

New PES-Praestol 859 UF membranes for hemicellulose purification

T. Hliavitskaya¹, T. Plisko¹, A. Bilydukevich¹, F. Lipnizki², G. Rodrigues^{2,3}, M. Sjölin²

¹ Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, Surganov str. 13, 220072 Minsk, Republic of Belarus (thliavitskaya@gmail.com)

² Department of Chemical Engineering, Lund University, Box 124, 221 00 Lund, Sweden (frank.lipnizki@chemeng.lth.se)

³ Department of Bioengineering, Instituto Superior Técnico, Portugal

Abstract: Novel approach for membrane modification to improve separation performance and antifouling stability was proposed. It involves using of 0.1 - 0.3 % aqueous solutions of Praestol 859 (cationic polyelectrolyte based on copolymer of acrylamide and 2-acryloxyethyltrimethylammonium chloride) as coagulants upon membrane preparation via nonsolvent induced phase separation. It was shown that addition of small amounts (0.1-0.3 %) of Praestol 859 into the coagulation bath leads to the increase in membrane pure water flux from 51 up to 68 L/(m²h) without decreasing membrane retention. Contact angle for modified membranes decreased from 64° down to 55°. Immobilization of Praestol 859 on the surface of a selective membrane layer was confirmed by FTIR spectroscopy. It was found that addition of Praestol 859 into the coagulation bath suppressed the macrovoid formation in the membranes supporting layer due to the decrease of "solvent-non-solvent" exchange rate which is attributed to the significant increase of viscosity of coagulation bath. The separation performance of modified membranes in thermomechanical pulp mill process water fractionating for concentration and purification of hemicellulose for further processing was studied. It was found that membrane modification by Praestol 859 leads to 2-6 times increase of flux, increase of fouling recovery ratio and improvement of cleaning efficiency without decreasing membrane rejection with regard to hemicelluloses (91.5-93 %) and lignin (21-22 %) as reference components.

Key words: polyether sulfone, membrane, modification, ultrafiltration, thermomechanical pulp mill process water, hemicellulose.

1. Introduction

Despite their great potential membrane processes are currently underutilized in the concept of lignocellulosic biorefineries. One potential application for membranes could be the concentration and purification of hemicellulose from process water in thermomechanical pulp mills (ThMP). Hemicellulose has a wide range of potential applications, for example as an oxygen barrier or as a hydrogel (Van Tuil *et al.*, 2000; Hansen and Plackett, 2008). One major challenges of using current *polyether sulfones* (PES) membranes for fractionation of biomass is fouling on the membrane outer and inner surfaces. PES membranes have rather hydrophobic surfaces (Howe and Clark, 2002; Luo *et al.*, 2005) which promote the deposition of dissolved substances on the membrane surfaces or within its pores leading to a decrease in filtration capacity (Xu *et al.*, 2016; Ghiggi *et al.*, 2017; Deng *et al.*, 2008). A possible approach to improve the PES membrane's antifouling performance – is membrane modification in order to increase hydrophilicity and charge as well as to decrease roughness of the membrane selective layer. Adjusting membrane surface properties is known to minimize attractive interactions between the membrane surface and components of the feed which suppresses membrane fouling.

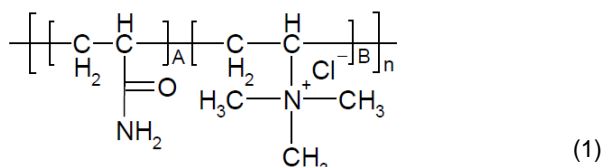
Additive blending - a method when surface-modifying agent is incorporated into a casting solution - is considered to be the most common method to improve separation performance and foulingresistant properties of PES ultrafiltration membranes (Zhao *et al.*, 2013; Miller *et al.*, 2017; Zhu *et al.*, 2018; Liu *et al.*, 2003; Zou *et al.*, 2010). Nanoparticles (Plisko *et al.*, 2018; Sawada *et al.*, 2012) and different polymeric additives (Polyethylene glycol (PEG) (Chakrabarty *et al.*, 2008_a; Chakrabarty *et al.*, 2008_b), polyvinylpyrrolidone (PVP) (Han and Nam, 2002; Lang *et al.*, 2011), commercial PEG and polypropylene glycol (PPG) block copolymers (Pluronic (Susanto *et al.*, 2009; Chen *et al.*, 2009), Tetronic (Wang *et al.*, 2006; Rahman *et al.*, 2008)) and others e.g.

(Shockravi *et al.*, 2017; Li *et al.*, 2010)) are widely used as additives to the membrane casting solution. Another novel approach to improve the performance and to increase antifouling properties of membranes is the addition of hydrophilic polymer to the gelation media (coagulation bath) upon membrane formation via non-solvent induced phase separation (NIPS) (Bilydukevich *et al.*, 2017; Rahimpour *et al.*, 2010; Alsari *et al.*, 2001). It was shown that addition of 5-20 % acrylic acid (AA) and 2-hydroxyethylmethacrylate HEMA in the water coagulation bath upon NIPS leads to a decrease in the pore size and surface roughness of the membrane selective layer (A. Rahimpour *et al.*, 2010). It was reported that a PVP solution was used as a bore fluid in the dry-jet wet spinning process of polysulfone hollow fibers (Bilydukevich *et al.*, 2017). The result was that the addition of PVP had an influence on the membrane structure, performance and antifouling properties. The immobilization of PVP in the inner selective layer of the membrane and not on the outer surface was confirmed by FTIR and contact angle measurements (Bilydukevich *et al.*, 2017). Increasing the concentration of PVP in the bore fluid was found to yield in the formation of a thicker inner skin layer, smoother surface of the skin layer and increased hydrophilicity which resulted in an decrease of the pure water flux, increase of the rejection coefficient and increase of the flux recovery ratio of the hollow fiber membranes. In the case of using polymers as additives to the coagulation bath upon membrane formation in NIPS, membrane modification was the result of mutual diffusion of the components present in the casting solution and coagulation bath (see Fig. 1). The water-soluble polymer is embedded in the membrane structure and fixed in the matrix of the membrane-forming polymer upon polymer precipitation and solidification in NIPS (Bilydukevich *et al.*, 2017). Moreover, the addition of polymer(s) or polyelectrolyte(s) to the coagulation bath yields in changes of kinetics and thermodynamics of phase inversion which resulted in the modifications of the membrane structure. The simplicity of this membrane modification method as well as that only few studies

reported about this modification method is the background for using this approach for membrane modification in this work.

