

The interplay role of vanillin, water, and coagulation bath temperature on formation of antifouling polyethersulfone (PES) membranes: Application in wood extract treatment

Esmaeili Mohammadamin, Lahti Jussi, Virtanen Tiina, Mänttari Mika, Kallioinen Mari

This is a Post-print version of a publication
published by Elsevier
in Separation and Purification Technology

DOI: 10.1016/j.seppur.2019.116225

Copyright of the original publication: © 2019 Elsevier

Please cite the publication as follows:

Esmaeili, M., Lahti, J., Virtanen, T., Mänttari, M., Kallioinen, M. (2019). The interplay role of vanillin, water, and coagulation bath temperature on formation of antifouling polyethersulfone (PES) membranes: Application in wood extract treatment. Separation and Purification Technology, vol. 235. DOI: 10.1016/j.seppur.2019.116225

**This is a parallel published version of an original publication.
This version can differ from the original published article.**

The interplay role of vanillin, water, and coagulation bath temperature on formation of antifouling polyethersulfone (PES) membranes: Application in wood extract treatment

Mohammadamin Esmaeili^{a,*}, Jussi Lahti^{a,b}, Tiina Virtanen^a, Mika Mänttari^a, Mari Kallioinen^{a,b}

^a*LUT School of Engineering Science, Department of Separation and Purification Technology, LUT University, P.O. Box 20, 53851 Lappeenranta, Finland*

^b*LUT Re-Source Platform, LUT University, P.O. Box 20, 53851 Lappeenranta, Finland*

Abstract

In this study vanillin was tested as the hydrophilicity promoter in a PES membranes to improve the feasibility of the membranes in the treatment of a biorefinery stream, namely a pressurized hot water extract (PHWE). The commercial PES membranes are typically prepared by phase inversion technique and thus, phase inversion is also used in this study. The ultimate structure of the phase inversion prepared membranes is asymmetric and it can be affected by various key parameters such as the temperature and the concentration of the PES solution, the solvent and additives which are used in PES solution, the coagulation bath temperature as well as the thickness of the cast PES film. In the present study, the effect of vanillin (0–6 wt.%) as a hydrophilic promoter agent, water as strong non-solvent additive in dope solution (0–2 wt.%) and coagulation bath temperature (CBT) on the formation of PES membranes was investigated in order to improve the understanding on the manufacturing of PES/vanillin membranes. The mentioned fabrication parameters were optimized and their effects on the membrane morphology, hydrophilicity, thickness, PHWE permeability, fouling and rejection properties were sequentially analyzed. It can be concluded that a small quantity of vanillin and water together in dope solution can preferably change the membrane morphology and increase the surface hydrophilicity and thus lead to formation of membrane with better wood extract permeability and antifouling characteristics.

Keywords: vanillin; hydrophilic promoter; antifouling; pressurized hot-water extract

1. Introduction

It has been shown that ultrafiltration is a potential process alternative to be used in the recovery of hemicelluloses from the biorefinery streams. The biggest challenge limiting the efficient use of ultrafiltration in these recovery processes is membrane fouling caused by aromatic compounds, such as lignin and wood extractives [1, 2]. Fouling problem is especially challenging with the polyethersulfone (PES) membranes, which have very good

mechanical properties, superior thermal strength and excellent oxidative and hydrolytic stability [3]. However, they have a relatively low hydrophilic nature, which has been identified as major contributing factor effecting directly on membrane fouling [3, 4]. Thus, to improve the possibilities to utilize PES membranes in the treatment of biorefinery streams there is a need to improve their hydrophilicity. It has been shown that vanillin (4-hydroxy-3-methoxybenzaldehyde) increases clearly the hydrophilicity of commercial PES membranes when it is adsorbed on the membranes surface [5, 11, 12]. In addition to its influence on hydrophilicity, vanillin can also improve antioxidant and antimicrobial characteristics of the membrane [13]. Similarly than typical polymeric hydrophilic additives, such as PEG, vanillin might leach out

*Corresponding author, Tel.: +358 44 968 3768

Email addresses: Mohammadamin.Esmaeili@lut.fi (Mohammadamin Esmaeili), Jussi.Lahti@lut.fi (Jussi Lahti), Tiina.Virtanen@lut.fi (Tiina Virtanen), Mika.Manttari@lut.fi (Mika Mänttari), Mari.Kallioinen@lut.fi (Mari Kallioinen)

¹<https://doi.org/10.1016/j.seppur.2019.116225>

Table 1. Comparison of different studies in which vanillin was used as antifouling/antibiofouling agent either in feed solution or in fabrication and modification of membranes. *Membrane performance tested in terms of permeability and selectivity.

The aim of the study	Tested*	How vanillin was introduced	Vanillin concentration	Effects	Ref.
Improvement of model compound permeability and performance of membrane in treatment of Pine hydrolysate (PHWE).	Yes	Physical adsorption on the surface	0–2.8 g/L	The PEG solution permeability improved up to 35–38%.; No significant improvement in pine hydrolysate permeability was observed.; Hydrophilicity improved by 30%.	[5]
Reduction of biofilm formation on the polystyrene surface.	No	Introduced into the feed solution	0–0.25 mg/ml	Biofilm formation of bacterium “ <i>Aeromonas hydrophila</i> ” was minimized.	[6]
Reduction of biofilm formation on the surface of membrane.	No	Introduced into the feed solution	0.16 mg/ml	Initial attachment and dynamics of biofilm growth of “ <i>Aeromonas hydrophila</i> ” bacterium were minimized due to quorum quenching mechanism of vanillin.	[7]
Reduction of biofilm formation on the surface of RO membrane.	No	Introduced into the feed solution	1200 mg/L	Biofilm formation of mix culture of marine bacteria was significantly reduced by more than 79%.	[8]
Reduction of biofilm formation on the surface of RO membrane.	Yes	Physical adsorption on the surface	1200 mg/L	QSI of vanillin on reduction of biofilm formation was observed.; No improvement in membrane performance (i.e. salt rejection and permeability) was observed.	[9]
Improvement of membrane performance and antifouling characteristics in presence of model compound solution.	Yes	Blending modification at 10 °C CBT	0–2 wt.%	The permeability improved up to ~10 (kg/m ² h).; At highest vanillin content, both antifouling and biofouling improved.	[10]
Reduction of biofouling.					
Improvement of permeability and performance of membrane during filtration of wood originated streams (e.g. PHWE). Preparation of antifouling membranes.	Yes	Blending modification in presence of water as another NSA at various CBTs	0–6 wt.%	Membranes with 102–160 (kg/m ² h) pure water flux permeability were fabricated. PHWE permeance (VRF: 1.1) was significantly improved compare to reference [5]; ~13 times higher. Small amount of water and vanillin preferably changed the surface chemistry, morphology and antifouling characteristics of membrane.	Current study

from the membrane structure during membrane formation and filtration processes due to its affinity to water [14–17]. The possible leaching of vanillin out from the membrane structure can be also beneficial as it can reduce the bacterial growth which in turn minimizes the biofilm formation. The desorbed vanillin could be possibly recovered similarly than in a molecular imprinting technique by a simple addition of vanillin to the feed [18]. The role of vanillin as a natural quorum sensing inhibitory (QSI) agent in reduction of biofilm formation has been the subject of many studies recently [6–8, 19]. For instance, Kateb et al. (2017) studied the in situ antibiofouling potential of vanillin by physical adsorption on the surface of polyamide thin-film composite reverse osmosis membranes using a mixed culture of biofilm forming marine bacteria. The results of their study reveal that vanillin as a quorum sensing (QS) inhibitory agent decreases the biomass production of polysaccharide (~12%), live bacteria (~58%) and dead bacteria (~16%) on the surface of the membrane (SWC5, Oceanside, CA) by disrupting QS pathways which in turn reduces the biofilm formation [9]. Vanillin possesses hydroxyl group on the phenyl ring and the double bond that are demonstrated to be important parameters which affect the antibiofilm compound

activity [20]. To the best of the authors’ knowledge, typical pore formers, such as PEG and PVP do not possess the quorum sensing inhibitory (QSI) characteristics. In addition, vanillin is an interesting membrane additive also from that point of view, that it originates from biomass and not from oil. Thus, it is a “green” and sustainable membrane performance promoter.

Table 1 demonstrates the proposed approach of the current paper in comparison with other studies in which vanillin was used as antifouling/antibiofouling agent either in feed solution or in fabrication and modification of membranes. To the best of the authors’ knowledge, neither vanillin nor water has been used in fabrication of membrane for the treatment of wood extract or other biorefinery streams. In general, most studies up to now in the field of the treatment of wood originated streams have focused on using commercial membranes but the reported fluxes have been very low even close to zero in the filtration of wood extracts with PES and polysulphone membranes (Table S2 in Supplementary material) [5, 21, 22]. Thus, there is a need for attempts focused on fabrication of new generation membranes that can be used in these areas where mixtures to be treated are extremely complex and challenging to treat. In this study vanillin is tested

as the hydrophilicity promoter in a PES membranes to improve the feasibility of the membranes in the treatment of a biorefinery stream, namely a pressurized hot water extract (PHWE). The commercial PES membranes are typically prepared by phase inversion technique and thus, phase inversion is also used in this study. The ultimate structure of the phase inversion prepared membranes is asymmetric and it can be affected by various key parameters such as the temperature and the concentration of the PES solution, the solvent and additives which are used in PES solution, the coagulation bath temperature as well as the thickness of the cast PES film [23]. In addition, the formation of complex between water and NMP through multiple hydrogen bonding and the interactions between water and vanillin can affect the kinetic parameters and thermodynamic properties during membrane formation. Thus the impacts of these interactions on the performance and morphology of membrane are of interest.

Sathis Kumar et al. [10] have also been inspired on the possibility to use vanillin as antifouling agent. They fabricated PES/vanillin membranes by phase inversion technique and tested their antibiofouling propensity. They found that vanillin modified membranes had better antibiofouling resistance compared to the pure PES membranes against the model biofouling organisms, which they used. They, however, did not examine the benefits of vanillin addition in the treatment of wood extract or other biorefinery streams, which are extremely complex mixtures and challenging to treat compared to model solutions. Moreover, they examined the effect of vanillin addition on the resulting membrane morphology only at one temperature (10 °C). To date, there is no research in which the interaction of vanillin, water and coagulation bath temperature (i.e. not more than one factor at the time) in membrane fabrication, has been investigated.

In the present study, the effect of vanillin (0–6 wt.%) as a hydrophilic promoter agent, water as strong non-solvent additive in dope solution (0–2 wt.%) and coagulation bath temperature (CBT) on the formation of polyethersulfone membranes is investigated in order to improve the understanding on the manufacturing of PES/vanillin membranes. The mentioned fabrication parameters were optimized and their effects on the membrane morphology, hydrophilicity, thickness, PHWE permeability, fouling and rejection properties were sequentially

analyzed.

