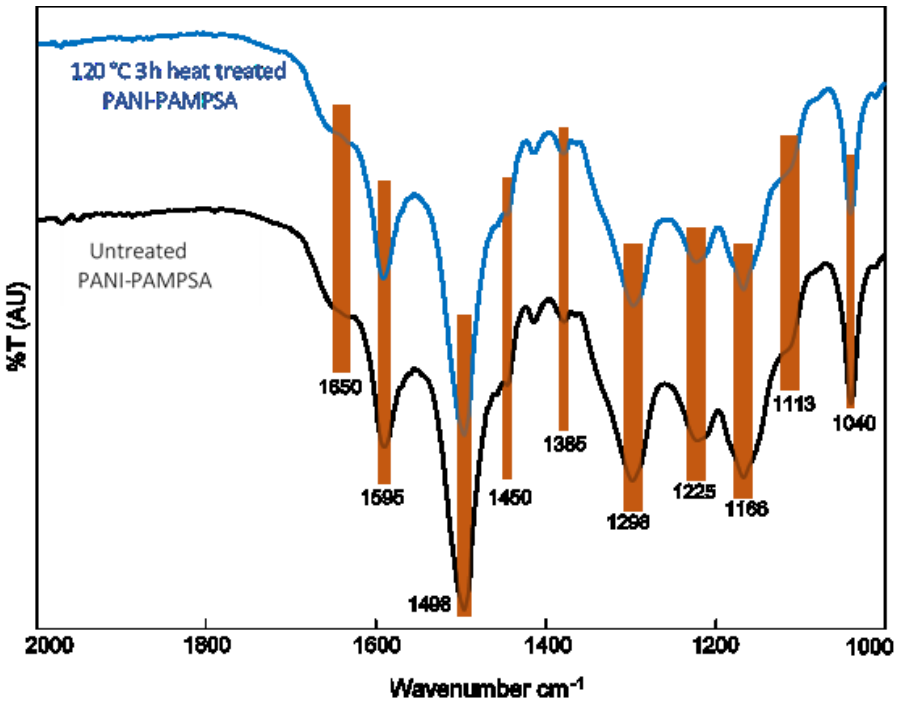


Figure 2. FTIR spectra for untreated and 120°C 3h heat treated PANI-PAMPSA membranes

3.2. SEM and AFM analysis

The cross-section and surface SEM images of the membranes are shown in Figure 3 and 4, respectively.

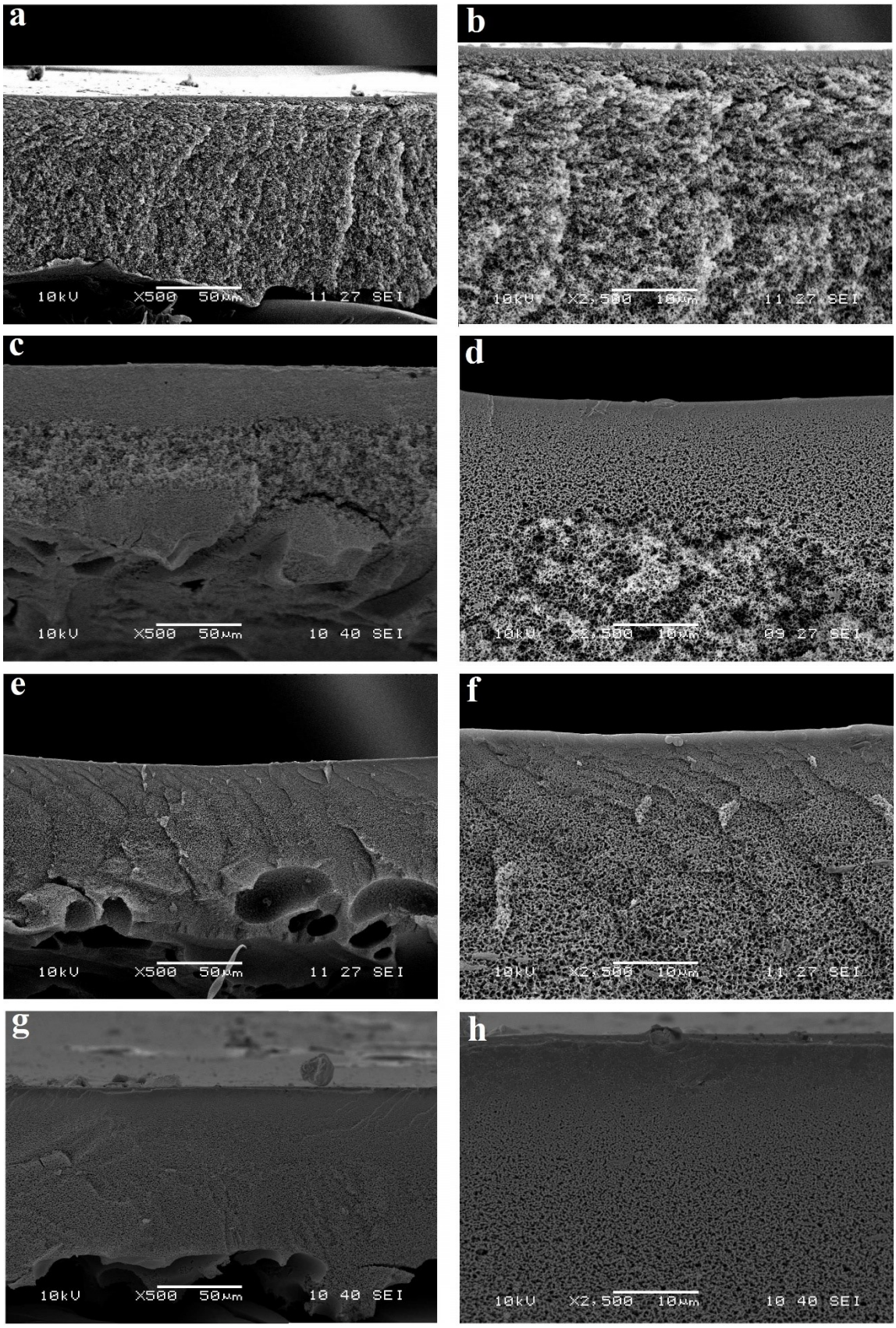


Figure 3. Cross-section SEM images of (a, b) Untreated, (c, d) 110°C 1h, (e, f) 120°C 1h, (g, h) 120°C 3h heat treated PANI-PAMPSA membranes with two different magnifications.