The aim of this research was to study the effect of water-soluble polyelectrolyte additive in water coagulation bath on the structure and properties of PES ultrafiltration membranes, and evaluate the membrane separation and antifouling performance using ThMP process water.

As a polyelectrolyte for membrane modification, cationic polyelectrolyte (PE) Praestol 859 was selected. Praestol 859 is a cationic high-molecular weight polyacrylamide-based flocculant with high content of charged groups (90%), see (1).



The main component of PRAESTOL 859.

Flocculants are widely used for wastewater treatment, for instance, in dissolved air flotations or in combination with clarifiers or microsieves (Rattanapan *et al.*, 2011; Kängsepp *et al.*, 2019). More details on flocculation principles and mechanisms can be found in (Tarleton, 2007). It is expected that introduction of Praestol 859 in the coagulation bath changes the phase inversion kinetics, which then should affect the performance and structure of membranes. The novelty of this study is that a polyacrylamide-based flocculant is used for the first time for membrane modification as an additive to the coagulation bath. The advantages of Praestol 859 is its relative low costs and availability due to its large scale production.

The tests of the modified membrane will be done with reference to lignocellulosic biorefineries. Forest related industries are amongst the most important industries in both Europe and North America. Environmental protection, recovery and valorization of by-products or energy savings are some of the most important reasons for implementing membranes processes in large scale industrial processes (Bokhary *et al.*, 2017).

ThMP process water used in these ultrafiltration trials contains mainly hemicelluloses and lignin. These compounds have a wide range of potential applications

which can lead to an increase in the profits of the industries by producing valuable by-products from what used to be a waste (Bokhary *et al.*, 2017). For example, hemicelluloses could be purified and used for biomedical applications as well as coatings or films for food products (Hansen and Plackett, 2008).

During the development of new types of membranes, with higher performance capacities, it is important that they are able to perform better not only at lab scale but also when using real industrial process streams instead of synthetic feed, and from full-scale applications. Considering the potential value that the pulp and paper industry presents for membrane processes as well as the main challenges it presents, a study was conducted to understand the possible advantages when introducing Praestol 859 in membrane production, regarding flux improvements, fouling impact and cleaning efficiency during and after ultrafiltration (UF), and considering the retention capacities for the main constituents of ThMP – hemicelluloses and lignin.

2. Methods

2.1 Materials

PES (Ultrason E 6020P) was purchased from BASF (Germany). N,Ndimethylacetamide (DMAc, BASF, Germany) was used as the solvent, glycerol (QREC) and polyethylene glycol <Mn> = 400 g/mol (PEG-400, BASF, Germany) were used as non-solvent additives (pore-forming agents) to the casting solutions. Distilled water and 0.1-0.3 % aqueous solutions of Praestol 859 (Ashland Inc., USA) were used as coagulation bath. Praestol 859 is a cationic polyelectrolyte, copolymer of acrylamide and 2-acryloxyethyltrimethylammonium chloride (M_n = (10-14)·10⁶ g/mol, content of charged groups is 90%).

ThMP process water used in the filtering test was provided by Stora Enso (Kvarnsveden Mill, Sweden). This waste stream contains less than 1 % of total solids, mainly hemicelluloses and lignin. Other components such as salts, fibers and extractives are also present. Prior to the test, the process water was stored in a freezer at -18 °C, and a biocide was added to the ThMP water as a preservative, with a 0.1 % . The product used was FennoCide BZ26 (Kemira, Helsinki, Finland).

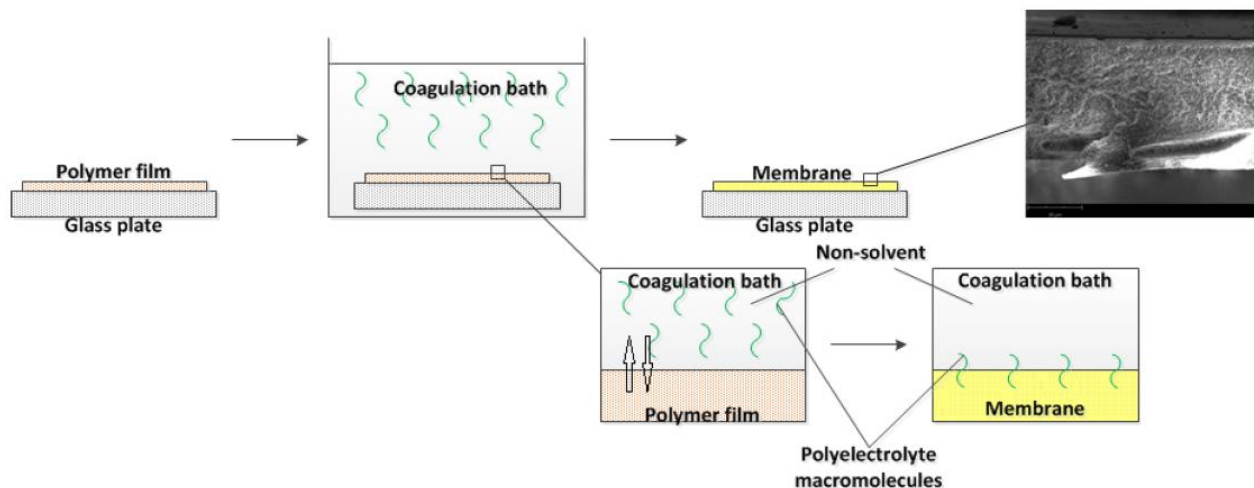


Fig. 1 – Schematic presentation of solvent-nonsolvent mutual diffusion in NIPS process.

Table 1 – Initial composition of the ThMP process water.

Compound	Concentration
Total solids (g/L)	6.4
Hemicelluloses (g/L)	2.01
Total Lignin (g/L)	0.89
Ash (mg/g)	1.22
Acid Soluble Lignin (g/L)	0.11
Klason Lignin (mg/g)	0.54
Turbidity (NTU)	256
Conductivity (mS/cm) at 30°C	1.7

2.2 Membrane preparation

The membranes were prepared by the phase inversion method. The casting solution was prepared by mixing polymer (PES) and pore-forming agents (Glycerol and PEG-400) with solvent (DMAc). Concentration of PES was 22 %, content of glycerol and PEG-400 - 10 % each. The solution was heated to 90 °C and stirred at 400 rpm during 4 hours. The resulting solution was degassed and casted on a glass plate in a uniform thickness of about 200 µm. The glass plates were then immediately immersed into distilled water or Praestol 859 aqueous solution (coagulation bath). Prepared membranes were finally placed in distilled water rinse bath for a 12 h and soaked in 30 % glycerol solution for 3 h before drying.