2. Materials and methods

2.1. Chemicals

Vanillin used in this study (purity 99%, Mw. 152.15 g/mol, CAS: 121-33-5) was provided by Acros Organics (Geel, Belgium). The non-woven polyester (PET) support material (grade 3329, basic weight 96.5 g.m⁻², thickness 0.135 mm, air permeability 41 L.m⁻².sec⁻¹) was provided by Ahlstrom Filtration LLC. The following chemicals were used for preparation of casting solution in membrane manufacturing: Polyethersulfone (58,000 g/mol, Goodfellow Cambridge Ltd, UK) as the basic polymer, N-Methyl-2-Pyrrolidone (NMP, CAS: 872-50-4) and N, N-dimethylformamide (DMF) as solvents were provided by Merck Co. (Germany) and Fluka Chemie AG (Buchs, Switzerland, ≥ 99%), respectively. Ultra-pure deionized water (DI, 15 MΩ) was produced for all the experiments with the CENTRA-R 60/120 system (Elga purification system, Veolia Water, UK).

2.2. Membrane preparation

Asymmetric PES based and vanillin modified membranes were fabricated via wet phase inversion technique according to the procedure described in details by Mulder [24]. The preparation of dope solution was initiated by dissolving desired amount of DI water (0–2 wt.% based on the weight ratio of DI water to PES solution) and vanillin (0–6 wt.% based on the weight ratio of vanillin to PES solution) into NMP solvent under constantly agitation at room temperature. Once the dissolution of additives were completely obtained, an adequate amount of dry PES beads were gradually added into the mixture to attain desired polymer concentration (20 wt.%). After being fully mixed, the homogeneous dope solution was laid aside to degas overnight in order to eliminate any air bubbles which might be present in the dope solution. In addition, the polymer solution was kept in dark place in order to avoid the aging process [25].

High porosity of polyester (air permeability 41 L.m⁻².sec⁻¹) might increase the risk of dope solution penetration through the PET support which can result in formation of PES layer underneath the PET fabric. In order to avoid this unfavorable

event, the PET was initially immersed into the solution of water and DMF solvent (containing 60–65 vol.% water) for 1 min [26]. Afterwards, the excess solution on the surface of PET was drained and then the PET was attached to a spotless glass plate using paper clips. The PES dope solutions were then hand-casted via a film applicator with a thickness of 200 μm on (i) non-woven pretreated PET for permeation tests and (ii) on a glass plate for characterization tests. Thereafter, the cast film was instantaneously immersed into the coagulation bath containing DI water. The condition of fabricated membranes by various preparation parameters is presented in Table 2.

2.3. Membrane characterization

2.3.1. Fourier transform infrared spectroscopy

To characterize the presence of vanillin in modified membranes, FTIR spectra of both virgin and modified PES membranes were measured by using the Perkin Elmer Frontier spectrometer with an universal ATR module (Diamond crystal). FTIR spectra of six random spots from each membrane were measured at 4000–400 cm^{-1} wavenumber range with the resolution of 4 cm^{-1} . All the spectra were measured with the acquisition of 20 scans with the data interval of 1 cm^{-1} at the absorbance mode. At the final step, the co-added spectra were processed with ATR correction, baseline correction, and normalization.

2.3.2. Scanning electron microscopy

The cross sectional morphology of membranes was qualitatively investigated using scanning electron microscope (SEM) (Hitachi SU 3500, Japan) at an acceleration voltage of 15 kV in high vacuum condition. The membrane samples were subsequently coated with a thin layer of gold using Edwards Scancoat six Pirani 501 sputter coating system (Edwards High Vacuum International, Crawley, UK). Finally, the cleaved edge was examined perpendicular to cut plane by SEM. The cross-section SEM images of each membrane sample were analyzed using ImageJ software (National Institutes of Health, Bethesda, Maryland, USA) and the averaged membrane thickness of six different locations for each membrane were measured.

2.3.3. Casting solution viscosity measurement

Regarding the considerable role of casting solution viscosity on pore formation and the final structure of the membrane, the dynamic viscosities of

dope solutions were measured using Modular Compact Rheometer MCR 302 (Anton-Paar, Austria, PP50/P2 spindle) at 20 °C.

2.3.4. Contact angle measurements

Static contact angles of fabricated membranes were measured using the both captive bubble and sessile drop methods. Roughly 5 μL of DI water and 3–4 μL of air bubble volumes were placed on the surface of the membrane samples with the aid of micro syringe (sessile drop) and U-shaped needle (captive bubble) at room temperature, respectively. To increase the reliability of the measurements, the contact angles of six independent points for each samples were tested and the average of recorded data was considered as the final CA. The CA was measured using KSV CAM 101 instrument (KSV Instruments Ltd., Finland) connected to a CCD camera (DMK 21F04, The Imaging Source Europe GmbH, Bremen, Germany). The captured images were treated by curve fitting analysis with CAM 2008 software in order to determine the CA.

2.3.5. UV/Vis analysis

UV/Vis spectrophotometer (Jasco V-670 spectrophotometer, Japan) was utilized to measure the concentration of lignin in feed, permeate, and concentrate samples of pressurized hot-water extract (PHWE) by UV absorption at wavelength of 280 nm.

2.4. Experimental design and procedure

2.4.1. Pressurized hot water extraction process and characterization

The autohydrolysis process was performed in a batch extractor set up (15 L, stainless steel). The pine wood sawdust with the particle size distribution below 2.8 mm was used to prepare wood extract (hydrolysate). A 5.6 : 1 weight ratio of water to wood was applied. The wood and water were heated to 160 °C and processed for 90 min at pressure of 5–6 bar. The extract was cooled down to 25 °C followed by 30 min centrifugation at 3000 rpm (Sorvall RC-28S centrifuge, RCF= 920G GSA fixed angle rotor, Du Pont, USA) to separate the hydrolysate from the wood chips for the fouling study. pH and conductivity of the produced PHWE were 3.8 and 600 $\mu\text{S}/\text{cm}$ at 25 °C.

Table 2. Standard array of experimental runs (Std), the measured viscosity of each polymer solution (at 20 °C), contact angle, thickness, pure water mass flux before (PWF_b) filtration test, and pure water flux reduction (PWF_R) of fabricated membranes (errors are based on 95% confidence interval).

Std	Water content (wt.%)	Vanillin Content (wt.%)	CBT (°C)	Viscosity (Pa.s)	CA sessile drop (°)	CA captive bubble (°)	Thickness (μm)	PWF_b (kg/m ² hbar)	PWF_R (%)
1	0	0	10	1.28	61.51 ± 0.93	62.68 ± 3.49	73.28	102.74	57.30
2	2	0	10	1.63	59.04 ± 1.93	61.33 ± 1.07	67.59	127.45	61.30
3	0	6	10	1.96	55.97 ± 2.00	58.75 ± 0.51	62.08	147.79	59.11
4	2	6	10	2.63	57.70 ± 0.77	54.19 ± 1.01	61.23	163.39	65.40
5	0	3	0	1.60	65.53 ± 2.48	64.33 ± 1.06	70.38	152.21	57.30
6	2	3	0	2.03	64.12 ± 3.51	61.37 ± 1.47	75.66	157.19	73.66
7	0	3	20	1.60	53.10 ± 0.63	52.79 ± 1.66	74.98	117.10	46.70
8	2	3	20	2.03	57.48 ± 1.15	58.12 ± 0.71	73.67	167.89	65.08
9	1	0	0	1.43	57.94 ± 1.60	59.25 ± 1.26	75.18	104.32	58.42
10	1	6	0	2.22	66.13 ± 1.01	69.88 ± 2.27	60.97	135.34	68.83
11	1	0	20	1.43	54.74 ± 0.45	53.22 ± 1.45	75.26	159.68	70.31
12	1	6	20	2.22	51.76 ± 0.41	52.19 ± 0.21	75.53	139.37	61.60
13-14	1	3	10	1.73	54.50 ± 1.13	54.00 ± 0.30	67.59	141.74	42.19

2.4.2. Fouling tests of membranes with hydrolysate

The fouling behavior of hydrolysate for both virgin and vanillin modified PES membranes was investigated in a batch mode with a dead-end filtration system using the stirred cell (Millipore, USA, Cat No.: XFUF07611, diameter of mixer: 60 mm).

Membranes with an effective filtration diameter of 70 mm were prepared. As a preliminary step, the compaction of membranes at 5 bar for 20 min and subsequent 15 min stabilization at 3 bar with 300 mL DI water was conducted. Then pure water flux at 3 bar and 25 °C was measured before hydrolysate filtration. Thereafter, 300 g of centrifuged hydrolysate was filtered for 90 min at 3 bar and the filtrate weight was recorded every one minute at a stirring rate of 500 rpm. At the end of filtration test, the final weights of permeate and concentrate were recorded in order to evaluate the mass balance. Then, the membrane coupon was taken out from the filter and the surface of the membrane was rinsed six times by dipping it in the DI water. Finally, the pure water flux was measured with the same conditions which were used before the filtration of the hydrolysate. The lignin and TOC rejections were calculated using Eq. (1):

$$R(\%) = \left(1 - \frac{2 \times c_p}{c_f + c_r}\right) \times 100 \quad (1)$$

where C_p , C_f and C_r are the concentrations of lignin or TOC in permeate, initial feed (*i.e.*, $t = 0$) and retentate (at the end of filtration process), respectively. The concentration of lignin was calcu-

lated from Beer–Lambert law by using the adsorption coefficient of Pine lignin (ε , *i.e.* absorptivity) at 280 nm, 25 L. g⁻¹.cm⁻¹ [27, 28]. Membrane fouling was evaluated based on pure water flux reduction (PWF_R) using Eq. (2):

$$PWF_R(\%) = \left(\frac{PWF_a - PWF_b}{PWF_b}\right) \times 100 \quad (2)$$

where PWF_b (kg/m²hbar) and PWF_a (kg/m²hbar) are pure water mass flux before and after the filtration of PHWE (hydrolysate).

3. Results and discussion

3.1. The effect of vanillin and water content on viscosity of polymer solution

The results obtained from the viscosity measurements of dope solutions as a function of vanillin and water content are summarized in Table 2 and depicted in Fig. 1.

As shown in Fig. 1, the viscosity of polymer solution increases with increasing the vanillin and water content in the solution. In the case of vanillin, the results can be ascribed to two reasons: (i) vanillin (152.15 g/mol) has a higher molecular weight compared to NMP (99.13 g/mol), (ii) the entanglements of polymer chains or intermolecular aggregations stemming from adding vanillin which has a non-solvent character for PES when compared to NMP. Increase of viscosity of casting solution as a consequence of the addition of organic additives has

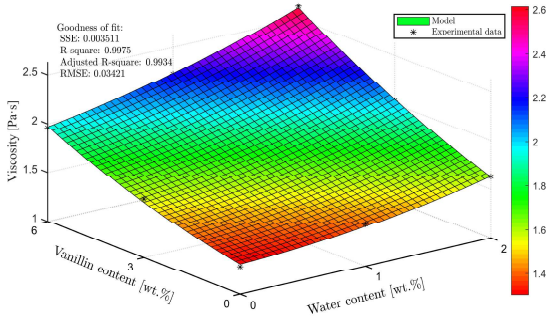


Fig. 1. The effect of vanillin and water content on the viscosity of PES polymer solution at 20 °C.

been reported in many studies [29–31] however, the effect of vanillin on viscosity of polymer solution has not been investigated in existing literature up to now. Within experimental domains in this study, the viscosity of polymer solution at 20 °C (Z , Pa.s) can be expressed by an empirical quadratic polynomial equation with RMSE (root-mean-square error) of 0.034 based on water (X , in percentage) and vanillin content (Y , in percentage) as follows:

$$Z = 1.306 + 0.03833X + 0.06278Y + 0.06167X^2 + 0.02667XY + 0.007963Y^2 \quad (3)$$

This model was validated by measuring the viscosity at 20 °C of two unknown polymer solution and the results are presented in the Table 3.