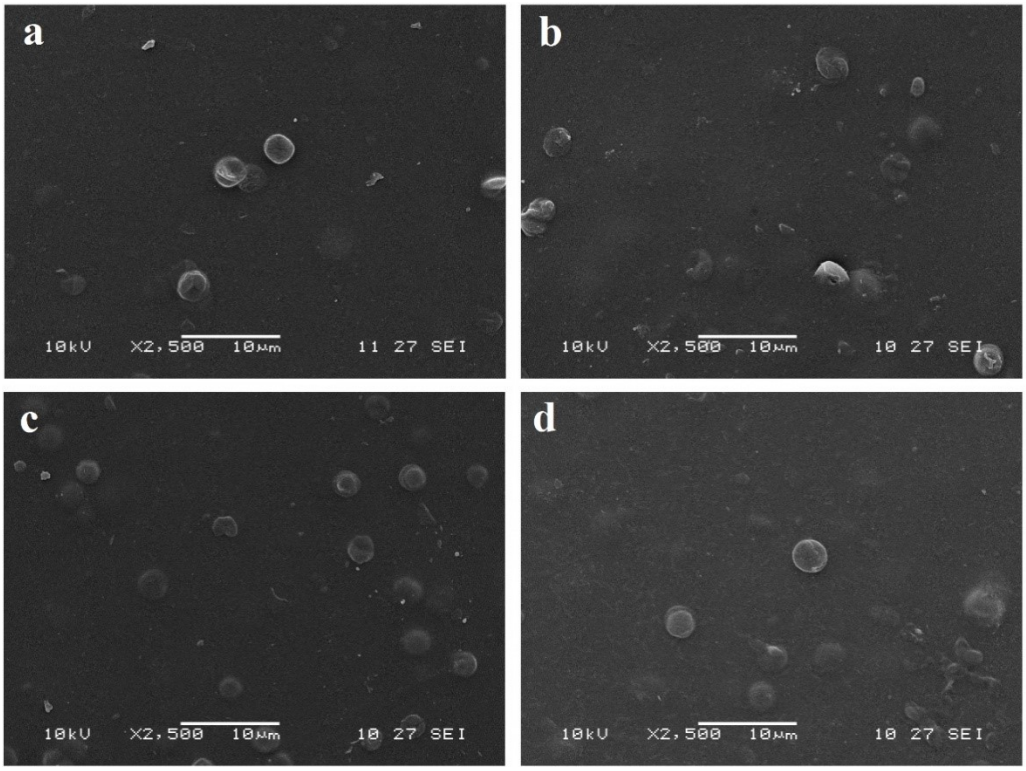


Figure 4. Surface SEM images of (a) Untreated, (b) 110°C 1h, (c) 120°C 1h, (d) 120°C 3h heat treated PANI-PAMPSA membranes

Fig. 3 shows that the cross-section of the untreated PANI-PAMPSA has an asymmetric structure, with relatively dense but still porous thin top layer and a more porous spongy layer underneath. With the heat treatment process the membrane became denser (Fig 3b-d) and the pore sizes of the matrix decrease as the temperature increased. The top layer turned into a denser layer, and furthermore, the thickness of the dense top layer appeared to increase with the increasing temperature. These changes, especially to the top layer, will play an important role in MWCO of the membranes because the separation takes place at the top layer of the membrane. This is in line with the results obtained by other researchers [27, 57] that showed that increasing the temperature increased the density of the top layer.

Figure 4 shows that both untreated and heat treated membranes present surface structures with randomly distributed, drop-like, round shape and similar-sized bulges. The heat treated membrane have a larger number of bulges, but there is no observable pin holes or deformations etc. on the surfaces on either of the membranes.

Since no difference was observed in membrane surfaces using SEM imaging, AFM was used to identify if there were any differences in the surface roughness between the untreated and

heat tread membrane. Figure 5 shows the 2D and 3D AFM images of the PANI-PAMPSA membranes untreated and 120 °C 3h heat treated membrane as a representative sample. Table 2 show roughness values (mean roughness, R_a and root mean square roughness, R_q).

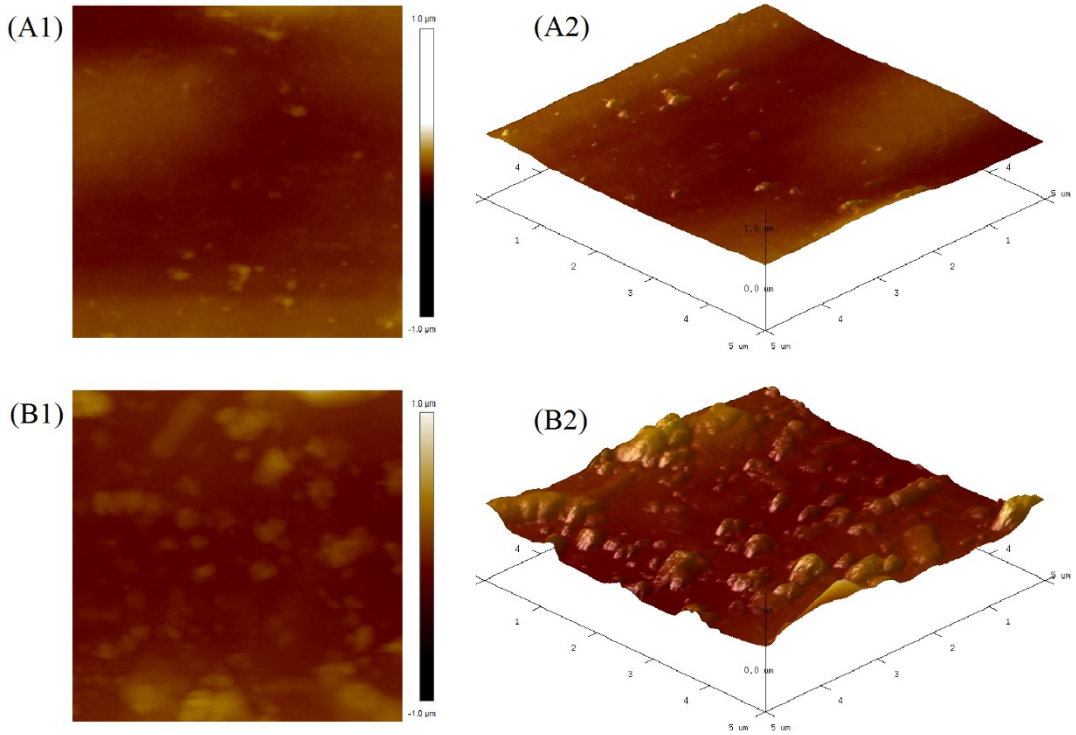


Figure 5. AFM images of PANI-PAMPSA membranes
(A1 and A2 untreated, B1 and B2 120°C 3h heat treated)

Figure 5 shows that the surface of the untreated membrane is quite smooth and that after the heat treatment, the surface became rough. The observed increase in roughness can be attributed to the formation of a mesoscopic structure associated with agglomeration of polymer chains [49] and the degradation of the surface at that temperature [48]. Evaporating the residual solvent or trap gases may have contributed to the formation of these island type structures on the surface [49]. The increase of surface roughness of the membrane after heat treatment was further confirmed by the surface roughness parameters in Table 2. The Ra and Rq values are 29.0 and 34.1 nm for untreated membrane and they increased significantly to 79.6 and 105 nm after heat treated process. The results are in line with other studies that reported an increase in surface roughness of PANI [49] and polyethersulfone [48] membranes on heat treatment.

Table 2. Some roughness values for PANI-PAMPSA membranes

Membrane	Ra (nm)	Rq (nm)
Untreated	29.0	34.1
120°C 3h heat treated	79.6	105

3.3. Dynamic contact angle analysis

Dynamic contact angle analysis was performed to evaluate the surface wettability rate and roughness of the prepared membranes. Dynamic contact angle results for untreated and heat treated membranes are given in Figure 6. The contact angle pictures at the start and end point obtained in 2 minutes for untreated and 120 °C 3h heat treated PANI-PAMPSA membranes are shown in Figure 7.