2.3 Preparation and characterization of gelation media

The coagulation bath aqueous solutions containing Praestol 859 were prepared dissolving Praestol 859 in distilled water. The content of Praestol 859 was varied from 0 up to 0.3 %. Temperature of coagulation bath was 25 °C. Dynamic viscosities of Praestol 859 aqueous solutions were measured using a rotary viscometer (Brookfield DV III – Ultra, Brookfield Engineering Laboratories Inc., USA).

To study the effect of Praestol 859 addition to the gelation media on the thermodynamics of the phase separation of PES solution in DMAc coagulation value (CV) was measured as the amount (g) of the non-solvent needed to cause the phase separation of 100 mL (1 dL) of 1 % PES solution by titration method. CV is the indication of the coagulation power of the non-solvent toward the polymer solution. The CV were determined by titration of 100 ml of a 1 % PES solution in DMAc by distilled water and 0.05-0.3 % Praestol 859 aqueous solutions with constant stirring of the titrated solution on a magnetic stirrer at room temperature. Three different samples of polymer solution were titrated by each non-solvent and the average CV was calculated. The cloud point was recorded if, after 20 minutes of stirring, the solution remained cloudy.

2.4. Membrane characterization

The morphology of the membranes was investigated by scanning electron microscope Phenom Pro (PhenomWorld, Netherlands). Membrane samples were quenched by liquid nitrogen.

The structure of membranes selective layer was studied by atomic force microscopy (AFM, NT - 206,

Microtestmashines, Belarus). Standard silicon cantilevers (NSC35, Mikromasch, Estonia) with a rigidity 3.5 N/m (according to the manufacturer's specification) were used for this study. Contact angle of membrane surface was determined from "membrane–0.02 M NaCl–air" system. The membrane was fixed in 0.02 M NaCl solution in a way that the selective layer was oriented downwards (see Fig. 2). An air bubble with a constant volume (0.01 cm³) was placed to the membrane selective layer by using a special dispenser. Images of the bubble were recorded by a goniometer LK-1 (Open Science, Russia).

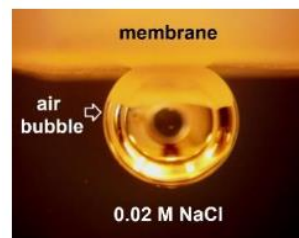


Fig. 2 – Representation of the membrane contact angle measurements from "membrane – 0.02 M NaCl – air" system.

2.5 FTIR analysis

FTIR spectra of membrane surfaces were carried out using Nicolet Is50 spectrometer (Thermo Fisher Scientific, USA). Prior to measurements, the membranes were three times washed with distilled water and dried for 48 h.

2.6 Ultrafiltration experiment

2.6.1 UF set-up

The system used for this study (see Fig. 3) included a 15 L feed tank plus an immersion heater (Baker, Elektro-Varme, Sweden), where temperature was regulated by a control unit (Model MCM, Shinko, Technos Co., Ltd, Japan). Pressure on the system was controlled using two digital pressure valves (DCS40.0AR, Trafag AG, Switzerland) placed on the feed and retentate sides. Adjusting the pressure was possible due to a needle valve placed on the retentate side and the flow was set with a positive displacement pump (Hydra-cell D25XL, Wanner, USA) which was controlled by a frequency converter (ELEX 4000, Bergkvist & Co., AB, Sweden). The crossflow over the membranes was measured using a flowmeter (FCH-34-PP-Chemica, B.I.O-TECH e.K., Germany) placed on the retentate side of the equipment and the permeate fluxes were measured with a scale (PL6001-1, Mettler Toledo Inc., USA) recording weight changes underneath each one of the three parallel flat-sheet modules. The average of the difference in pressure between the retentate and the feed sides is assumed to be the transmembrane pressure (TMP).

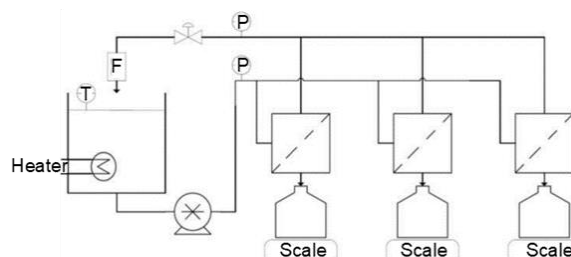


Fig. 3 – Schematic illustration of the experimental set-up for UF experiment.

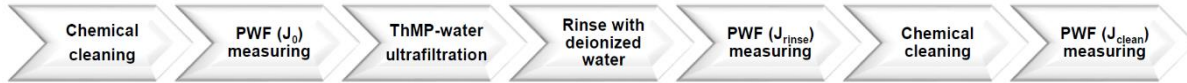


Fig. 4 – Scheme of the ultrafiltration experiment

2.6.2 Ultrafiltration experiment.

Fig. 4 presents the general scheme of the ultrafiltration experiment. All membranes were cleaned for 1 h at 50 °C, before and after ThMP filtration, with a 1 % solution of the cleaning agent Ultrasil 10 (Ecolab, Sweden). During the cleaning procedure, operational conditions at the membrane surface were of 2 bar TMP and a cross flow velocity (CFV) of 0.5 m/s. After each cleaning round and removal of the cleaning solution, the system was rinsed at least 3 times with deionized water to ensure that the complete cleaning agent solution had been removed. Pure water flux (PWF) measurements were conducted after each cleaning cycle. An additional measurement of PWF occurred after the filtration step with ThMP.

For each of the three PWF measurements (initially for cleaned membranes, J_0 , for membranes rinsed with deionized water after ThMP process water ultrafiltration, J_{rinse} , and for fouled membranes that have been chemically cleaned, J_{clean}) the conditions of operation were similar: temperature of 30 °C, CFV of 0.3 m/s and TMP of 1.0, 2.0 and 3.0 bar, and the PWF was evaluated by average permeability.

The ThMP process water ultrafiltration test was performed at 70 °C, with a CFV of 0.3 m/s and TMPs of 1.0, 3.0 and 5.0 bar.

Fluxes were stabilized before starting the logging of the data for both PWF and ThMP filtration. Samples of ThMP permeate were collected while logging and ThMP feed samples were collected immediately after the logging period.