Table 3. Experimental validation of model results of viscosity measurements at 20 °C.

Water content [%]	Vanillin content [%]	Empirical data [Pa.s]	Model [Pa.s]
1.5	4	2.03	2.04
0	2	1.46	1.46
0.5	2	1.55	1.52

Complex formation between water and NMP can be considered as a possible explanation for the influence of water on the viscosity of polymer solution. In other words, this can be attributed to the growth of a 2D hydrogen network which links several molecules together as demonstrated by Wang *et al.* [32]. Another possible elucidation for the increase of viscosity in this case can be ascribed to the role of water as non-solvent in accelerating the polymer chain precipitation process and reducing the thermodynamic miscibility of casting solution.

In fact, the dope solution system is tended to a state close to the cloud point in presence of water wherein the viscosity increases. These results are consistent with Yunos *et al.* [33] and Wang *et al.* [32] findings which showed the increase of viscosity of dope solution with increasing water content.

3.2. Chemical structure of the membranes

Spectra of polyethersulfone membranes fabricated based on the factors in Table 2, are presented in Fig. 2 over a wavelength range of 4000–400 cm^{-1} . Two signals at 1486 and 1578 cm^{-1} are the identical peaks for PES membrane [34, 35]. One unanticipated peak at 1680 cm^{-1} in spectrum of unmodified PES is associated with carbonyl group of residual NMP solvent in membrane [36]. In order to assure that this peak is related to NMP, the FTIR of unmodified PES was analyzed after drying in oven for 2 h (Fig. S2). This spectrum confirms the association between the peak with carbonyl group of NMP since the peak disappeared as a result of complete evaporation of NMP solvent. Considering the fact that there is always a little amount of inevitable trapped water inside the porous membranes fabricated via phase inversion techniques, the presence of two peaks at 3553 and 3636 cm^{-1} can be attributed to O–H stretching vibration of water molecules. These peaks match those observed in earlier studies performed by Belfer *et al.* [34].

From the spectrum given in Fig. 2, it can be seen that most of the vanillin peaks overlap with the peaks of a virgin PES membrane (std1, (0,0,10), Table 2) due to similarities in their functional groups. However, a clear trend of increase in intensity of vanillin peaks can be noticed as the wt.% of vanillin in dope solution increases at 781, 1029, 1267, and 1510 cm^{-1} . These peaks are associated with the aromatic native structure of vanillin, in-plane C–H deformation, OCH_3 group, and the coupled skeletal vibrations of the aromatic ring of vanillin, respectively [37, 38]. The most clearly the effect of vanillin on the FTIR spectra can be seen at 1510 cm^{-1} . The observed increase in intensity of this peak can be explained based on four prominent factors, vanillin concentration, temperature of coagulation bath (CBT), viscosity of casting solution, and water content. Overall, the intensity at 1510 cm^{-1} increases as the concentration of vanillin in dope solution increases from 0–6 wt.%. Comparing the spectra of the samples std10 (1,6,0) and std12 (1,6,20) or std6 (2,3,0) and std8 (2,3,20), in which the water and vanillin content are the same

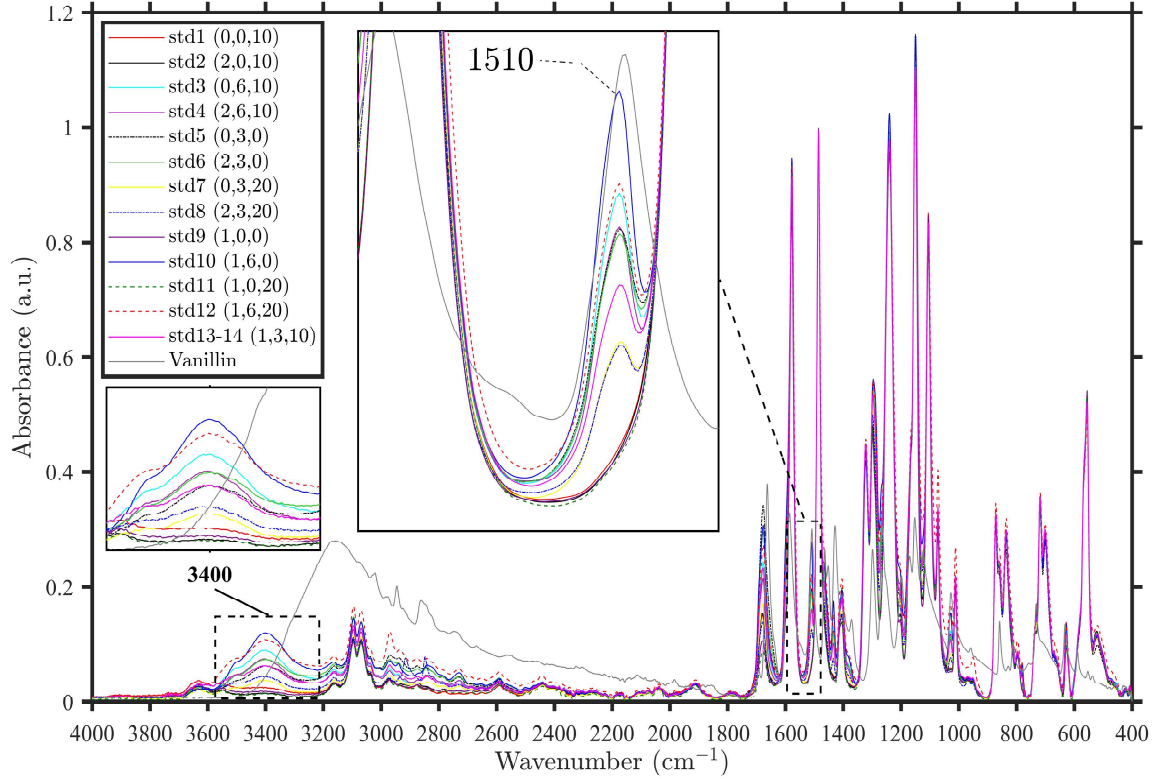


Fig. 2. ATR-FTIR spectra of virgin and modified membranes in the region of 4000–400 cm^{-1} . The values in parentheses show water content (wt.%), vanillin content (wt.%) and coagulation bath temperature ($^{\circ}\text{C}$), respectively.

but the coagulation bath temperatures different, it can also be seen that the intensity of this peak at 1510 cm^{-1} is significantly dependent on the CBT. The intensity of the peak at 1510 cm^{-1} decreased as the CBT increased. This might be due to the fact that the miscibility of vanillin in coagulation bath declines as the temperature decreases. As a result, the amount of vanillin, which is remained inside the membrane structure increases during the immersion precipitation process.

The thickness of the membrane and interdiffusion of solvent and non-solvent during the phase-inversion process can be affected as the viscosity of polymer solution changes [26]. In the same CBT conditions, the intensity of vanillin peak at 1510 cm^{-1} increased as the viscosity of dope solution increased since the exchange rate between solvent and non-solvent in coagulation bath during the precipitation process was decreased (see Fig. 2, compare the samples std4 (2,6,10) and std13–14 (1,3,10)).

From Fig. 2 and Table 2, it should be also noticed

that at the same CBT and vanillin content (wt.%), the increase in water content decreases the intensity of the mentioned peak even though it increases the viscosity of polymer solution. In such conditions (constant CBT and vanillin content), water as non-solvent reduces the effect of viscosity factor due to the formation of macrovoids in the cast film and also reduces the thermodynamic miscibility of casting solution [33]. Consequently, the more non-solvent, i.e. water, will diffuse into the film and it can wash out the more vanillin from the cast film. The FTIR spectra of std3 (0,6,10) and std4 (2,6,10) or std5 (0,3,0) and std6 (2,3,0) show the effect of water content in reducing the impact of polymer viscosity in increasing the intensity of vanillin peak at 1510 cm^{-1} .

From the spectra it was noticed that when vanillin was added, the absorption peaks of O–H stretching at 3200–3700 cm^{-1} region, benzene stretching at 1677 cm^{-1} , and sulfone groups vibrations at 1152 cm^{-1} become apparently wide and

strong which indicates the formation of hydrogen bonds between OH groups of vanillin and oxygen atoms in ether and sulfone groups of PES. The area of C–H aromatic stretching vibration (3100–3000 cm^{-1}) and aliphatic stretching vibration (2922–2875 cm^{-1}) become also more intense as the vanillin concentration increases. The main FTIR peak assignments of PES are summarized in Table 4.

Table 4. The main peak assignments for ATR-FTIR spectra of fabricated PES membrane over wavenumber of 4000–1000 cm^{-1} .

FTIR-peaks (cm^{-1})	Peak assignments
1105	S=O stretching vibration
1151	Symmetric stretches SO_2 of sulfone group
1240	Aromatic ether band
1322	Asymmetric SO_2 of sulfone group
1486 & 1578	Aromatic skeletal vibration
1677	C=O carbonyl group (vanillin)
2878	γ s CH_3 asymmetric aliphatic stretch
2925	γ a CH_2 asymmetric aliphatic stretch
2952	γ a CH_3 asymmetric aliphatic stretch
3069 & 3069	C–H aromatic stretch
broad band 3200–3600	Hydrogen bonded OH band

Virtanen et al. have suggested the H-bonding of the hydroxyl group with the sulfur oxygens of polyethersulfone membrane when the vanillin is in protonated form and vanillin is adsorbed on the membrane surface [11]. Based on the findings from the FTIR spectra, this interaction (depicted in Fig. 3.) has most possibly taken place also in this study.

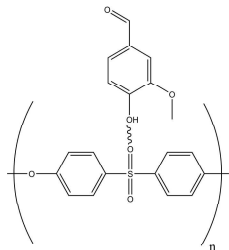


Fig. 3. Schematic representation of the intermolecular interactions between the polyethersulfone and vanillin.

3.2.1. Hydrophilicity of the membranes

The hydrophilicity of the membranes was evaluated based on the water contact angle using both the captive bubble and sessile drop methods. Any significant hysteresis between the results from the captive bubble and sessile drop methods could not be seen (Table 2). The negligible inconsistency in results between these two techniques can be associated to the applied volume of water and air bubble and to the gravity.