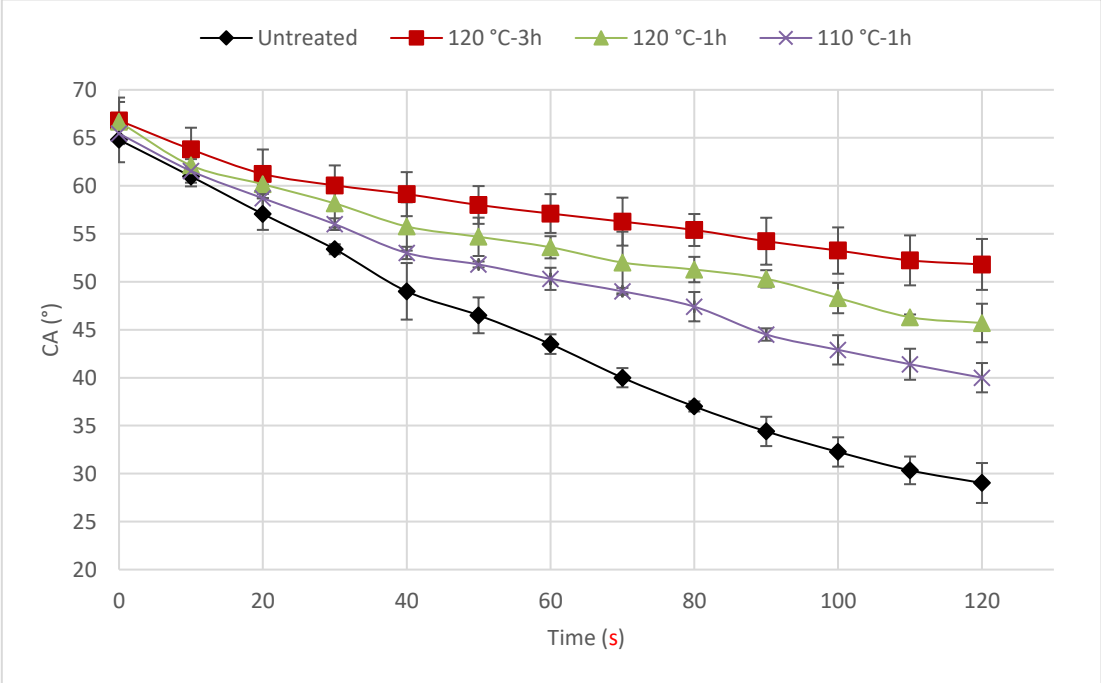


Figure 6. Dynamic contact angle results of a selection of PANI-PAMPSA membranes

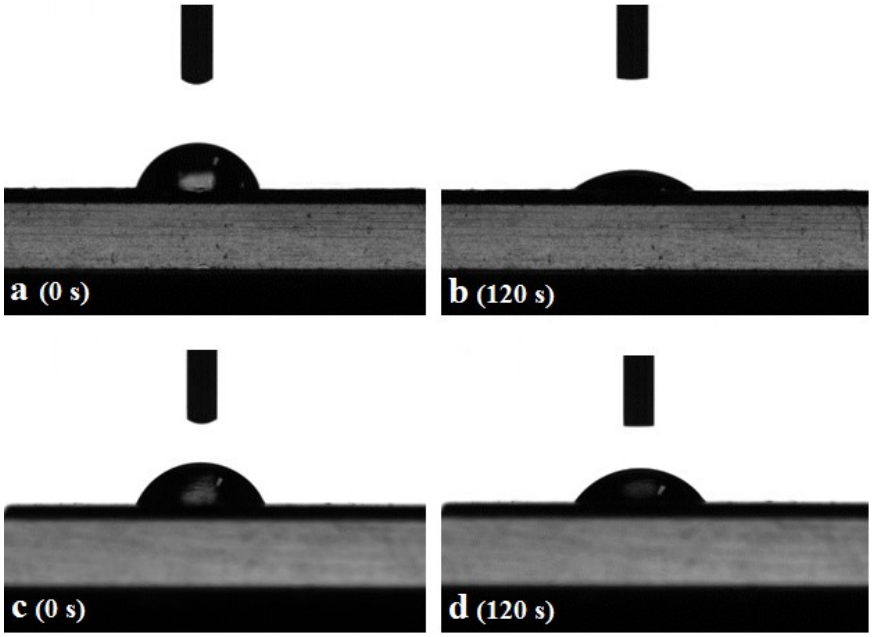


Figure 7. Contact angle pictures of PANI-PAMPSA membranes at the start (0 Second) and end point (120 second). (a, b) Untreated, (c, d) 120°C 3h heat treated PANI- PAMPSA

It can be observed in Figures 6 and 7 that contact angles of untreated and 120°C 3h heat treated PANI-PAMPSA membranes decreased from 65° to 29° and 67° to 52° in 2 minutes respectively. This shows that the main difference between the membranes is the reducing rate of the contact angle. The rate at which the contact angle decrease is higher for the untreated membranes, whereas the heat treated membranes show a slower reducing rate. Although the heat treated membranes do have a rougher surface, which should decrease the contact angle [50], they also have a more dense structure skin layer with smaller pores resulting in the droplets entering the pores slower. As determined by IR, heat treatment did not lead to any significant change in the chemical structure of the heat treated membranes, thus the hydrophilicity/hydrophobicity of the membranes is similar before and after the heat treatment. Therefore the results suggest that smaller pore size along with the shrunk and denser structure of the membrane skin layer lead to slower reducing rate of the contact angle.

3.4. Swelling and stability results

Table 3 shows the swelling degree (%) and stability (%) results obtained for the untreated and 120 °C 3h heat treated membrane in different solvents.

Table 3. Stability and swelling degree results of the membranes in different solvents

	Stability (ΔWeight**) (%)**	**Swelling (%)**

Solvent	Untreated	120°C 3h treated	Untreated	120°C 3h treated
Water	0.81 ± 0.15	0.33 ± 0.02	115 ± 4.3	110 ± 2.8
Methanol	1.43 ± 0.10	0.66 ± 0.06	111 ± 5.2	90.5 ± 7.7
2-propanol	0.80 ± 0.17	0.32 ± 0.01	73.1 ± 2.5	71.4 ± 3.7
Acetone	1.00 ± 0.65	0.29 ± 0.01	88.9 ± 2.2	78.4 ± 6.7
Toluene	1.28 ± 0.56	0.65 ± 0.04	69.2 ± 0.35	48.9 ± 1.7
Hexane	0.48 ± 0.16	0.16 ± 0.01	22.9 ± 6.6	20.0 ± 3.0

The stability test results (after one week) (Table 3) show that the weight loss percentages for both untreated and heat treated membranes are low in all tested solvents. For the heat treated membrane, there was no significant difference of weight after one week for all tested solvents. Furthermore, the filtration stability tests performed in 2-propanol, acetone and methanol for a total filtration time of 24h (8h for each solvent) resulted in a total weight loss percentage of the 120 °C 3h heat treated membrane of1. 92%. This weight loss can be attributed to the removal of unreacted chemicals (monomers etc.), low molecular weight PANI structures inside the membrane bulk structure and the pores because of high pressure. Membrane filtration stability was further confirmed during an eight hour pure solvent filtration study (Fig S1) and cross-SEM images before and after the filtration (Fig S2). Fig. S1 show that the pure solvent permeances for 8 hours of filtration (for each solvent) remained constant. If the membranes were not stable, the permeance would increase due to the deformation/degradation of the membrane structure. Fig. S2 show the cross-section SEM images of the 120 °C 3h heat treated membrane before and after the filtration study. It can be observed that there is no significant difference and no deformations on the membrane cross sectional structure after 8h of filtration, further confirming the filtration stability of the heat treated membrane.