2.6.3 Fouling and cleaning efficiency

Flux recovery ratio after rinsing membranes with deionized water (FRR_{rinse}) and flux recovery ratio after cleaning membranes with Ultrasil 10 (FRR_{clean}) were calculated as a percentage of the initial PWF using the following equation:

$$FRR_{rinse} = \frac{J_{rinse}}{J_0} \times 100 \quad (2)$$

$$FRR_{clean} = \frac{J_{clean}}{J_0} \times 100 \quad (3)$$

2.6.4 Retention Coefficients

Retention or rejection values for each membrane were measured based on the following equation:

$$Retention = \frac{X_{Feed} - X_{Permeate}}{X_{Feed}} \times 100 \quad (4)$$

Retentions values, in percent, were calculated for both hemicellulose and lignin in order to evaluate the membranes retention capacities. X_{Feed} and $X_{Permeate}$ are content of hemicellulose or lignin in the feed and permeate solutions, respectively.

2.7 Analytical methods

All analyses were performed in accordance with the standardized NREL procedure (Sluiter *et al.*, 2008; Sluiter *et al.*, 2012).

2.7.1 Turbidity

Turbidity was measured at 30 °C using a portable 2001P ISO Turbidimeter (Hach Co., USA).

2.7.2 Total solids and ash

Samples were dried in oven at 105 °C for 24 h. The content of total solids was determined as difference in weight before and after drying. After the total solids test, the samples were placed in a furnace, heated until 250 °C at a 10 °C/min gradient and temperature was maintained for 30 min. After this, the temperature was once again increased at a 20 °C/min rate, until the final temperature of 575 °C. This temperature was maintained for 180 min. Ash content was calculated as the difference in weight before and after the ashing procedure.

2.7.3.1 Total Lignin

Total soluble lignin was measured using an UV spectrophotometer (Shimadzu UV spectrophotometer UV-1800, Japan) at 280 nm wavelength and an absorptivity value of 17.8 L/(g cm). Feed and permeate samples were diluted with deionized water prior to the measurements and the system was calibrated using only deionized water. Each sample was measured in triplicates and in between the measurements the plastic vial was rinsed with deionized water. A similar procedure was previously presented in (Örså *et al.*, 1997).

2.7.3.2 Klason Lignin

An acid hydrolysis was performed with both permeate and feed samples collected from the tests, where lignin materials are fractionated into acid soluble and insoluble lignin (Klason lignin). A vacuum filtration step was performed using ceramic filters to separate the soluble lignin from the insoluble forms. The used filters were placed in a 105 °C oven for 24 h and an additional 30 min in the desiccator before and after filtration, and before being weight again. The difference in weight of the filters corresponds to the insoluble lignin found in each sample.

2.7.3.3 Acid Soluble Lignin

After acid hydrolysis and filtration of the hydrolysates, soluble forms of lignin can be measured through UV at a wavelength of 320 nm, in the same spectrophotometer apparatus and using the same procedure as previously describe in section 2.7.3.1. The absorptivity value used for calculations was of 30 L/(g cm), according to the official NREL procedure (Sluiter *et al.*, 2012).

2.7.4 Hemicelluloses

To determine hemicellulose composition in each sample and ultimately retention of hemicellulose for each membrane, an acid hydrolysis was performed on both permeate and feed samples collected during the filtration with ThMP. 1.5 mL of 72 % sulfuric acid was added to 20 ml sample and put in an autoclave (Systec DX-150, Germany), for hydrolysis for 1 h at 120 °C. Hydrolysates were cooled down to room temperature before filtering through ceramic filters to separate acidinsoluble solids. Filtrates were diluted in deionized water and analyzed by high-performance anion exchange chromatography for monosaccharide concentrations in an ICS-3000 (Dionex Corp., USA) chromatography system equipped with a Carbo Pac PA1 analytical column and a pulsed amperometric system. The analysis temperature was 30°C and the injection loop volume was of 10 μ L. The eluent solution composed of deionized water at a flow rate of 1.0 mL/min and the post column eluent addition was of 200 mM NaOH at a flow rate of 0.5 mL/min. The wash eluent solution used was 200 mM NaOH and 170 mM Sodium Acetate. Well-defined sugar solutions of Glucose, Galactose, Arabinose, Mannose and Xylose were used as calibration standards.

3. Results and discussion

3.1 Characterization of gelation medium

Two key factors can influence the structure and performance of polymeric membranes when polymeric additives are added to the gelation medium: (1) increase of casting solution tolerance toward coagulant, and (2) increase of coagulant viscosity. Increase of casting solution tolerance toward coagulant means that more aqueous solution of polyelectrolyte is needed to induce phase separation of the PES casting solution compared to water which is known to be a very strong coagulant for membrane – forming polymers. It is due to the lower activity of the water in the aqueous polyelectrolyte solution and more water bound to hydrophilic polyelectrolyte which results in the milder conditions for polymer film precipitation upon Praestol 859 addition to the gelation medium. From another point of view, the increase in the coagulant viscosity results in the decrease of the “solvent–non-solvent” exchange rate in NIPS upon membrane formation. These two factors are expected to have a significant impact on phase separation of the casting solution which results in the significant change of membrane structure and, hence, membrane performance.

To check the first assumption the coagulation values (CV) of distilled water and 0.05-0.3 % Praestol 859 aqueous solution for 1 % of PES solution in DMAc were determined by titration method. It was found, that CV of distilled water for 1 % PES solution in DMAc is 10.6 g/dL and addition of 0.05-0.3 % Praestol 859 doesn't change CV. Thus, it was revealed that addition of cationic polyelectrolyte to the coagulation bath does not influence the thermodynamics of casting solution phase inversion since the PES casting solution tolerance toward coagulant does not change.

To check the second assumption, the viscosity of the Praestol 859 aqueous solutions was measured. According to Fig. 5a, Praestol 859 aqueous solutions

viscosity was found to be significantly dependent on Praestol 859 concentration. For example, a viscosity of 0.1 % Praestol 859 in solution was found to be 0.27 Pa·s at 25 °C, while a viscosity of 0.2 % Praestol 859 in solution was 1.12 Pa·s and a viscosity of 0.3 % Praestol 859 in solution was 3.62 Pa·s. Thus, it was shown that an increase of Praestol 859 concentration by 3 times resulted in a viscosity increase of 13 times. It is assumed that different viscosities of coagulation bath could also affect the kinetics of phase separation. For this purpose, solutions with different concentrations of Praestol 859 (0.1 and 0.3 %) were selected for membrane preparation. It was established that the viscosity of Praestol 859 solution strongly affects coagulation time – the time from the moment when polymer solution film is immersed into the coagulation bath to the moment until the film is completely separated from the glass plate. Increase in the concentration of Praestol 859 in solutions from 0.1 % up to 0.3 % led to an increase in coagulation time from 7 sec (for 0.1 %) up to 1 min 50 sec (for 0.3 %) respectively. The dependence of membrane coagulation time on the viscosity of Praestol in solution is presented in Fig. 5b. Praestol 859 in solutions with concentrations above 0.3 % were not used, since they were unsuitable due practical considerations related to high viscosity and long membrane formation times.