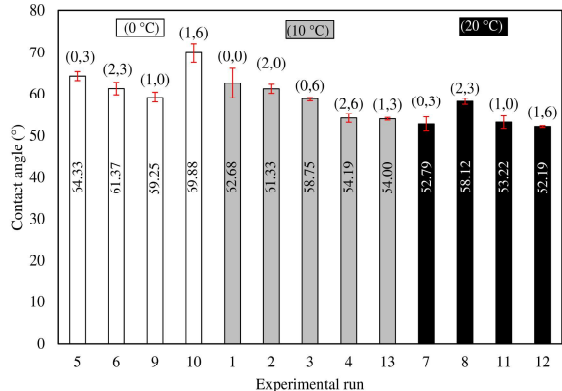


Fig. 4. Contact angle (captive bubble) of fabricated membranes arranged based on CBT. (water wt.%, vanillin wt.%)

Generally it can be conducted that the apparent contact angles of the membranes manufactured at the lowest coagulation bath temperature (0 °C) demonstrate the higher hydrophobicity compared to the other membranes (Fig. 4). It can be speculated that the surface coverage of membrane with vanillin is reduced due to the lower molecular thermal motion and also the stronger affinity between vanillin segments and PES chains during membrane formation which inhibits washing out of vanillin at lower temperature. In addition, the contact angle cannot be just ascribed to surface chemistry of membrane but also it relies on the pore size, porosity, and surface roughness of the membrane. In general, the slower exchange rate of solvent and non-solvent occurs at lower CBT, which in turn can lead to the formation of a membrane with denser structure. At higher coagulation bath temperature (20 °C), the pore sizes of the membrane are larger (higher water flux, lower retention, Supplementary material Table S1) and its roughness is higher than at 0 °C. These lead to lower apparent contact angle of the membrane coagulated at 20 °C. Based on Wenzel (1936) method [39], if the surface is chemically hydrophilic ($<90^\circ$), it will become even more hydrophilic when surface roughness increases.

At higher temperatures, especially in presence of water as non-solvent additive, it is also important to keep in mind that the surface coverage of membrane with vanillin might be reduced due to higher solubility and diffusivity of vanillin and thus vanillin can be easily washed out from the surface and from the membrane structure during the experiments. As indicated previously, the quantity of residual vanillin

in the structure of membrane reduces when the water content increases to 2 wt.% as the coagulation bath temperature increases. This can be considered as an explanation for the increase of contact angle in std8 (CBT: 20 °C, 2 wt.% water, 3 wt.% vanillin) where the intensity of vanillin peak is the lowest one compared to the other membranes containing vanillin.

3.3. Morphology of the membranes

3.3.1. Thickness of the membranes

From Table 2 it can be seen that the thickness of membranes at coagulation bath temperature of 20 °C is higher when compared to 0 and 10 °C. It is generally accepted that the instantaneous demixing process leads to faster precipitation of polymer chains, which in turn increases the thickness of membrane while the delayed demixing prolongs the completion of precipitation process. In higher temperature, the mutual diffusivity between NMP (solvent) and water (non-solvent) enhances which consequently accelerates the exchange rate between solvent and non-solvent and thus the precipitation process can be finalized in shorter time. Saljoughi and Mousavi [40] have presented the results demonstrating the increase of membrane thickness with successive increase of CBT. However, Wang *et al.* [32] have reported that CBT does not have the dominant role in the exchange rate between solvent and non-solvent, particularly in presence of additives in dope solution. Several studies reported that the addition of a suitable non-solvent additives into the dope solution can shift the binodal curve closer to the initial composition of casting solution which in turn reduces the thermodynamic miscibility of the dope solution. Therefore, it facilitates the solidification process resulting in fabrication of membrane with higher thickness. In this study both explanations support that the membrane thickness is higher at higher temperatures. On the other hand, it should also be noted that the higher amount of additives, in this case vanillin and water, increases the viscosity of dope solution (Fig. 1) and consequently hinders the kinetics of solvent outflux and non-solvent influx which in turn declines the overall thickness of the membrane.

The outcomes of the lowest temperature needs to be discussed in detail. At the lower temperature, the local polymer chain entanglement through the hydrogen bonding among the PES segments causes the formation of small nuclei owing to the quick reduction in mobility of PES chains. Consequently,

the cast film might immediately form a strong gel before the initiation of phase separation as demonstrated by Cha *et al.* [41]. The macromolecular network possessing a moderately low entanglement density will be formed in the gel and the overall thickness of membrane will not change with further solvent and non-solvent exchange. As was pointed out, the presence of non-solvent additives can accelerate the precipitation process which can also be considered as an explanation for the increase of membrane thickness in lower temperature. Among the membranes at coagulation bath temperature of 0 °C, the presence of 6 wt.% vanillin in std10, shows the lowest thickness ($\sim 61 \mu\text{m}$). This discrepancy could be attributed to highest peak intensity of vanillin in std10 (1,6,0) among all membranes which has been shown in Fig. 2. In other words, the intensity of this peak shows that the higher amount of vanillin is remained in the structure of the membrane which in turn amplifies the role of viscosity in delayed demixing process and consequently leads to the reduction of membrane thickness.

It can be also noticed that the viscosity of dope solution plays a vital role in the reduction of membrane thickness at the CBT of 10 °C. Closer inspection of the Table 2 shows that at the 6 wt.% vanillin content and at 2 wt.% water content, the role of viscosity is outstanding compared to aforementioned roles for vanillin and water.

3.3.2. Physical structure of the membranes

The SEM cross-sectional structures of PES membranes and ones modified with vanillin and water are depicted in Figs. 5 and 6. An asymmetric structure including a thin dense top layer and porous sublayer was observed in all the cross-sectional structures. As can be seen from the SEM images, the sublayers appear to possess cavities and morphologically different finger-like macrovoids in their structures.

In order to identify the role of vanillin and water in morphology of cross-section structure, it is worth to investigate the formation of macrovoids in the structure of the membrane. The formation of a skin layer at early stage, which declines the penetration of large amount of coagulant (water) into the cast film is the necessity for the initial macrovoid formation. In addition, instantaneous demixing process stemming from rapid exchange between solvent and non-solvent can form a thin skin layer which avoids the formation of extra nuclei after the formation of few nuclei (where the solvent

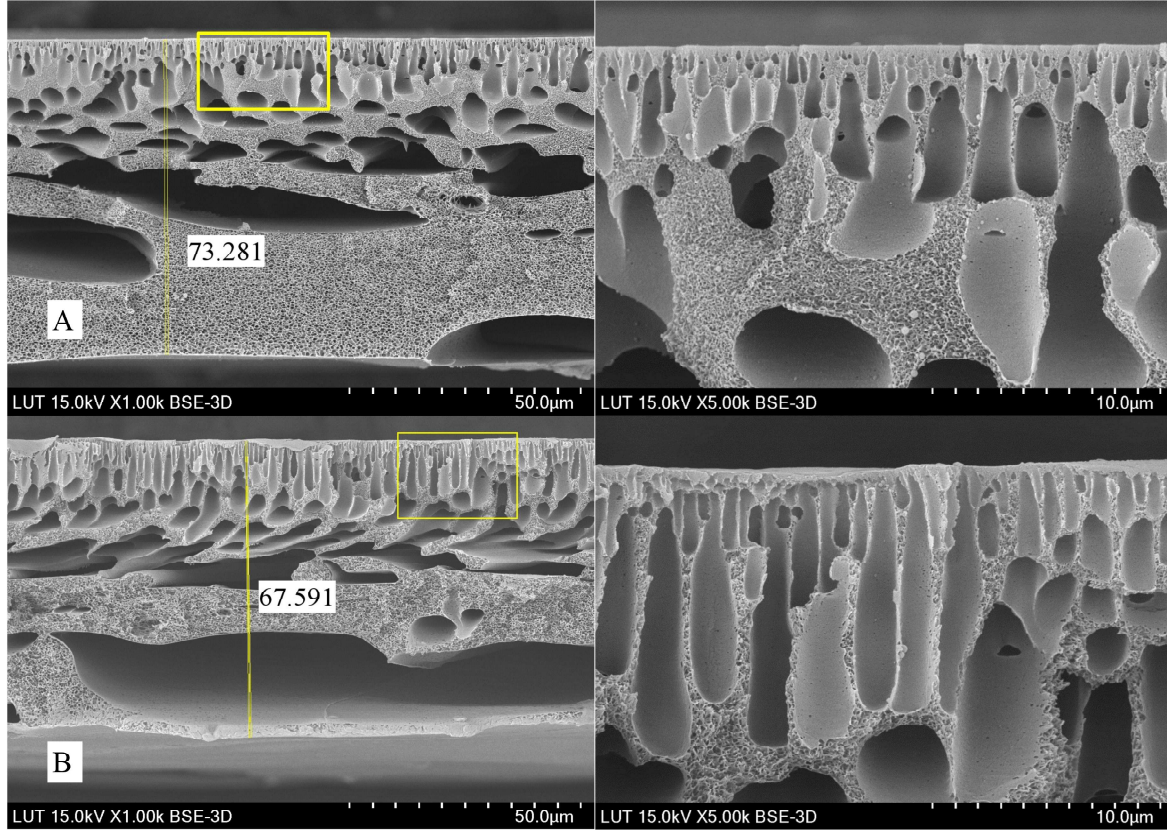


Fig. 5. SEM images of the PES membranes prepared by varying the water content in 20 wt.% PES/NMP solution at CBT of 10 °C: (A) 0 wt.%, (B) 2 wt.% . The cross-sections are on the right and the zoom sections of marked top layers are shown on the left.

existed). Another theory which might explain the observation of macrovoids could be the relatively hydrophobic characteristics of PES materials. As mentioned earlier, the PES polymer chains repel water due to their hydrophobic features and thus there would not be enough coagulant beneath the skin layer to induce phase inversion, which in turn can lead to the formation of macrovoids.

3.3.2.1. Effects of water as non-solvent additive on membrane morphology. The PES membrane without any additives (Fig. 5, std1) has a very small finger-like macrovoids from the top half of the cross-section to the top surface of skin layer which, probably introduces pinhole defects to the surface of the membrane.

The effects of successive increase of water content from 0 to 2 wt.% on the structure of the membrane cross-sections is depicted in Fig. 5. It can clearly

be seen that the size and the length of finger-like macrovoids increase with increase of water content in dope solution. This can be ascribed to the role of water as a strong non-solvent additive (NSA) in the reduction of thermodynamic miscibility of dope solution, which in turn shifts the binodal curve close to the dope solution and accelerates the diffusional exchange rate between solvent (NMP) and non-solvent (water). These results are in agreement with Yunos' *et al.* [33] findings demonstrating the similar behavior on the morphology of PSf membrane cross-sections as a consequence of using water as strong non-solvent additive on the dope solution. Similarly, the same behavior of water as NSA on the morphology of polysulfone (PSf) has also been observed by Azizi Namaghi *et al.* [42]. It can also be noticed that the pore walls at the bottom of matrix become thinner with the increase of water in the dope solution. The presence of some trapped