In order to investigate the interactions between the membranes and the solvents, swelling studies (Table 3) were performed. The heat treated membrane swelled less than the untreated membrane in all solvents, and the polarity of the solvents was directly related to the swelling degrees of the membranes. Polarities of the solvents from low to high are in the order of: hexane, toluene, 2-propanol, acetone, methanol and water. Due to the polar structure of the PANI membrane, more polar solvents resulted in a higher swelling due to the stronger interactions between the membrane and the solvent [51]. The highest swelling degree in organic solvents was with methanol, this is because of the polarity (as per above) and H-

bonding properties [51] but it is also related to the size and shape of the solvents [27]. Methanol is a small polar molecule that better interacts with the charged backbone of polyaniline [52].

3.5. Nanofiltration tests and MWCO determinations

Nanofiltration experiments were performed to investigate the rejection levels of the membranes in different solvents by using different molecular weight of PPGs. The rejection results in 2-propanol, acetone and methanol are shown in Figure 8, 9 and 10, respectively. Figure 11 shows the rejection properties of the best membrane obtained, 120 °C 3h heat treatment in three solvents.

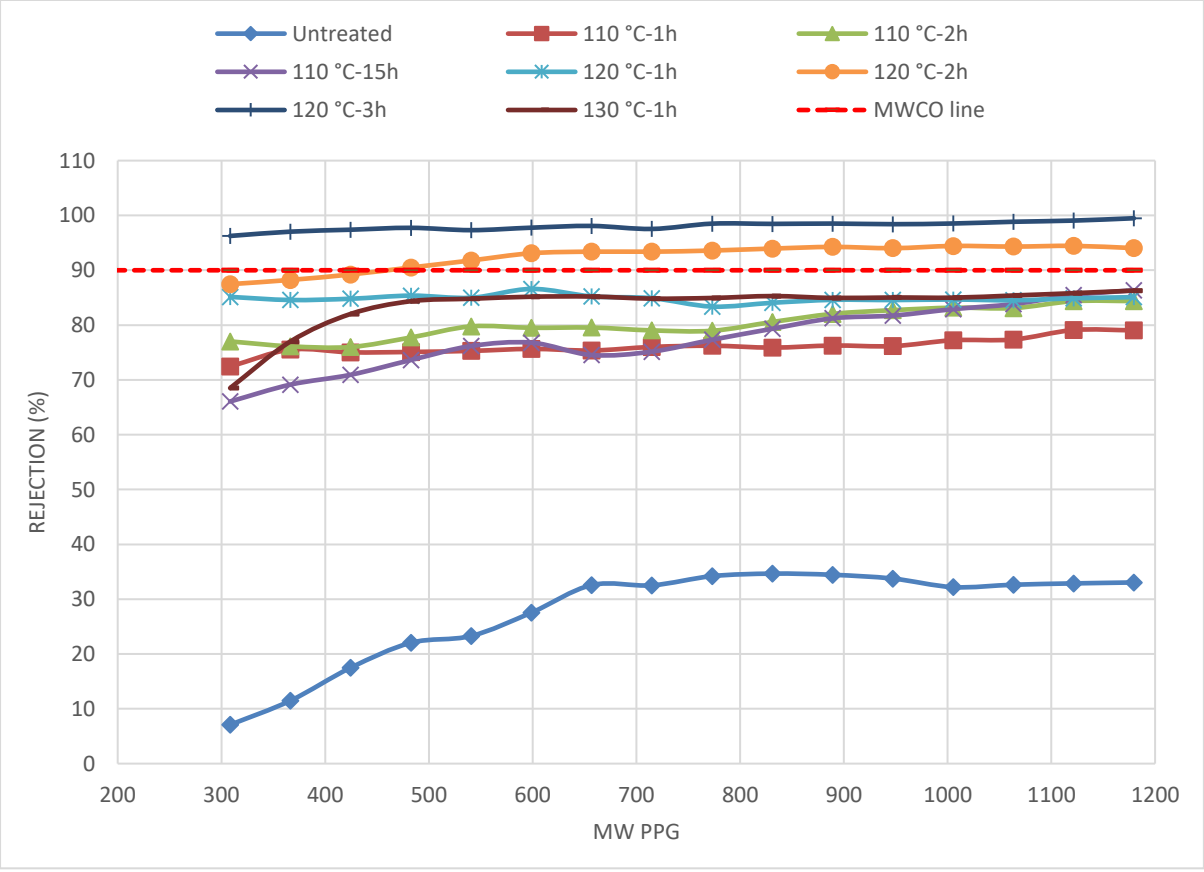
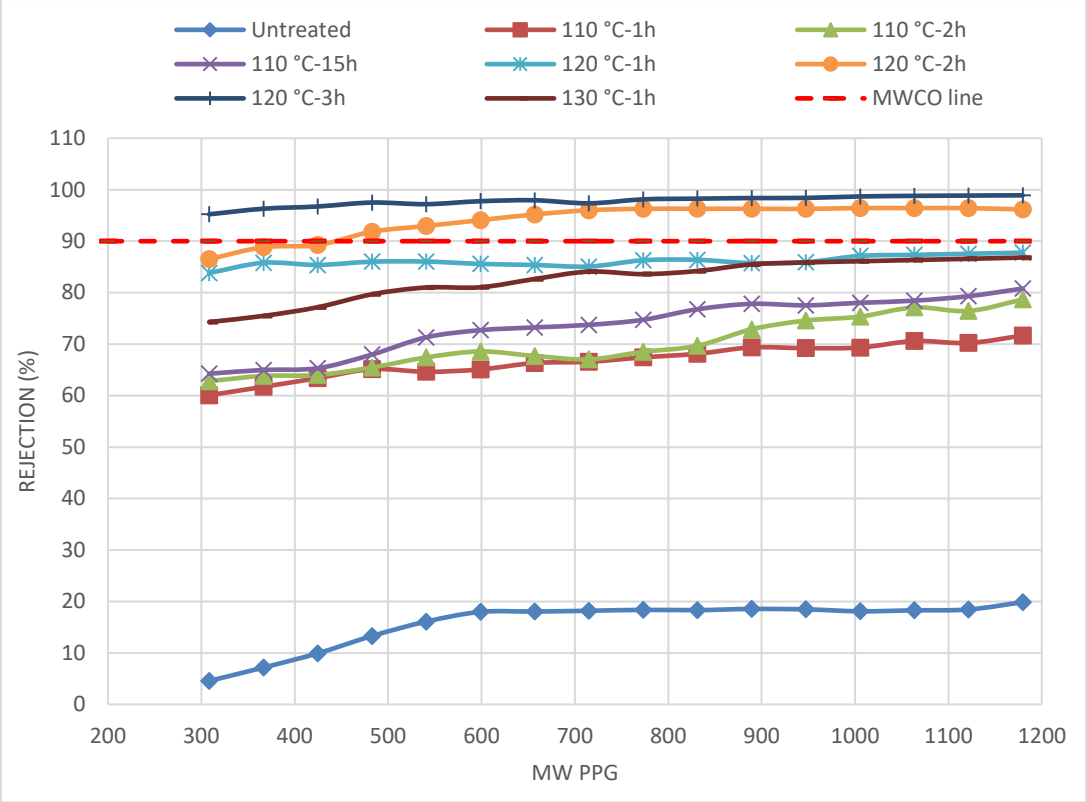