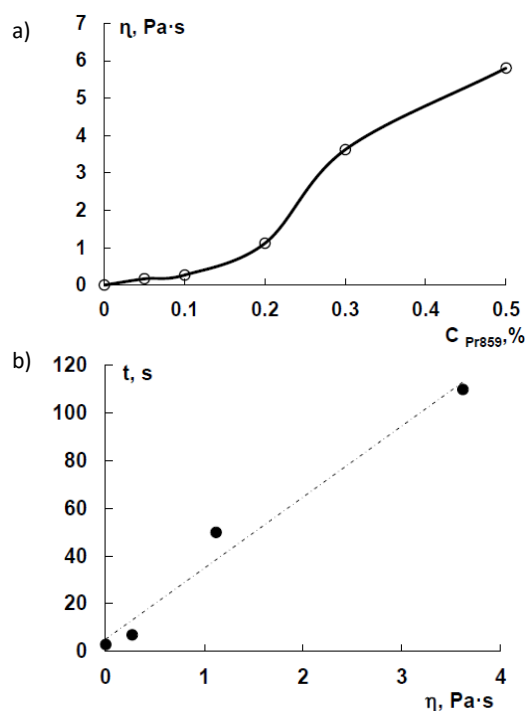


Fig. 5 – (a) Dependence of the viscosity of Praestol 859 in solutions on Praestol 859 concentration; (b) Correlation of time of membrane formation vs viscosity of the Praestol 859 in aqueous solutions as a gelation medium (coagulation bath).

3.2 Characterization of modified membranes

Immobilization of Praestol 859 on the surface of a selective membrane layer was confirmed by the results of FTIR spectroscopy. The FTIR spectra of unmodified membrane surface (distilled water was used as coagulation bath) and surface of membranes prepared by using Praestol 859 aqueous solution as coagulation bath are shown in the Fig. 6. For all samples, the S=O bonds were observed at 1322, 1300 and 1155 cm^{-1} . IR peaks at 1580, 1485 and 1105 cm^{-1} indicated the presence of C=C

bonds of aromatic ring of the PES. Ether bond $-C-O-C-$ was observed at 1245 cm^{-1} . Contrary to the unmodified membrane, on the FTIR spectra of membrane surface prepared by using Praestol 859 in aqueous solution, the presence of an IR peak in the range of $3500-3150\text{ cm}^{-1}$ and a peak at 1670 cm^{-1} appeared. Intensities of these peaks increased with increasing of concentration of Praestol 859 in the coagulation bath. IR peak at 1670 cm^{-1} correspond to $C=O$ bonds from amide group of Praestol 859. Absorbance in the range of $3500-3150\text{ cm}^{-1}$ with the maximum at 3365 cm^{-1} correspond to the NH_2 group of Praestol 859. For comparison, Fig. 6 also shows the spectrum of pure Praestol 859 powder (see Curve 5), which have absorbance at the similar range.

The results imply that there are differences in the composition of the selective membrane layers of the modified and pristine membranes. Thus, it is confirmed that the introduction of Praestol 859 into coagulation bath leads to membrane modifications.

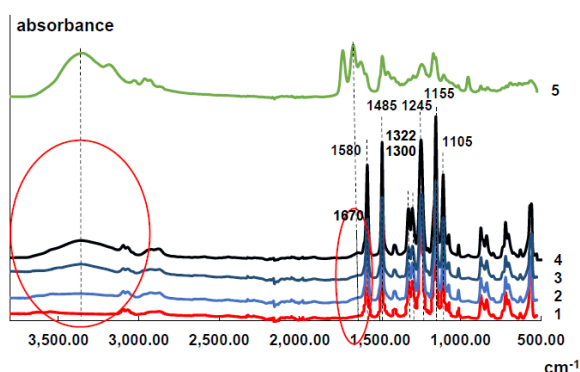


Fig. 6 – The FTIR spectra of the surface of the membrane prepared by using distilled water coagulation bath (1); surface of the membrane prepared by using 0.1 %, 0.2 %, 0.3 % Praestol 859 solution as coagulation bath (2), (3), (4) (respectively) and Praestol 859 powder (5).

3.3 Effect of Praestol 859 on membrane morphology and properties

Fig. 7 presents the results of scanning electron microscopy of the pristine membranes and membranes prepared by using Praestol 859 in solutions as a coagulation bath at $25\text{ }^{\circ}\text{C}$. It was established that the introduction of Praestol 859 into coagulation bath leads to suppression of macrovoid formation in the membrane cross-sectional structure. Several large macrovoids were

detected in the structure of supporting layer (sublayer) of reference PES membrane (see Fig. 7a). The longitudinal size of macrovoids reaches up to $90\text{ }\mu\text{m}$. The formation mechanism of such membrane structures was described in (Radovanovic *et al.*, 1992; Guillen *et al.*, 2011).

It was revealed that the addition of Praestol 859 into the coagulation bath lead almost to the complete disappearance of macrovoids in the structure of the membrane sublayer (see Fig. 7 b, c). Macrovoids pass deep into the supporting layer with sizes below $30\text{ }\mu\text{m}$. The supporting layer of the modified by cationic polyelectrolyte membranes was shown to have well-defined spongy structure. The change of the membrane structure upon Praestol 859 addition to the gelation medium is due to the dramatic increase of the viscosity when cationic polyelectrolyte is added and when its concentration increases (Fig. 5a). Increase of the viscosity yields the substantial increase of membrane formation time which confirms the decrease of the “solvent–non-solvent” exchange rate (Fig. 5a,b). This means that both the rates of coagulant in-diffusion to the as cast polymer film and solvent out-diffusion decrease leading to the delayed demixing mechanism of phase separation which is generally attributed to the macrovoid-free membrane structure formation (Fig. 7).

It is known that macrovoids in the supporting layer are an undesirable phenomenon since under applied pressure this can cause destruction of the membrane (Liu *et al.*, 2003; Holda and Vankelecom, 2015). Therefore, a spongy structure (Fig. 7b, c) is the preferred membrane crosssectional structure.