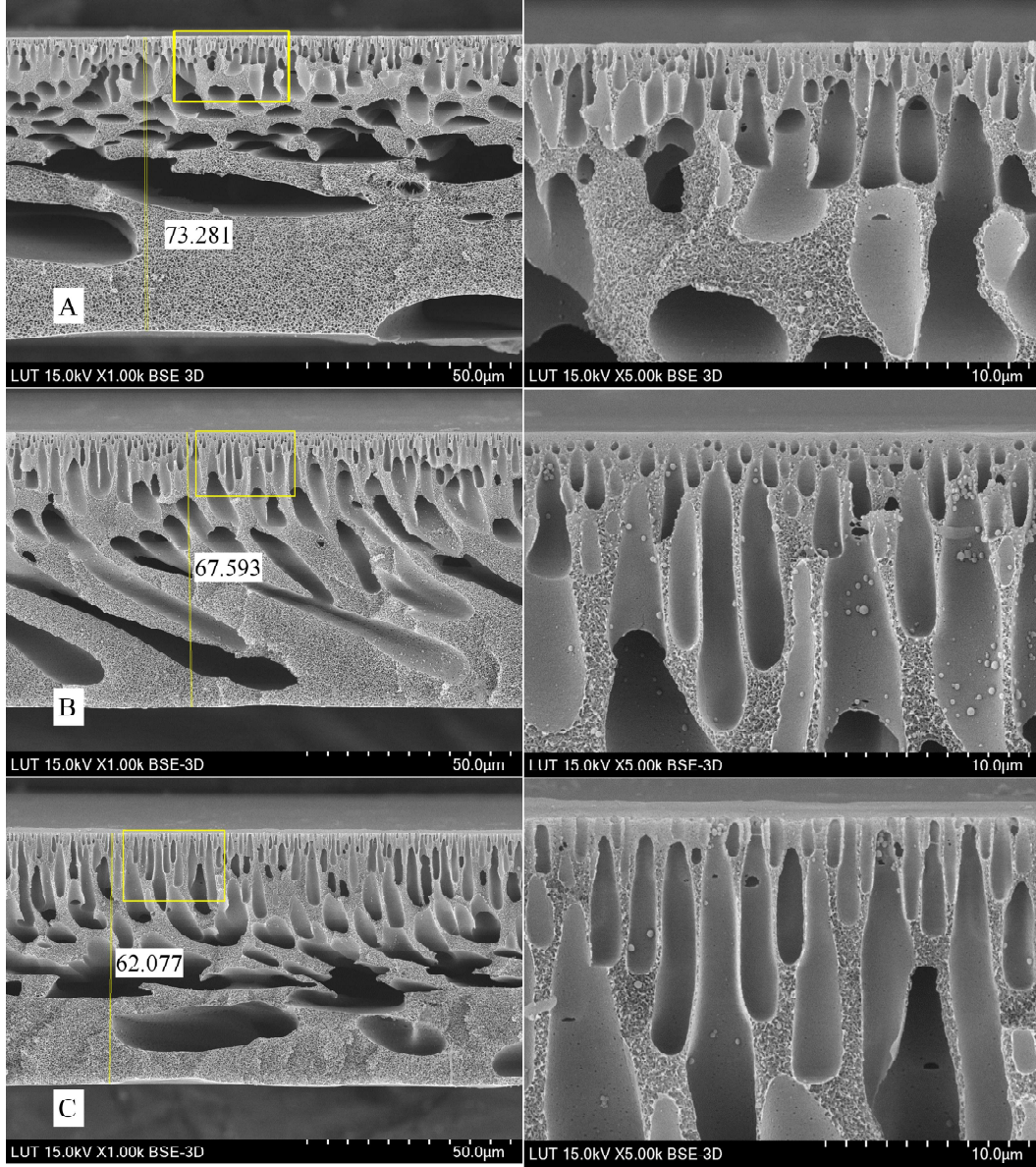


Fig. 6. SEM images of the PES membranes prepared by varying the vanillin content in 20 wt.% PES/NMP solution at CBT of 10 °C: (A) 0 wt.%, (B) 3 wt.% (1 wt.% water content), (C) 6 wt.%. The cross-sections are on the right and the zoom section of marked top layers are shown on the left.

particles (0.2–0.5 μm) in the membrane matrix can be clearly seen from Fig. 5 (zoom section of top layer). This might be attributed to the precipitation of highly localized concentrated PES as a consequence of crystallization. The same crystallization related precipitation conducts have been also observed by Yeow *et al.* [43] for PVDF membranes

cast and coagulated at 20 °C. The more trapped particles have been observed in lower gelation temperature, i.e. 0 and 10 °C. This can be explained by the fact that at lower temperature, the gelation prompted by crystallization arises first in the membrane formation processes and thus the crystals can grow as a result of delayed demixing [43].

3.3.2.2. Effects of vanillin as non-solvent additive on membrane morphology. The presence of vanillin as a hydrophilic additive can enhance the instantaneous demixing in coagulations bath. The key aspects of this phenomenon can be listed as follows:

1. The presence of vanillin increases the thermodynamic instability of dope solution due to the non-solvent characteristics of vanillin.

2. The diffusion of water molecules can be facilitated due the formation of a thin layer of vanillin on the surface of the membrane, specifically at CBT of 10 °C and 3 wt.% vanillin concentration. The contact angle measurements which have been presented in Table 2 demonstrate the presence of this layer on the surface of the membrane.

It can be seen clearly from Fig. 6 that the membrane structures in presence of 3 wt.% vanillin become more regular with fully developed finger-like macrovoids that stem from instantaneous demixing. A clear boundary existing between finger-like macrovoids beneath the skin layer and spongy-structure in pure PES was vanished as a result of 3 wt.% vanillin in the cast film. In fact, 3 wt.% vanillin content in dope solution improved the interconnectivity of membrane pore structures, enlarged the finger-like structures, and also almost joined them to the macrovoids at the spongy-structure of bottom layer. However, the suppression of macrovoids when the amount of vanillin content increased from 3 to 6% can be also noticed due to the increase of the viscosity of casting solution, which in turn hampers the instantaneous demixing process. As explained earlier (3.3.1), with regards to membrane thickness at constant CBT of 10 °C, the viscosity of dope solution plays a dominant role and reduces the thickness of the fabricated membranes as it increases due to delay in demixing process. It seems that with further increase of vanillin content to 6 wt.%, the surface becomes more dense and less porous which can be also ascribed to the dominant role of viscosity in lowering the diffusion rate between solvent and non-solvent. These results are in accordance with previous researches demonstrating the effect of poly (vinylpyrrolidone) [31], glycerol [43] and IGEPAL [40] as hydrophilic additives on the morphology of PES, PVDF and PSf membranes respectively.

3.3.2.3. Effects of coagulation temperature bath on membrane morphology. Effects of two coagulation bath temperature (CBT) (0 and 20 °C) at constant vanillin and water content on the morphology

of membrane are demonstrated in Figs. 7 and 8. It is clearly obvious that the number and sizes of finger-like macrovoids increase as CBT increases. It means that the more porous structure can be achieved at higher CBT (20 °C). According to these figures, the thickness of membrane at higher temperature increases at constant vanillin and water content. The abovementioned observations can be attributed to the faster demixing process at higher temperature since the mutual diffusivity between solvent (NMP) and non-solvent (water) is accelerated. Faster demixing of solvent and non-solvent in turn can accelerate the solidification process and thus increase the thickness of membrane as it was discussed in section 3.3.1. The abovementioned observations are in agreement with Saljoughi and Mousavi [40]. Moreover, by comparing Figs. 7 and 8, it can be clearly seen that at constant CBT, the thickness of membrane decreases as vanillin and water content increases, which demonstrates the dominant role of higher viscosity of dope solution in hindering the faster demixing process; a 38.75% increase of dope solution viscosity at 6 wt.% vanillin and 1 wt.% water compared to 3 wt.% vanillin.

3.4. Effect of additives on the wood hydrolysate flux and rejection

The effect of vanillin and water concentration in the dope solution on the permeate flux, fouling and rejection of membrane was studied by filtering wood hydrolysate. Wood hydrolysate was selected because it was shown to foul significantly PES membranes in previous study [2]. Vanillin concentration of 0 and 6 wt.% and coagulation bath temperature of 10 °C was used in the membrane preparation.

As Fig. 9 shows when vanillin was added to dope solution (6 wt.%) the permeate flux (at 50% VRF) improved approximately 40% compared to the membrane without vanillin but the rejections of organic compounds (TOC) or compounds absorbing UV light (mainly lignin) were not changed (Fig. 10). Addition of water (2 wt.%) in the dope solution (no vanillin addition) increased the permeate flux of wood hydrolysate about 12% (Fig. 10) and rejection stayed more or less constant (Fig. 10). By combining addition of water and vanillin to the dope solution (1 wt.% water and 3 wt.% vanillin, Table 1) and by casting the membrane at 10 °C the permeate flux in the filtration of hydrolysate increased about 40% (Fig. 9) and membrane fouling based on the PWF_R decreased almost

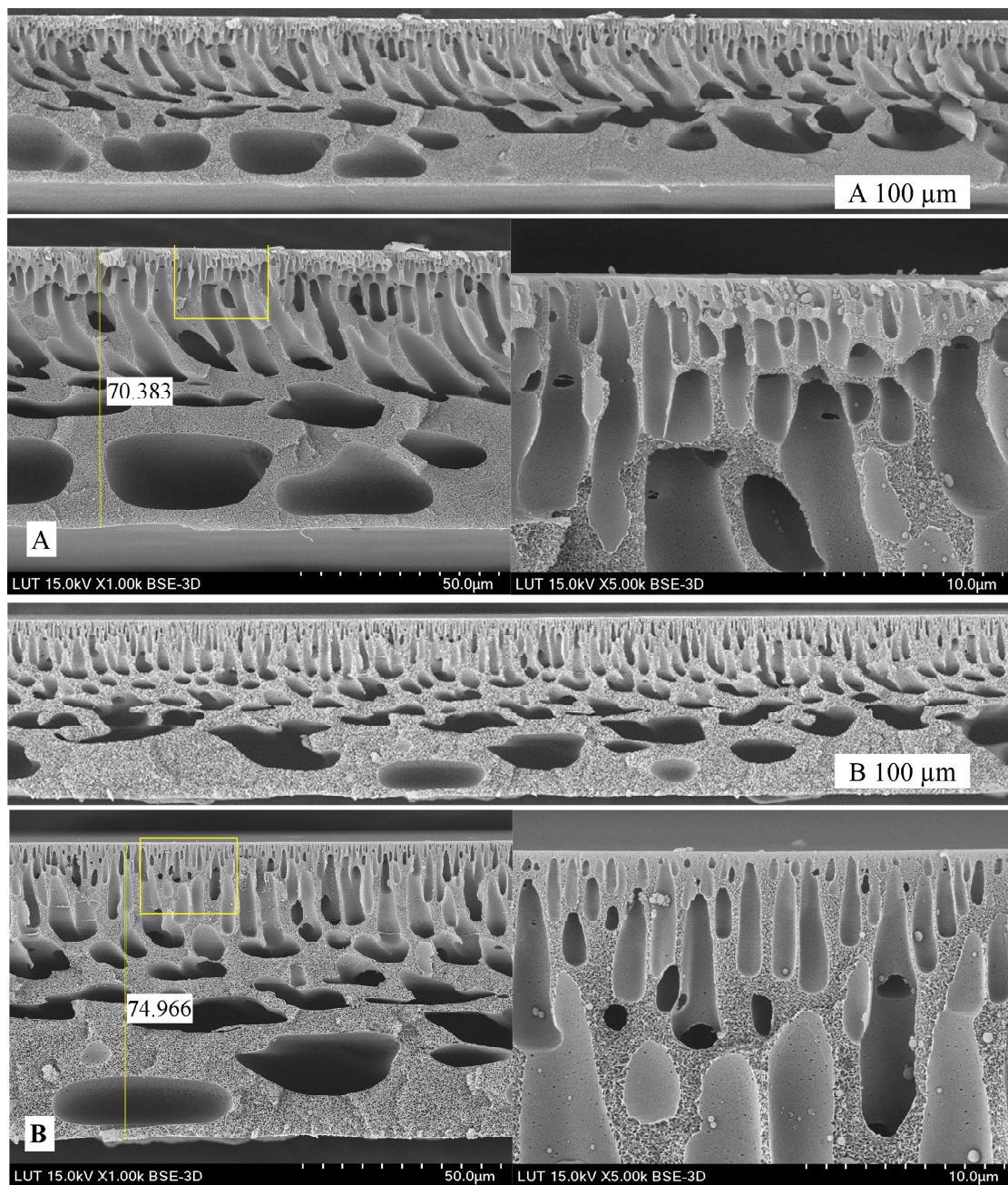


Fig. 7. SEM images of the PES membranes prepared by varying the CBT at 3 wt.% vanillin content without water in 20 wt.% PES/NMP solution:(A) At CBT of 0 °C, (B) At CBT of 20 °C. The cross-sections are on the right and the zoom section of marked top layers are shown on the left.