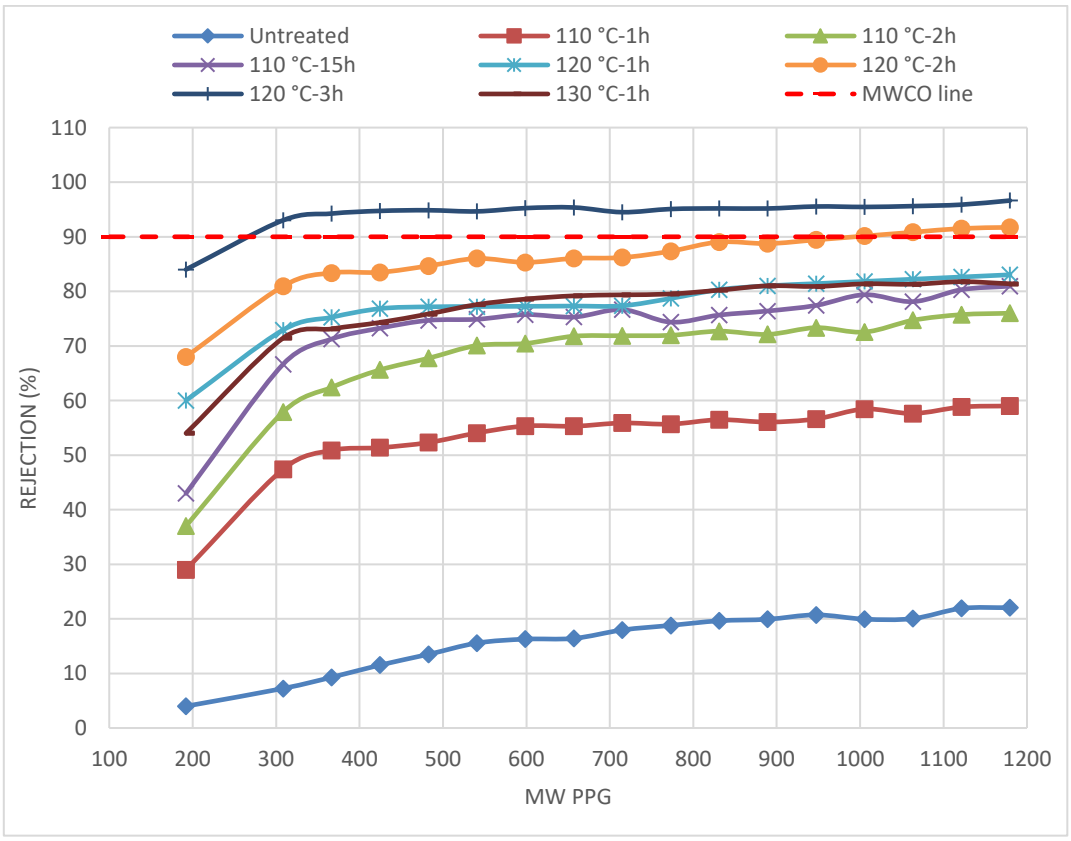
Figure 8. MWCO-curves of the membranes in 2-propanol



373

374 **Figure 9.** MWCO-curves of the membranes in Acetone

375



376

377 **Figure 10.** MWCO-curves of the membranes in Methanol

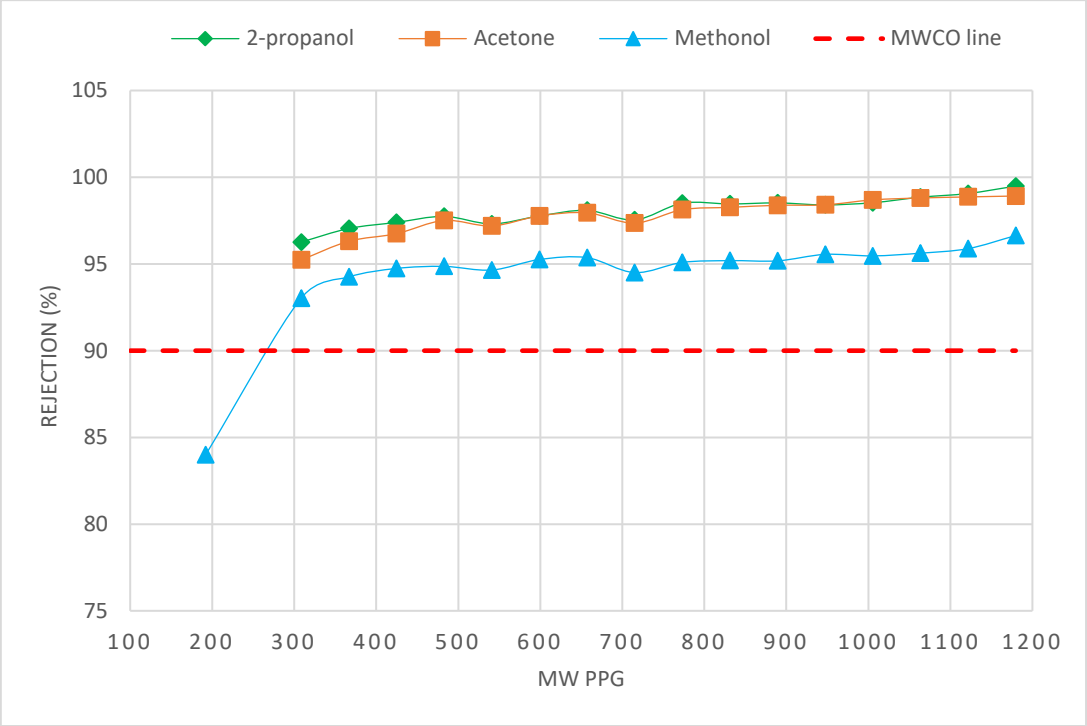


Figure 11. MWCO-curves of the 3h heat treated membrane in three solvents

In all solvents the best rejection was obtained for 120°C 3h heat treated PANI-PAMPSA membrane with a MWCOs lower than 300 Da. The exact MWCO values could not be determined for 2-propanol and acetone because there was no signal below 300 Da in these solvents (Figures 8 and 9). For the methanol results (Figures 10 and 11) there was a signal on 192 Da related to tripropylene glycol so by using this signal the MWCO of the treated membrane could be determined as 266 Da.