Fig. 8 shows the AFM images of the pristine and 0.1 % Praestol 859-modified membranes. The bright area indicate the highest point of the membrane surface and dark regions indicate valleys (or structural elements) of the membrane. It was established that introduction of Praestol 859 leads to slight increase in membrane surface roughness. The introduction of Praestol 859 into the coagulation bath leads to an increase in average roughness (R_a) and root-mean-squared surface roughness (R_q). For a $25\text{ }^{\circ}\text{C}$ coagulation bath both R_a and R_q increased from 10.4 to 15.6 nm and 13.9 to 19.8 nm respectively. For membranes which were prepared by using distilled water (reference membranes) as a coagulation bath (Fig. 8a) structural elements are evenly distributed over membrane surface (diameter of valleys does not exceed 200 nm).

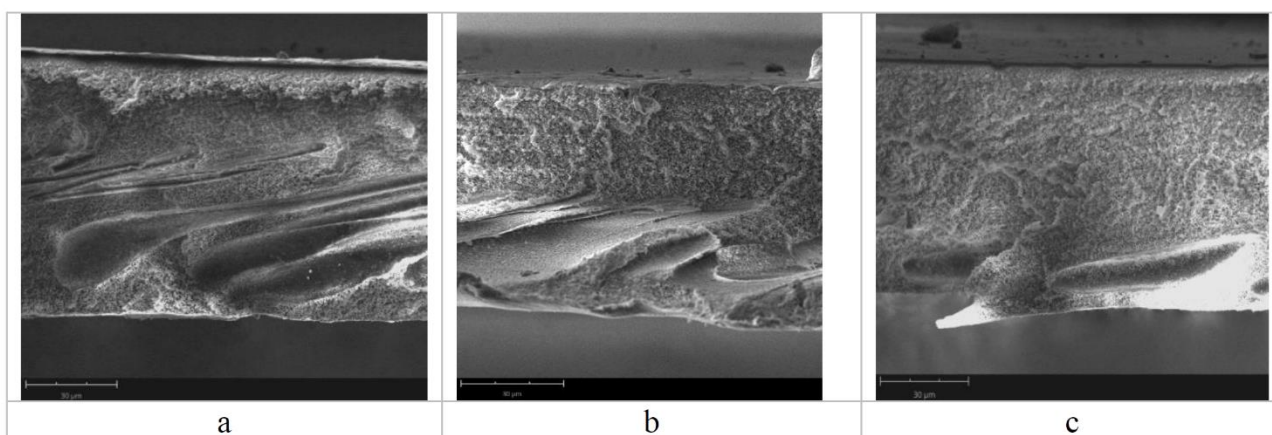


Fig. 7 – SEM images of cross-section structure of PES membranes. Concentration of Praestol 859 in coagulation bath: (a) – 0 %; (b) – 0.1 %; (c) – 0.3 %.

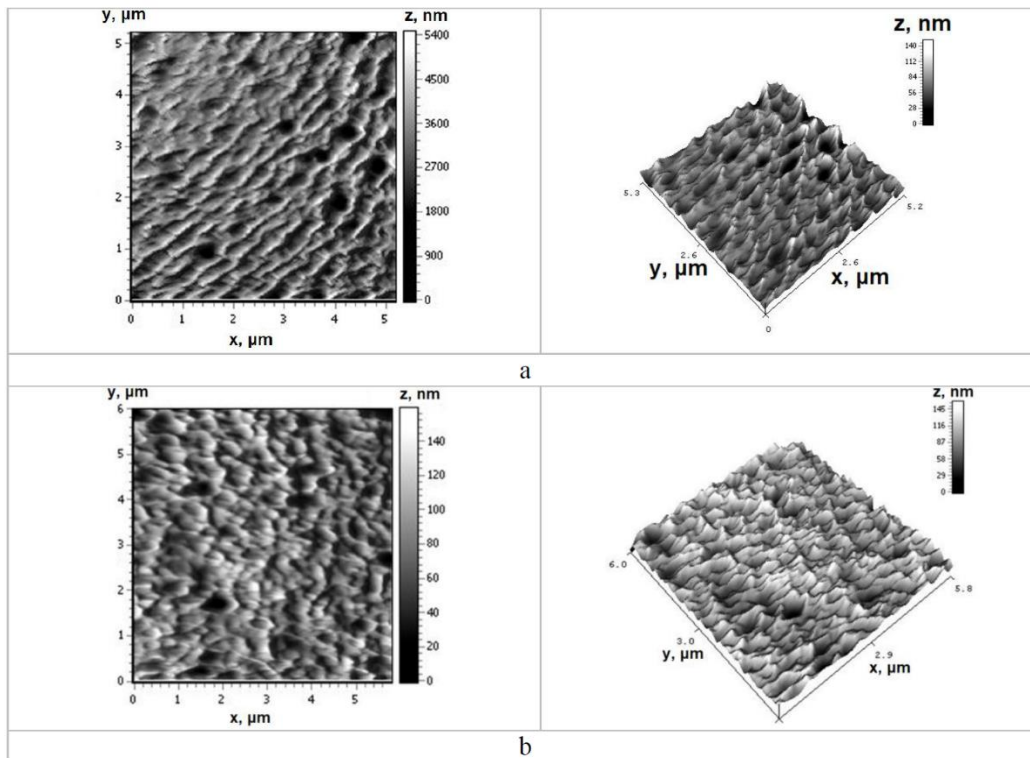


Fig. 8 – AFM images of the surface of the selective layer of membranes. Concentration of Praestol 859 in coagulation bath: (a) – 0 %; (b) – 0.1 %.

Formation of the structure with higher surface roughness upon cationic polyelectrolyte addition to the coagulation bath is due the substantial increase of coagulant viscosity and heterogeneity and decrease of “solvent–non solvent” exchange rate. It yields the formation of larger polymer nodules due to decrease of the rate of phase separation which results in the formation of greater valleys.

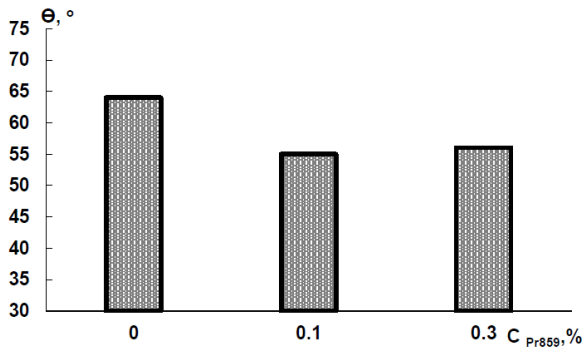


Fig. 9 – Effect of Praestol 859 content in the gelation medium on the membranes contact angle (θ).