15% units. The results prove that vanillin had positive effect on the membrane performance. A small quantity of vanillin (3 wt.%) and water (1 wt.%)

can preferably change the membrane morphology and increase the surface hydrophilicity thus lead to formation of membrane with better wood extract

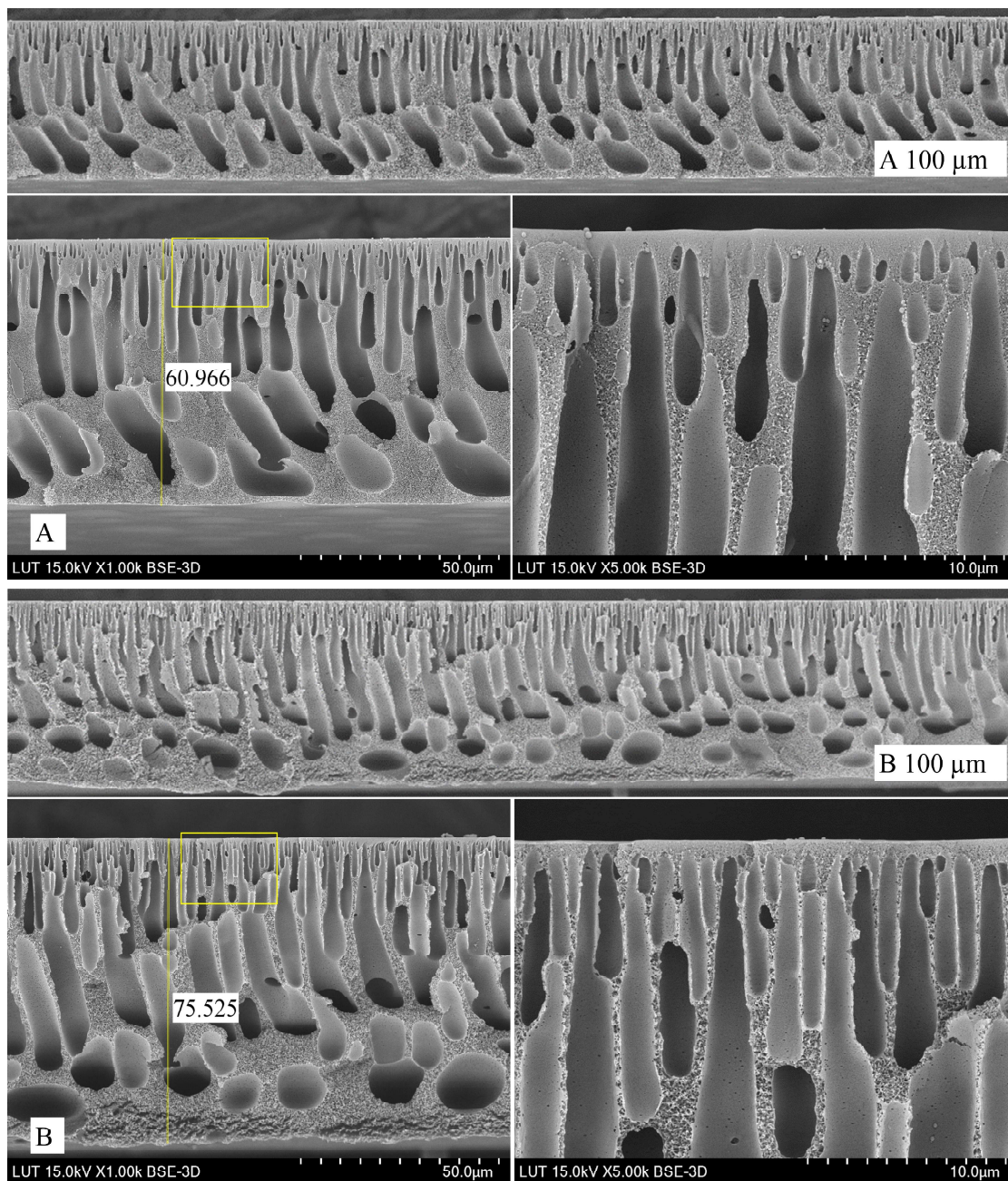


Fig. 8. SEM images of the PES membranes prepared by varying the CBT at 6 wt.% vanillin content and 1 wt.% water content in 20 wt.% PES/NMP solution:(A) At CBT of 0 °C, (B) At CBT of 20 °C. The cross-sections are on the right and the zoom section of marked top layers are shown on the left.

permeability and antifouling characteristics.

The effect of CBT at two levels (0 °C and 20 °C) on the hydrolysate permeance in presence of only

3 wt.% vanillin and 6 wt.% vanillin with 1 wt.% water is presented in Fig. 11.

As the gelation bath temperature increases, the

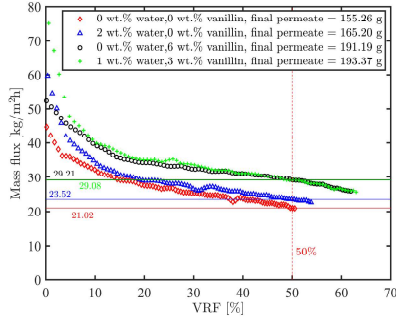


Fig. 9. The effect of vanillin and water on the hydrolysate permeance at constant CBT of 10 °C.

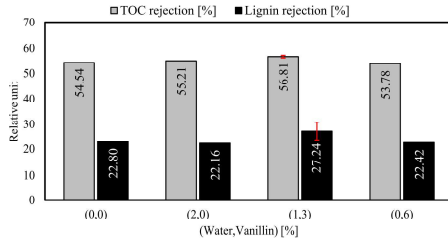


Fig. 10. Effect of water and vanillin on TOC rejection, lignin rejection at constant CBT of 10 °C.

permeate flux at 30% VRF for both higher and lower level of vanillin concentration increases by about 95% and 60%, respectively. In general, as it was discussed in previous sections (3.2.1 and 3.3.1), the faster demixing process at higher temperature accelerates the precipitation process which in turn results in the formation of membrane with more porous structure (7 and 8) and it can consequently increase the permeate flux. Moreover, the results of contact angle measurements are in agreement with the permeate flux behavior and permeate flux at 30% VRF shown in Fig. 11. The contact angle decreased approximately by 18% (at constant 3% vanillin) and 25% (at constant 6% vanillin and 1% water) as CBT increased from 0 °C to 20 °C.

The inverse relationship between permeate flux at 30% VRF and TOC rejection in Fig. 12 can be explained by the trade-off relationship between the CBT and membrane pore structure which was previously stated (section 3.2). This inherent trade-off can be also linked to the viscosity of dope solutions and the results of FTIR analysis. As indicated earlier, at CBT of 0 °C, the vanillin remains inside the cast film due to the lower diffusional motion compared to higher temperature which in turn hin-

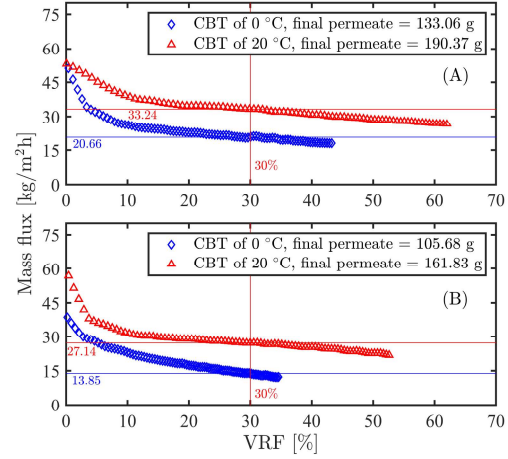


Fig. 11. Effect of CBT on the hydrolysate permeance: (A) 3 wt.% vanillin (B) 6 wt.% vanillin and 1 wt.% water.

ders the demixing process and consequently forms a membrane with denser structure and better rejection characteristic.

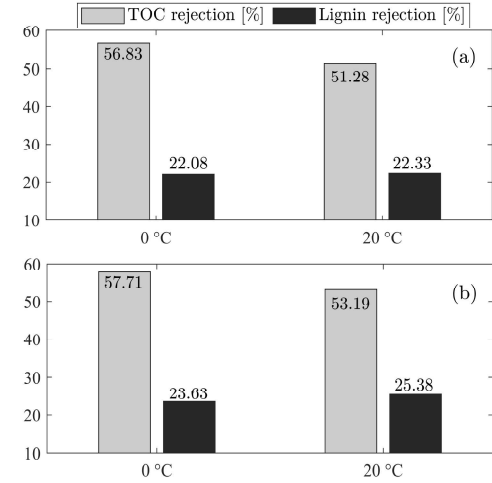


Fig. 12. Effect of CBT on TOC rejection and lignin rejection: (A) 3 wt.% vanillin (B) 6 wt.% vanillin and 1 wt.% water.

At constant CBT, the reduction in permeate flux at 30% VRF and slight increase in TOC and lignin rejection at different vanillin concentrations, presented in Fig. 11 and Fig. 12, can be attributed to the effect of viscosity discussed in section 3.1. As an example, at CBT of 0 °C or 20 °C, the TOC and lignin rejection slightly enhanced and permeate

flux (at t 30% VRF) decreased as vanillin content increased from 3 to 6 wt%. Similar flux and rejection behavior at different concentrations of Tween-20 as a hydrophilic additive by varying the CBT have been observed by Mousavi *et al.* [44].

Overall, these results indicate the combined impacts of hydrophilicity and surface porosity on the hydrolysate permeance and rejection which are connected to the amount of additive and gelation temperature (CBT).

4. Conclusions

This study set out to find some practical membrane-based applications of vanillin as phenolic modifier in which vanillin can minimize the membrane fouling phenomenon by increasing the hydrophilicity of the membrane and by acting as an antifouling agent. The results of this study indicate that vanillin as a hydrophilic additive has substantial roles in the dope solution and membrane morphology which can be classified into several divisions: the suitable amount of vanillin (a) acts as a hydrophilic promoter, (b) acts as pore former, (c) improves interconnectivity of membrane pore structures, and (d) enlarges the finger-like structures (e) preferably increases the viscosity of solution. In general, water as a strong non-solvent additive was applied to achieve the following tasks: reduce the dissolving power of NMP (solvent), increase the viscosity of dope solution, and move the dope solution closer to the binodal curve. The presence of vanillin in membrane structure was confirmed by observable change in FT-IR spectra after modification and was supported by structural changes in SEM images, in contact angle results and in wood extract fouling behavior. It was generally found that a small quantity of vanillin (3 wt.%) and water (1 wt.%) at constant coagulation bath temperature, particularly at CBT of 10 °C, can preferably change the membrane morphology and increase the surface hydrophilicity and thus lead to formation of membrane with better wood extract permeability (40%) and antifouling characteristics. The effect of phenolic antioxidants, such as vanillin, in reducing biofilm formation through quorum sensing mechanism in both feed pretreatment and membrane preparation is currently in the focus of our on-going research.