On the other hand 120 °C 2h heat treated membrane showed MWCO of 480, 430 and 950 Da in 2-propanol, acetone and methanol, respectively. Except these 2 membranes, all other membranes have MWCO higher than 1200 Da although they are all having a lower MWCO than the untreated membrane in all solvents for all PPGs. Heat treatment at 130 °C decreased the rejection contrary to other temperatures. This can be attributed to the deformation of membrane support layer at this temperature. The melting temperature of PE/PP support is around 130 °C (especially polyethylene) [53] so it might have been damaged at 130 °C.

Figure 11 shows the rejection performance of the best membrane (120 °C 3h) in three solvents. It was observed that the rejection in 2-propanol and acetone are quite similar but higher than in methanol. This can be explained by considering the swelling degree of the membrane in different solvents (in Table 2) because the swelling of the membrane in methanol is higher than

399 the 2-propanol and acetone, owing to its higher polarity, H-bonding ability and smaller shape.
400 Higher swelling make the membrane pores relatively open, therefore the rejection ratio in
401 methanol is lower, although it still remain in the nanofiltration range. Contrary to the rejection
402 results, higher swelling degrees of the membranes increased the permeance of the solvents,
403 through the relatively opened pores, and the permeance results obtained for acetone, 2-propanol
404 and methanol were 0.46, 0.60 and 0.74 L m^{-2} $h^{-1}bar^{-1}$, respectively. These results are similar
405 with other reported OSN studies [27, 34, 51, 54].
406

407 **3.6. Conductivity, cross-flow filtration and tuneability studies**

408 Conductivity measurements were performed to see if the PANI-PAMPSA membranes were
409 conductive and whether the heat treatment affects the conductivity. Conductivities of the
410 untreated and 120°C 3h heat treated membranes were $1.80x10^{-4}$ and $1.17x10^{-4}$ $S.cm^{-1}$,
411 respectively. This showed that both untreated and heat treated membranes are conductive and
412 that the heat treatment process did not cause a significant change in the conductivity. The slight
413 decrease of the conductivity after the heat treatment may be attributed to the poorer contact
414 between probe and membrane surface because of the higher surface roughness [55].

415 Cross-flow filtration studies were performed to compare the MWCO and permeance under
416 applied potential and to investigate the electrical tuneability of the 120°C 3h heat treated
417 membrane. Figure 12 shows the changes on the MWCOs and permeance for different applied
418 potentials (0, 5, 10, 20 V). For 5 V applied potential, there was no significant change in both
419 the permeance and MWCO because significant tuneability has previously only been observed
420 for potential with 7 V or more applied potential [32]. It was further observed that increasing
421 the applied potential from increased both the MWCOs and the permeance of the membrane
422 from 270 to 296 Da and 2.25 to 3.50 $Lm-^{2}h^{-1}$ bar^{-1}, respectively. The main reason for this
423 increase in MWCO and permeance is likely due to the applied voltage providing extra charge
424 to the already positively charged PANI-PAMPSA membrane surface. Providing this additional
425 charge would increase the steric hindrance between the chain and thus compel the chains to
426 loosen or the pores to open slightly [56, 57]. Overall, these results show that this in-situ doped
427 and low temperature heat treated PANI-PAMPSA membranes show promise to be applied in
428 electrical tuneable separations in OSN.

429

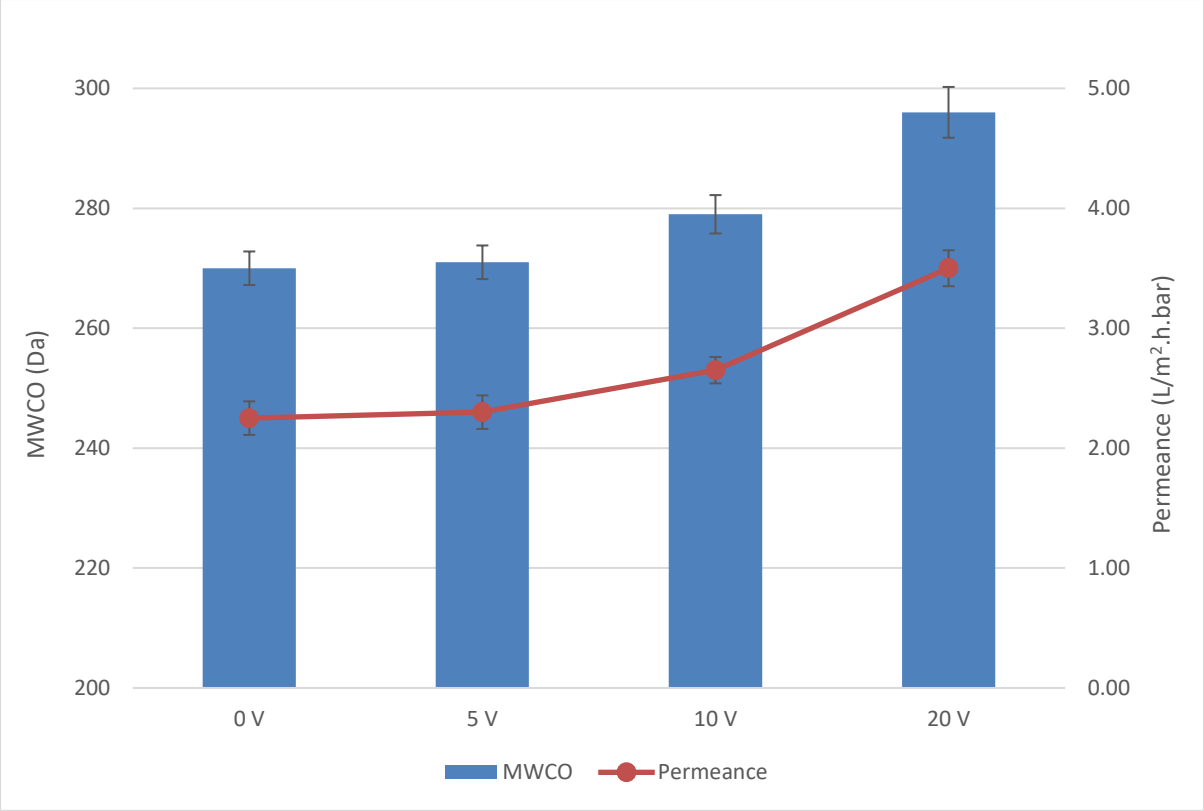


Figure 12. MWCO and permeance values of 120 °C 3h heat treated membrane under applied potentials of 0, 5, 10 and 20 V

4. Conclusion

Novel PANI-PAMPSA OSN membranes with electrically tuneable properties were developed. Heat treatment, below the crosslinking temperature, was used to prepare in-filtration durable NF-membranes, without thermal crosslinking. Results showed that the heat treated PANI-PAMPSA membranes were stable in organic solvents with different polarities with no loss in performance after repeated use. Besides, IR spectra of both untreated and heat treated membranes confirmed the absence of any chemical alteration affecting the PANI-PAMPSA membranes, however SEM and AFM images indicated that the top skin layer of the heat treated membranes became more dense, with an increase in surface roughness. These results were supported by dynamic contact angle and filtration experiments. Dynamic contact angle measurements indicated that with the heat treatment, the surface pores became smaller, and consistently, the permeance decreased and the rejection increased. Filtration studies showed that the 120°C 3h heat treated PANI-PAMPSA membranes had NF range rejections with the MWCOs lower than 300 Da for all tested solvents (e.g., 266 Da in methanol). The conductivity

was successfully retained after the heat treatment, and the application of 20 V potential led to an increase of 10.4 % and 55.6 % for MWCO and permeance of membrane, respectively. Therefore, the prepared OSN membrane can be controlled in-situ by applying electrical potential during the filtration process. In summary, we have for the first time developed durable OSN membranes with electrical tuneability.