The proposed method of modification is effective for increasing the hydrophilicity of the membrane selective layer, as indicated by Fig. 9. It was established that introduction of 0.1% Praestol 859 lead to a decrease in contact angle value from 64° down to 55°. A further increase of Praestol 859 concentration from 0.1 up to 0.3 % did not influence the contact angle value further (55-56). The hydrophilization of the selective layer is due to the presence of hydrophilic NH₂ groups from Praestol 859 involved in hydrogen bond formation which was confirmed by FTIR (Fig. 6). These groups enable the formation of thin layer of water on membrane surface due to hydrogen bonds which results in the increase of the hydrophilicity of the membrane selective layer. Thus, it

was shown that Praestol 859 addition to the gelation medium upon membrane formation via NIPS yields in spongy macrovoid-free structure formation due to the decrease of the “solvent– non-solvent” exchange rate resulting in a dramatic increase of the coagulant viscosity. Praestol 859 immobilization into the selective layer was confirmed by FTIR and leads to the improvement of the hydrophilicity.

3.4 ThMP process water ultrafiltration – PWF, ThMP fluxes and Retentions

The results on the effect of the different concentrations of Praestol 859 on the membranes PWFs are presented in Fig. 9. Comparing PWFs before the filtration with ThMP (J_0), the modified membranes achieve higher fluxes – 58 L/(m² h) (in case of 0.1 % Praestol 859 solutions) and 68 L/(m² h) (for 0.3 % Praestol 859) – compared to the flux of 52 L/(m² h) of the reference membrane. This indicates an increase in PWFs of the modified membranes of 13 % and 32 % respectively, when compared to the reference PES membrane.

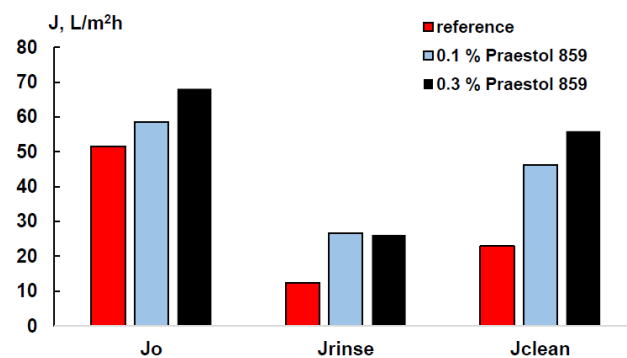


Fig. 10 – Dependence of membrane PWF on the Praestol 859 concentration in coagulation bath.

After the filtration of ThMP and rinsing with deionized water, PWFs (J_{rinse}) of membranes containing Praestol 859 in their composition (for 0.1 and 0.3 % Praestol 859 in the gelation medium) were found to have more than two times higher PWFs than the pristine membrane. This improved performance of the modified membranes is probably due to their enhanced hydrophilicity (see Fig. 8), which also results in less fouling of these membranes (Bokhary *et al.*, 2017).

It can be stated that adding Praestol 859 to the coagulation bath improves the filtration of ThMP process water (see Fig. 11a). Absolute fluxes were more than six times higher for modified membranes than for pristine membrane. During the ultrafiltration of ThMP process water, the transmembrane pressure (TMP) was increased from 1.0 to 3.0 bar and ultimately to 5.0 bar (Fig. 11a). Similar to previous studies by Thuvander *et al.*, 2008a, it was shown for all membranes that an increase in feed pressure leads to an increase in membrane fluxes. ThMP-water fluxes of the modified membranes were superior in flux compared to the reference membrane. Increasing the feed pressure, the difference between the fluxes of the reference and modified membranes increased as well (see Fig. 11a). Fig. 11a presents the dependence of flux vs. TMP for the reference membrane and indicates that critical flux was achieved, and approaching limiting flux region, at 5.0 bar at which irreversible fouling appears, while for the modified membranes, no significant deviation from linearity was

observed, indicating that these membranes may be more resistant to fouling (Bacchin *et al.*, 2006).

The results of retentions (Fig. 11b and 11c) for hemicellulose and lignin are similar for the modified and reference membranes. Hemicellulose retention was revealed to reach 90-93 % for modified polymeric membranes and 93% for the reference, and regarding lignin retention, the reference PES membrane retained 21 %, while retentions for modified membranes were in the range of 21-26 %.

3.5 Antifouling performance

Flux recovery ratios (FRR) of the membranes were calculated in order to better understand the influence of the fouling on the membranes performance. The recovery ratios for the pristine membrane during the ultrafiltration tests were relatively low, both before and after the alkaline cleaning step ($\text{FRR}_{\text{clean}}=43\%$, $\text{FRR}_{\text{rinse}}=24\%$), as shown in Fig. 10. These results support the assumption that the alkaline cleaning step was not efficient enough to remove the majority of the fouling particles attached to the membrane and that another or alternative cleaning treatment step(s) should be considered.

It was shown that modification of the membrane surface with Praestol 859 lead to a significant increase in FRR values. After the ThMP process water filtration, rinsing the system with deionized water and cleaning with the alkaline agent, PWF recovery ratios were between 79 %