5. Acknowledgements

The Academy of Finland (Grant no. 292253) is appreciatively acknowledged for the financial support. Mr. Toni Väkiparta is deeply thanked for his assistance in SEM analyses.

References

- [1] L. Puro, M. Kallioinen, M. Mänttari, G. Natarajan, D. C. Cameron, M. Nyström, Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters, *Desalination* 264 (3) (2010) 249–255. doi:10.1016/j.desal.2010.06.034.
- [2] E. Koivula, M. Kallioinen, T. Sainio, E. Antón, S. Luque, M. Mänttari, Enhanced membrane filtration of wood hydrolysates for hemicelluloses recovery by pretreatment with polymeric adsorbents, *Bioresour. Technol.* 143 (2013) 275–281. doi:10.1016/j.biortech.2013.05.129.
- [3] B. Van der Bruggen, Chemical modification of polyethersulfone nanofiltration membranes: A review, *J. Appl. Polym. Sci.* 114 (1) (2009) 630–642. doi:10.1002/app.30578.
- [4] K. C. Khulbe, C. Feng, T. Matsuura, The art of surface modification of synthetic polymeric membranes, *J. Appl. Polym. Sci.* 115 (2) (2010) 855–895. doi:10.1002/app.31108.
- [5] M. Esmaeili, T. Virtanen, J. Lahti, M. Mänttari, M. Kallioinen, Vanillin as an antifouling and hydrophilicity promoter agent in surface modification of polyethersulfone membrane, *Membranes* 9 (4). doi:10.3390/membranes9040056.
- [6] K. Ponnusamy, D. Paul, J. Kweon, Inhibition of Quorum Sensing Mechanism and *Aeromonas hydrophila* biofilm formation by vanillin, *Environ. Eng. Sci.* 26 (8) (2009) 1359–1363. doi:10.1016/S0031-9422(03)00149-3.
- [7] K. Ponnusamy, S. Kappachery, M. Thekeettle, J. H. Song, J. H. Kweon, Anti-biofouling property of vanillin on *Aeromonas hydrophila* initial biofilm on various membrane surfaces, *World J. Microbiol. Biotechnol.* 29 (9) (2013) 1695–1703. doi:10.1007/s11274-013-1332-2.
- [8] L. Katebian, E. Gomez, L. Skillman, D. Li, G. Ho, S. C. Jiang, Inhibiting quorum sensing pathways to mitigate seawater desalination RO membrane biofouling, *Desalination* 393 (2016) 135–143. doi:10.1016/j.desal.2016.01.013.
- [9] L. Katebian, M. R. Hoffmann, S. C. Jiang, Incorporation of Quorum Sensing Inhibitors onto Reverse Osmosis Membranes for Biofouling Prevention in Seawater Desalination, *Environ. Eng. Sci.* (2017) 1–9doi:10.1089/ees.2017.0129.
- [10] R. Sathish Kumar, G. Arthanareeswaran, Y. Lukka Thuyavan, A. Ismail, Enhancement of permeability and antibiofouling properties of polyethersulfone (PES) membrane through incorporation of quorum sensing inhibition (QSI) compound, *J. TAIWAN Inst. Chem. E.* 72 (2017) 200–212. doi:10.1016/j.jtice.2017.01.012.
- [11] T. Virtanen, P. Parkkila, A. Koivuniemi, J. Lahti, T. Viitala, M. Kallioinen, M. Mänttari, A. Bunker,

- Characterization of membrane-foulant interactions with novel combination of Raman spectroscopy, surface plasmon resonance and molecular dynamics simulation, *Sep. Purif. Technol.* 205 (2018) 263–272. doi:10.1016/j.seppur.2018.05.050.
- [12] M. Nyström, L. Kaipia, S. Luque, Fouling and retention of nanofiltration membranes, *J. Membr. Sci.* 98 (3) (1995) 249–262. doi:10.1016/0376-7388(94)00196-6.
 - [13] N. J. Walton, M. J. Mayer, A. Narbad, Vanillin, *Phytochemistry* 63 (5) (2003) 505–515. doi:10.1016/S0031-9422(03)00149-3.
 - [14] M. Sadrzadeh, S. Bhattacharjee, Rational design of phase inversion membranes by tailoring thermodynamics and kinetics of casting solution using polymer additives, *J. Membr. Sci.* 441 (2013) 31–44. doi:10.1016/j.memsci.2013.04.009.
 - [15] F. Siepmann, J. Siepmann, M. Walther, R. MacRae, R. Bodmeier, Polymer blends for controlled release coatings, *J. Control. Release* 125 (1) (2008) 1–15. doi:10.1016/j.jconrel.2007.09.012.
 - [16] C. Causserand, S. Rouaix, J.-P. Lafaille, P. Aimar, Ageing of polysulfone membranes in contact with bleach solution: Role of radical oxidation and of some dissolved metal ions, *Chem. Eng. Process.* 47 (1) (2008) 48–56. doi:10.1016/j.cep.2007.08.013.
 - [17] M. Esmaili, I. Anugwom, M. Mänttari, M. Kallioinen, Utilization of des-lignin as a bio-based hydrophilicity promoter in the fabrication of antioxidant polyethersulfone membranes, *Membranes* 8 (3). doi:10.3390/membranes8030080.
 - [18] N. N. Mohamad Yusof, T. Kobayashi, Efficient separation on vanillin operated with permeability performance of hollow fiber membranes embedded vanillin imprinted polymer particles, *Ind. Eng. Chem. Res.* 52 (47) (2013) 16951–16957. doi:10.1021/ie4029158.
 - [19] S. Kappachery, D. Paul, J. Yoon, J. H. Kweon, Vanillin, a potential agent to prevent biofouling of reverse osmosis membrane, *Biofouling* 26 (6) (2010) 667–672. doi:10.1080/08927014.2010.506573.
 - [20] N. Muñoz-Cazares, R. García-Contreras, M. Pérez-López, I. Castillo-Juárez, Phenolic compounds with anti-virulence properties, in: M. Soto-Hernandez, M. Palma-Tenango, M. del Rosario Garcia-Mateos (Eds.), *Phenolic Compounds*, IntechOpen, Rijeka, 2017, Ch. 8. doi:10.5772/66367.
 - [21] E. Koivula, Enhancement of ultrafiltration process by pretreatment in recovery of hemicelluloses from wood extracts, Ph.D. thesis, LUT University (2016).
 - [22] E. Koivula, M. Kallioinen, S. Preis, L. Testova, H. Sixta, M. Mänttari, Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates, *Sep. Purif. Technol.* 83 (2011) 50–56. doi:https://doi.org/10.1016/j.seppur.2011.09.006.
 - [23] C. Barth, M. Gonçalves, A. Pires, J. Roeder, B. Wolf, Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance, *J. Membr. Sci.* 169 (2) (2000) 287–299. doi:10.1016/S0376-7388(99)00344-0.
 - [24] M. Mulder, *Basic Principles of Membrane Technology*, 2nd Edition, Springer, 1996.
 - [25] A. Idris, K. Y. Lee, H. K. Hing, Preparation of cellulose acetate dialysis membrane for separation of bovine serum albumin, *Jurnal Teknologi* 42 (F) (2005) 35–46.
 - [26] H. Azizi Namaghi, A. Haghighi Asl, M. Pourafshari Chenar, Identification and optimization of key parameters in preparation of thin film composite membrane for water desalination using multi-step statistical method, *J. Ind. Eng. Chem.* 31 (2015) 61–73. doi:10.1016/j.jiec.2015.06.008.
 - [27] S. Y. Fengel, G. Dence, Wood: chemistry, ultrastructure, reactions, 1st Edition, Walter de Gruyter, 1984.
 - [28] D. Lin, C. W. Wegener, *Methods in Lignin Chemistry*, 1st Edition, Springer: Berlin, Heidelberg, 1992.
 - [29] J.-H. Kim, K.-H. Lee, Effect of PEG additive on membrane formation by phase inversion, *J. Membr. Sci.* 138 (2) (1998) 153–163. doi:10.1016/S0376-7388(97)00224-X.
 - [30] B. Torrestiana-Sanchez, R. Ortiz-Basurto, E. B.-D. L. Fuente, Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes, *J. Membr. Sci.* 152 (1) (1999) 19–28. doi:10.1016/S0376-7388(98)00172-0.
 - [31] M. Amirilargani, E. Saljoughi, T. Mohammadi, M. Moghbeli, Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes, *Polym. Eng. Sci.* 50 (5) (2010) 885–893. doi:10.1002/pen.21603.
 - [32] D. Wang, K. Li, W. Teo, Highly permeable polyethersulfone hollow fiber gas separation membranes prepared using water as non-solvent additive, *J. Membr. Sci.* 176 (2) (2000) 147–158. doi:10.1016/S0376-7388(00)00419-1.
 - [33] M. Z. Yunus, Z. Harun, H. Basri, A. F. Ismail, Effects of water as non-solvent additive on performance of polysulfone ultrafiltration membrane, *Adv. Mater. Res.* 488 (2012) 46–50. doi:10.4028/www.scientific.net/AMR.488-489.46.
 - [34] S. Belfer, R. Fainchtain, Y. Purinson, O. Kedem, Surface characterization by FTIR-ATR spectroscopy of polyethersulfone membranes-unmodified, modified and protein fouled, *J. Appl. Polym. Sci.* 172 (1) (2000) 113–124. doi:10.1016/S0376-7388(00)00316-1.
 - [35] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, *J. Membr. Sci.* 327 (1) (2009) 125–135. doi:10.1016/j.memsci.2008.11.025.
 - [36] N. Bolong, A. Ismail, M. Salim, D. Rana, T. Matsuura, Development and characterization of novel charged surface modification macromolecule to polyethersulfone hollow fiber membrane with polyvinylpyrrolidone and water, *J. Membr. Sci.* 331 (1) (2009) 40–49. doi:10.1016/j.memsci.2009.01.008.
 - [37] V. Balachandran, K. Parimala, Vanillin and isovanillin: Comparative vibrational spectroscopic studies, conformational stability and NLO properties by density functional theory calculations, *Spectrochim. Acta, Part A* 95 (2012) 354–368. doi:http://dx.doi.org/10.1016/j.saa.2012.03.087.
 - [38] J. Hu, D. Shen, S. Wu, H. Zhang, R. Xiao, Effect of temperature on structure evolution in char from hydrothermal degradation of lignin, *J. Anal. Appl. Pyrolysis* 106 (2014) 118–124. doi:http://dx.doi.org/10.1016/j.jaap.2014.01.008.
 - [39] R. N. Wenzel, Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem.* 28 (8) (1936) 988–994. doi:10.1021/ie50320a024.
 - [40] E. Saljoughi, S. Mousavi, Preparation and characterization of novel polysulfone nanofiltration membranes for

- removal of cadmium from contaminated water, *Sep. Purif. Technol.* 90 (2012) 22–30. doi:10.1016/j.seppur.2012.02.008.
- [41] W.-I. Cha, S.-H. Hyon, Y. Ikada, Gel spinning of poly(vinyl alcohol) from dimethyl sulfoxide/water mixture, *J. Polym. Sci., Part B: Polym. Phys.* 32 (2) (1994) 297–304. doi:10.1002/polb.1994.090320211.
 - [42] H. Azizi Namaghi, A. Haghighi Asl, M. Pourafshari Chenar, M. Hesampour, A. Pihlajamäki, M. Mänttari, Preparation of thin film composite membrane with emphasis on structure improvement of substrate via water as a strong non-solvent additive, in: *The 4th National Conference on Separation Science and Engineering*, 2017.
 - [43] M. L. Yeow, Y. T. Liu, K. Li, Isothermal phase diagrams and phase-inversion behavior of poly(vinylidene fluoride)/solvents/additives/water systems, *J. Appl. Polym. Sci.* 90 (8) (2003) 2150–2155. doi:10.1002/app.12846.
 - [44] S. M. Mousavi, F. Dehghan, E. Saljoughi, S. A. Hosseini, Preparation of modified polyethersulfone membranes using variation in coagulation bath temperature and addition of hydrophilic surfactant, *J. Polym. Res.* 19 (7) (2012) 9861. doi:10.1007/s10965-012-9861-1.