Acknowledgement

The authors acknowledge the financial support of the European Research Council (ERC) Consolidator grant TUNEMEM (Project reference: 646769; funded under H2020-EU.1.1.-EXCELLENT SCIENCE). Adem Sarihan thanks the "Scientific and Technological Research Council of Turkey (TUBITAK) BIDEB-2219 International Postdoctoral Research Fellowship Programme" for financial support. The authors thank the technician team at the Departments of Chemical Engineering and Physics, University of Bath for technical support.

References

[1] M. Bastin, K. Hendrix, I. Vankelecom, Solvent resistant nanofiltration for acetonitrile based feeds: A membrane screening, Journal of Membrane Science, 536 (2017) 176-185.

[2] Y. Feng, M. Weber, C. Maletzko, T-S. Chung, Facile fabrication of sulfonated polyphenylenesulfone (sPPSU) membranes with high separation performance for organic solvent nanofiltration, Journal of Membrane Science, 549 (2018) 550-558.

[3] Y.H. See-Toh, M. Silva, A. Livingston, Controlling molecular weight cut-off curves for highly solvent stable organic solvent nanofiltration (OSN) membranes, Journal of Membrane Science, 324 (2008) 220-232

[4] M. Amirilargani, M. Sadrzadeh, E.J.R. Sudhölter, L.C.P.M. de Smet, Surface modification methods of organic solvent nanofiltration membranes, Chemical Engineering Journal, 289 (2016) 562-582.

[5] S. Hermans, H. Marien, C.V. Goethem, I.F.J Vankelecom, Recent developments in thin film (nano)composite membranes for solvent resistant nanofiltration, Current Opinion in Chemical Engineering, (2015) 8 45-54.

[6] F. Yuan, Y. Yang, R. Wang, D. Chen, Poly(vinylidene fluoride) grafted polystyrene (PVDF-g-PS) membrane based on in situ polymerization for solvent resistant nanofiltration, RSC Adv. (2017) 7 33201.

[7] A.V. Volkov, G.A. Korneeva, G.F.Tereshchenko, Organic solvent nanofiltration: prospects and application, Russian Chemical Reviews, 77 (11) (2008) 983-993.

[8] A.R.S. Teixeira, J.L.C. Santos, J.G. Crespo, Solvent resistant diananofiltration for production of steryl esters enriched extracts, Separation and Purification Technology, 135 (2014) 243-251.

[9] D. Peshev, L.G. Peeva, G. Peeva, I.I.R. Baptista, A.T. Boam, Application of organic solvent nanofiltration for concentration of antioxidant extracts of rosemary (Rosmarinus officiallis L.), Chemical engineering research and design, 8 9 (2011) 318-327.

[10] R. Valadez-Blanco, F.C. Ferreira, R.F. Jorge, A.G. Livingston, A membrane bioreactor for biotransformations of hydrophobic molecules using organic solvent nanofiltration (OSN) membranes, Journal of Membrane Science, 317 (2008) 50-64.

[11] F.C. Ferreira, H. Macedo, U. Cocchini, A.G. Livingston, Development of a Liquid-Phase Process for Recycling Resolving Agents within Diastereomeric Resolutions, Organic Process Research & Development, (2006) 10 784-793

[12] G. Székely, J. Bandarra, W. Heggie, B. Sellergren, F. C. Ferreira, Organic solvent nanofiltration: A platform for removal of genotoxins from active pharmaceutical ingredients, Journal of Membrane Science, 381 (2011) 21-33.

[13] R. Abejon, A. Garea, A. Irabien, Analysis and Optimization of Continuous Organic Solvent Nanofiltration by Membrane Cascade for Pharmaceutical Separation, American Institute of Chemical Engineers, 60 3 (2014) 931-948.

[14] L.S. White, C.R. Wildemuth, Aromatics Enrichment in Refinery Streams Using Hyperfiltration, Ind. Eng. Chem. Res., 45 (2006) 9136-9143.

[15] L.S. White, Development of large-scale applications in organic solvent nanofiltration and pervaporation for chemical and refining processes, Journal of Membrane Science, 286 (2006) 26-35.

[16] D. Roy, J.N. Cambre, B.S. Sumerlin, Future perspectives and recent advances in stimuli-responsive materials, Progress in Polymer Science, 35 (2010) 278-301.

[17] H.H. Himsedt, K.M. Marshall, S.R. Wickramasinghe, pH-responsive nanofiltration membranes by surface modification, Journal of Membrane Science, 366 (2011) 373-381.

[18] M.A.C. Stuart, W.T.S.Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G.B. Sukhurukov, I. Szliefer, V.V. Tsukruk, M. Urban, F. Winnik, Z. Sauscher, I. Luzinow, S. Minko, Emerging applications of stimuli-responsive polymer materials, Nature materials, 9 (2010) 101-113.

[19] O. Azzaroni, UCST wetting transitions of polyzwitterionic brushes driven by self-association, Angewandte Chemie, 118 (2006) 1802-1806.

[20] A.G. Skirtach. A.M. Javier, O. Kreft, K. Kohler, A.P. Alberola, H. Mohvald, W.J. Parak, G.B. Sukhorukov, Laser-Induced Release of Encapsulated Materials inside Living Cells, Angewandte Chemie, 45 (2006) 4612-4617.

[21] C. Weidlich, K-M. Mangold, Electrochemically switchable polypyrole coated membranes, Electrochimica acta, 56 (2011) 3481-3484.

[22] L. Xu, S. Shahid, A.K. Holda, E.A.C. Emanuelsson, Stimuli responsive conductive polyaniline membrane: In-filtration electrical tuneability of flux and MWCO, Journal of Membrane Science, 552 (2018) 153-166.

[23] M.R. Anderson, B.R. Mattes, H. Reiss, R.B. Kaner, Gas Separation Membranes: A Novel Application for Conducting Polymers, Synthetic Metals, 41-43 (1991) 1151-1154.

[24] P.C. Rodrigues, G. P. de Souza, J.D.D.M. Neto, L. Akcelrud, Thermal treatment and dynamic mechanical thermal properties of polyaniline, Polymer, 43 (2002) 5493-5499.

[25] W. Hu, S. Chen, Z. Yang, L. Liu, H. Wang, Flexible Electrically Conductive Nanocomposite Membrane Based on Bacterial Cellulose and Polyaniline, J. Phys. Chem. B., (2011) 115 8453-8457.

[26] P. Rannou, M. Nechtschein, J.P. Travers, D. Bernera, A. Walter, D. Djurado, Ageing of PANI: chemical, structural and transport consequences, Synthetic Metals, 101 (1999) 734-737.