Supplementary material

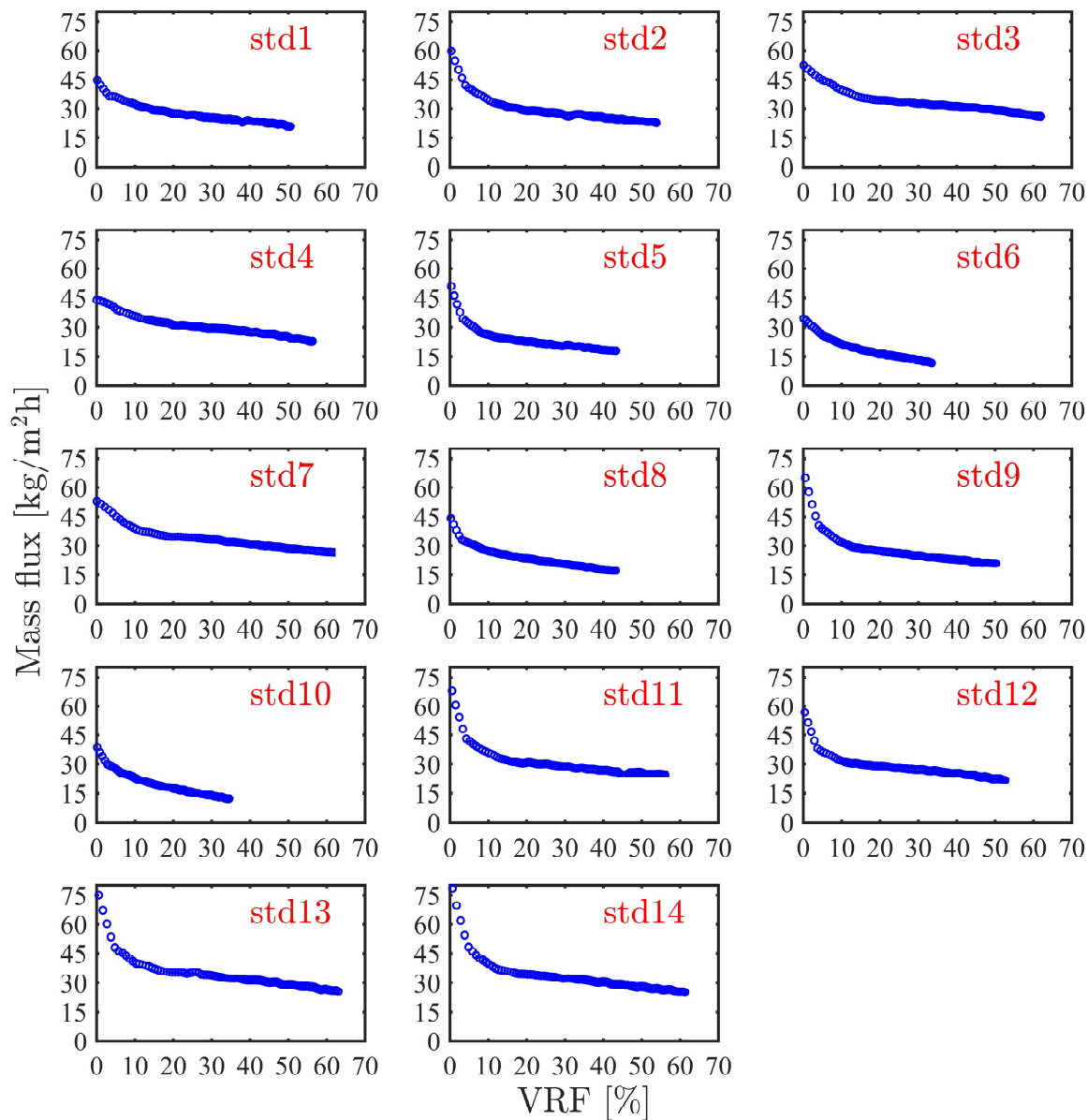


Fig. S1. Wood extract permeance behavior over 90 minutes filtration for all fabricated membranes.

Table S1. TOC rejection, lignin rejection, final collected permeate mass and permeate flux (at 30% and 50% VRF) of all fabricated membranes in wood extract performance.

Std.	TOC rejection [%]	Lignin rejection [%]	Final collected permeate mass [gr]	Permeate flux at 30% VRF [kg/m ² h]	Permeate flux at 50% VRF [kg/m ² h]
1	54.54	22.80	155.26	25.34	21.02
2	55.21	22.16	165.20	26.34	23.52
3	53.78	22.42	191.19	32.43	29.21
4	56.54	21.77	172.24	29.33	25.18
5	56.83	22.08	133.06	20.66	—
6	57.32	23.97	102.26	13.17	—
7	51.28	22.33	190.37	33.24	28.59
8	53.83	21.45	132.10	20.55	—
9	54.79	26.40	152.51	25.02	20.90
10	57.71	23.63	105.68	13.85	—
11	52.63	24.70	172.31	28.58	25.65
12	53.19	25.38	161.83	27.14	22.58
13	56.45	29.68	193.37	33.74	29.08
14	57.17	24.80	187.59	32.08	27.90

Table S2. Comparison of various membrane (PES and PSf) separation processes and their performance in treatment of different hydrolysate in dead-end filtration mode.

Feed Stream	Pretreatment method	Membrane Type	Operating condition	Pure water Flux (kg/m ² h)	Flux of permeate (kg/m ² h) at VRF 1.1	Ref.
Pine hydrolysate	No pretreatment	Commercial UF PES membrane	3 bar at 25°C	62	~3	[5]
Birch hydrolysate	No pretreatment	Commercial UF PSf membrane	5 bar at 55 °C	190	~0	[22]
	pH adjustment				~0	
	Activated carbon adsorption				~13	
	Ethyl acetate extraction				~12–13	
Birch hydrolysate	Prefiltration with RC 70PP membrane	Commercial UF PES membrane	5.5 bar at 60 °C	60–70	~0	[21]
	Oxidation with pulsed corona discharge				~11–13	
	No pretreatment				~2	
Pine hydrolysate	XAD16 adsorbent	Lab-made PES	3 bar at 25 °C	102–167	~24	Current study
	No pretreatment	modified with different concentrations of vanillin and water at different CBT			~21–40	

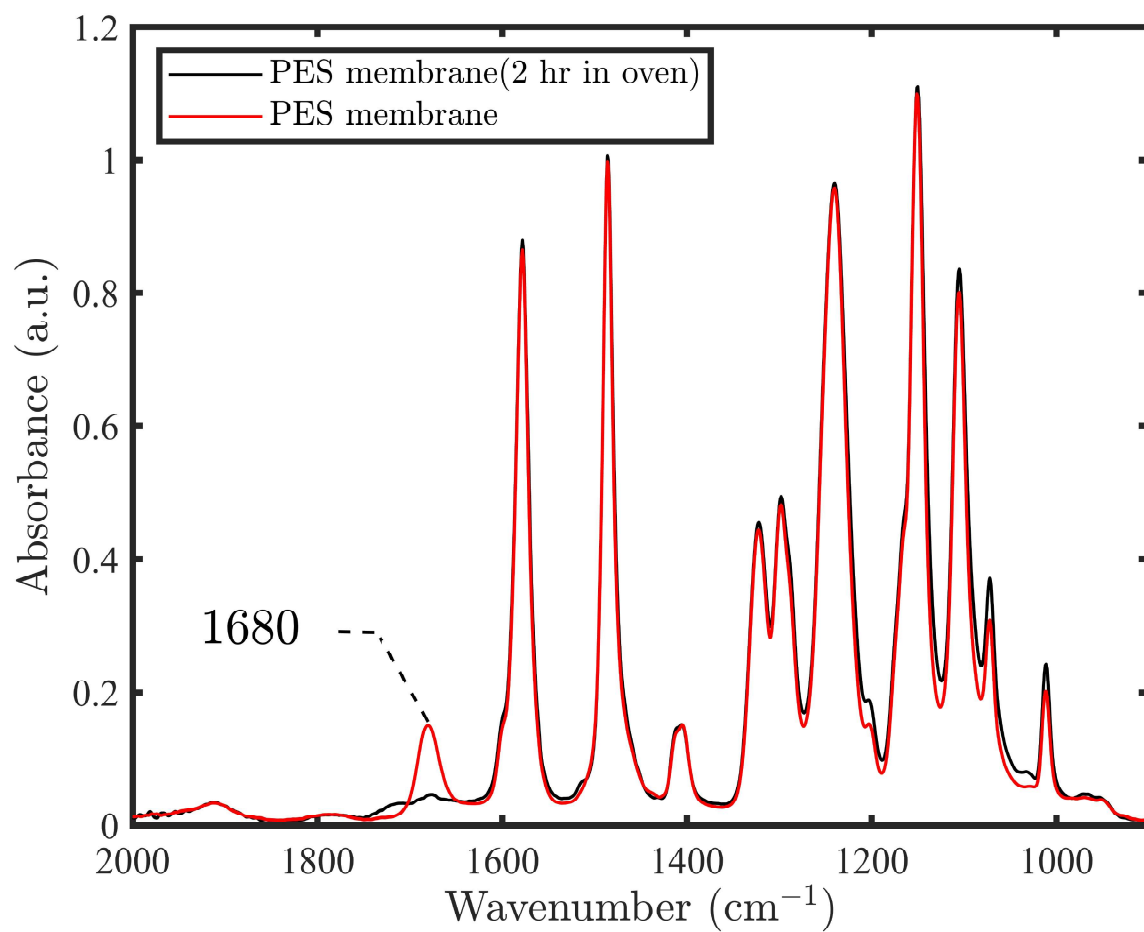


Fig. S2. The presence of carbonyl group at 1680 cm^{-1} as a result of residual NMP in the FTIR spectrum of virgin PES membrane.