[27] M. Sairam, X.X. Loh, K. Li, A. Bismarck, J.H.G. Steinke, A.G. Livingston, Nanoporous asymmetric polyaniline films for filtration of organic solvents, Journal of Membrane Science, 330 (2009) 166-174.

[28] Z. Fan, Z. Wang, M. Duan, J. Wang, S. Wang, Preparation and characterization of polyaniline/polysulfone nanocomposite ultrafiltration membrane, Journal of Membrane Science, 310 (2008) 402-408.

[29] J. Pellegrino, The Use of Conducting Polymers in Membrane-Based Separations, Annals New York academy of sciences, 984 (2003) 289-305.

[30] H. Hu, J.L. Cadenas, J.M. Saniger, P.K. Nair, Electrically Conducting Polyaniline-Poly(acrylic acid) Blends, Polymer International, 45 (1998) 262-270.

[31] L. Xu, Electrically Tuneable Membranes: Revolutionising Separation and Fouling Control for Membrane Reactors, PhD theses, University of Bath, (2016).

[32] R. Rohani, Linking the Microstructural and Separation Properties of Electrically Tuneable Polyaniline Pressure Filtration Membranes, MSc thesis, The University of Auckland, (2013).

[33] X.X. Loh, M. Sairam, A. Bismarck, J.H.G. Steinke, A.G. Livingston, K. Li, Crosslinked integrally skinned asymmetric polyaniline membranes for use in organic solvents, Journal of Membrane Science, 326 (2009) 635-642.

[34] X.X. Loh, M. Sairam, A. Bismarck, J.H.G. Steinke, A.G. Livingston, K. Li, Polyaniline hollow fibres for organic solvent nanofiltration , Chem. Commun, (2008) 6324-6326.

[35] J. Lin, Q. Tang, J. Wu, H. Sun, Synthesis, characterization and properties of polyaniline/expanded vermiculite intercalated nanocomposite, Sci. Technol. Adv. Mater., 9 (2008) 025010.

[36] S. Moon, Y.H. Jung, D.K. Kim, Enhanced electrochemical performance of a crosslinked polyaniline coated graphene oxide-sulfur composite for rechargeable lithium sulfur batteries, Journal of Power Sources, 294 (2015) 386-392.

[37] X. Wang, D. Liu, J. Deng, X. Duan, J. Guo, P. Liu, Improving cyclic stability of polyaniline by thermal crosslinking as electrode materials for supercapacitor, RSC Adv., 5 (2015) 5 78545.

[38] C-H. Chen, Thermal and Morphological Studies of Chemically Prepared Emeraldine-Base-Form Polyaniline Powder, Journal of Applied Polymer Science, 89 (2003) 2142-2148.

[39] J.A. Conklin, S-C. Huang, S-M. Huang, T. Wen, R.B. Kaner, Thermal Properties of Polyaniline and Poly(aniline-co-o-ethylaniline), Macromolecules, 28 (1995) 6522-6527.

[40] J. Shen, S. Shahid, A. Sarihan, D.A. Patterson, E.A.C. Emanuelsson, Effect of polyacid dopants on the performance of polyaniline membranes inorganic solvent Nanofiltration, Separation and Purification Technology, 204 (2018) 336-344

[41] Y.S. Kang, H.J. Kim, U.Y. Kim, Asymmetric membrane formation via immersion precipitation method. I. Kinetic effect, Journal of Membrane Science, 60 (1991) 219-232.

[42] R. Rohani, M. Hyland, D. Patterson, A refined one-filtration method for aqueous based nanofiltration and ultrafiltration membrane molecular weight cut-off determination using polyethylene glycols, Journal of Membrane Science, 382 (2011) 278-290.

[43] C.J. Davey, Z.X. Low, R.H. Wirawan, D.A. Patterson, Molecular weight cut-off determination of organic solvent nanofiltration membranes using poly(propylene glycol), Journal of Membrane Science, 526 (2017) 221-228.

[44] S.J. Kim, N.R. Lee, B.J. Yi, S.I. Kim, Synthesis and Characterization of Polymeric Acid-Doped Polyaniline Interpenetrating Polymer Networks, Journal of Macromolecular Sciencew, Part A: Pure and Applied Chemistry, 43 (2006) 497-505.

[45] L. Hechavarria, H. Hu, M.E. Rincon, Polyaniline-poly(2-acrylamido-2-methyl-1-propanosulfonic acid) composite thin films: structure and properties, Thin Solid Films, 441 (2003) 56-62.

[46] A.G. Willis, S. Haron, Synthesis and characterization of composite polyaniline as hydrogen gas detector, Malaysian Journal of Fundamental and Applied Sciences, 13 4 (2017) 559-562.

[47] A.J. Milton, A.P. Monkman, A comparative study of polyaniline films using thermal analyses and IR spectroscopy, J. Phys. D: Appl. Phys. 26 (1993) 1468.

[48] A. Idris, N.M. Zain, Effect of Heat Treatment on The Performance and Structural Details of Polyethersulfone Ultrafiltration Membranes, Jurnal Teknologi, 44 (F) (2006) 27-40.

[49] A. Bahramian, The effect of heat treatment on the surface structure of polyaniline nanostructured film: An experimental and molecular dynamics approach, Applied Surface Science, 311 (2014) 508-520.

[50] S-H. Yoon, Membrane Bioreactor Processes: Principles and applications, June 23, (2015) CRC Press,ISBN 9781482255836.

[51] A. Rahy, T. Rguig, S.J. Cho, C.E. Bunker, D.J. Yang, Polar solvent soluble and hydrogen absorbing polyaniline nanofibers, Synthetic Metals, 161 (2011) 280-284.

[52] D. Ballal, W.G. Chapman, Hydrophobic and hydrophilic interactions in aqueous mixtures of alcohols at a hydrophobic surface, The Journal of Chemical Physics 139 (2013) 114706.

[53] M. Polaskova, R. Cermak, T. Sedlacek, J. Kalus, M. Obadal, P. SAha, Extrusion of Polyethylene/Polypropylene Blends with Microfibrillar-Phase Morphology, Polymer composites, (2010) 1427-1433.

[54] M. Sairam, X.X. Loh, Y. Bhole, I. Sereewatthanawut, K. Li, A. Bismark, J.H.G. Steinke, A,G. Livingston, Spiral-wound polyaniline membrane modules for organic solvent nanofiltration (OSN), Journal of Membrane Science, 349 (2010) 123-129.

[55] A. Lodha, S.M. Kilbey II, P.C. Ramamurthy,R.V. Gregory, Effect of annealing on electrical conductivity and morphology of polyaniline films, Journal of Applied Polymer Science, 82 (2001) 3602-3610.

[56] P.L. Donald, A.C. Hillier, Electrochemically modulated transport through a conducting polymer membrane, Journal of Membrane Science, 208 (2002) 119-131.

[57] D.L.Pile, Y. Zhang, A.C. Hillier, Electrochemically Modulated Permeability of Poly(aniline) and Composite Poly(aniline)-Poly(styrenesulfonate) Membranes, Langmuir 22 (2006) 5925-5931.