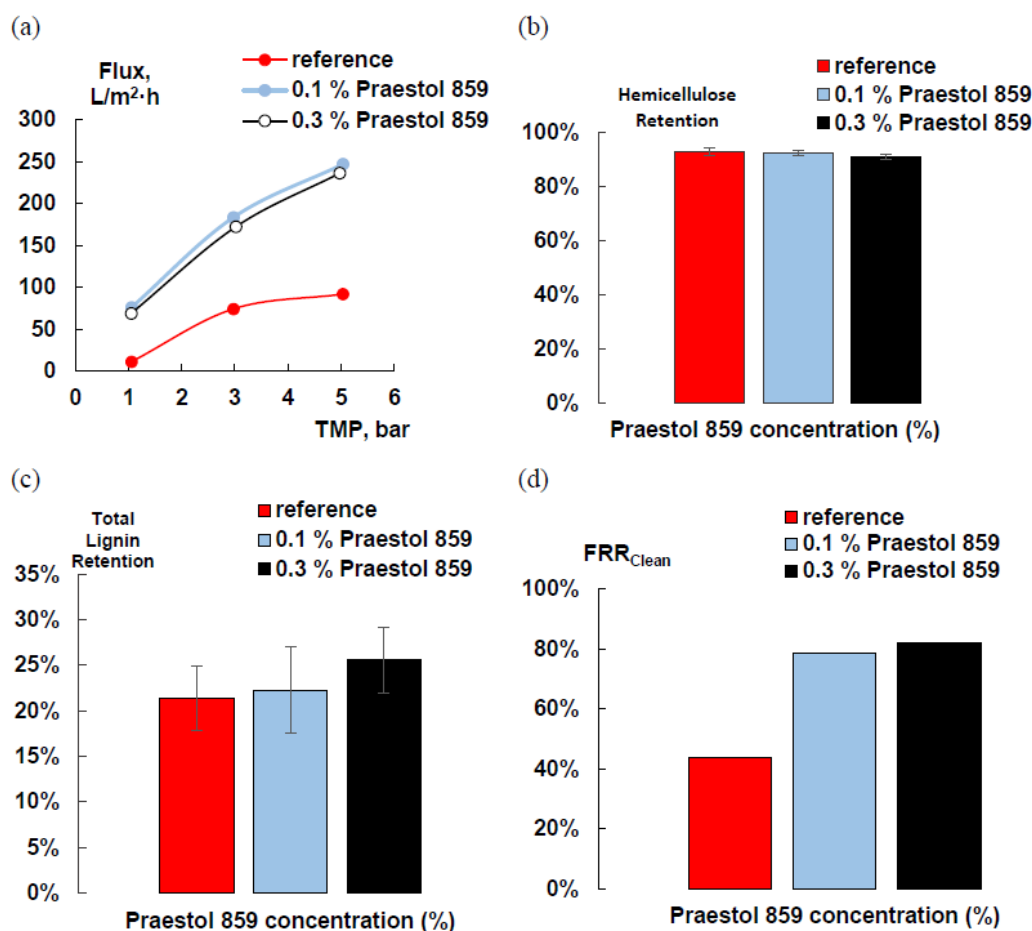


Fig. 11 – (a) Dependence of membrane flux on pressure during TMP test for PES membranes; (b) Hemicellulose retention for PES membranes considering different Praestol 859 concentrations on coagulation bath; (c) Total lignin retention for PES membranes considering different Praestol 859 concentrations on coagulation bath; (d) Fouling parameters of PES membranes.

and 82 % (depending on Praestol 859 concentrations), see Fig. 11d. Additionally, before the cleaning step, FRR were higher for modified membranes – at least 38 % – when compared to the 24 % of the reference membrane, which suggests that Praestol 859 was important for the reduction of fouling during the ThMP filtration.

The FRR results were in line with the FTIR spectrum of the selective layer of the pristine membrane after cleaning (see Fig. 12a). The spectrum of the cleaned membrane after UF of ThMP water showed the presence of one peak in the range of 3500-3100 cm^{-1} . This peak indicates the adsorption of polysaccharides on the membrane surface. Similar confirmation of the fouling in the FTIR spectra of membranes was observed by Thuvander *et al.*, 2018b.

The results obtained for the modified membranes indicate that it was possible to remove a larger part of the foulants from the membrane surface which can be related to the existence of less irreversible fouling. This was confirmed not only by the FRR values of modified membranes (the values of which were given above) but also by the FTIR-results (see Fig. 12). There are no obvious differences between the FTIR spectra of modified membranes (0.1 % Praestol 859) and modified membranes after cleaning after UF ThMP-water (see Fig. 12 b,c), which indicates no major detachments of Praestol from the membrane by the ThMP process water or the alkaline cleaning agent.

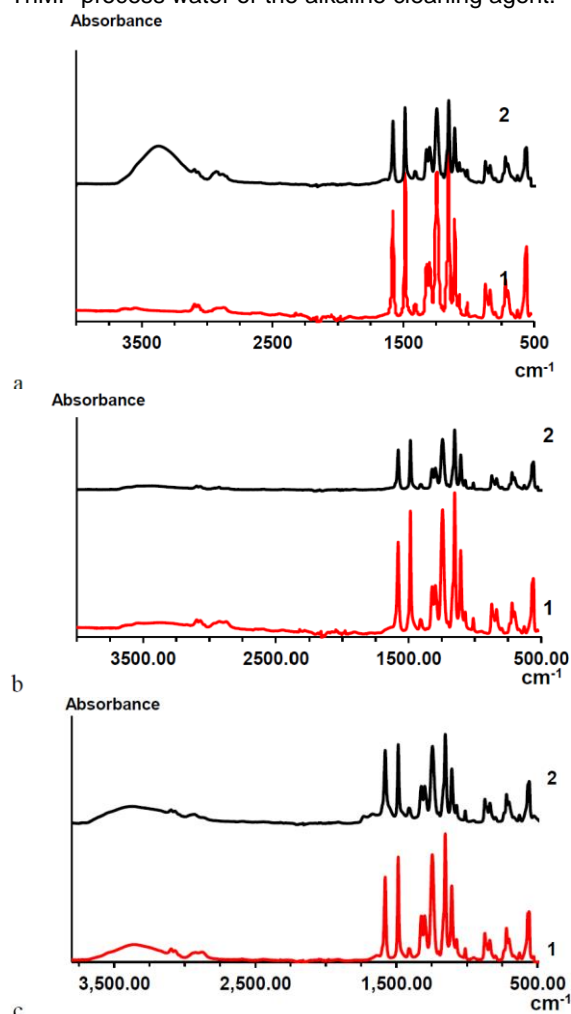


Fig. 12 – The FTIR spectra of: a – pristine membrane (1) and pristine membrane after cleaning after ThMP UF (2); b – surface of membrane modified with 0.1 % Praestol 859 solution (1) and this modified membrane after cleaning after ThMP UF (2); c – surface of membrane modified with 0.3 % Praestol 859 solution (1) and this modified membrane after cleaning after ThMP UF (2).

4. Conclusions

A novel modification method for PES membranes using polyelectrolyte solutions (Praestol 859 in aqueous solution) as a coagulation bath was proposed. It was shown that Praestol 859 addition to the gelation medium upon membrane formation via NIPS yields in spongy macrovoid-free structure formation due to the decrease of the “solvent–non-solvent” exchange rate which is a result of the dramatic increase of the coagulation bath viscosity. Praestol 859 immobilization into the selective layer was confirmed by FTIR and leads to the improvement of the membrane hydrophilicity.

The introduction of 0.1-0.3 % Praestol 859 into the coagulation bath increased the membrane separation performance and reduced membrane fouling, as experimentally shown in the UF of ThMP process water as well as by the FTIR analyses of the membranes before and after UF and cleaning. It was shown that the modified by cationic polyelectrolyte membranes maintained similar retentions compared to the reference membrane. The retention results for hemicelluloses (around 90 %) suggest that this group of membranes is promising for the retention of hemicelluloses from wastewater in addition to the fact that it is possible to purify the hemicelluloses from the lignin as they have very different retentions (21-26 % retention for lignin), meaning that a significant part of the lignin compounds can be recovered from the permeate stream while the hemicelluloses can be mainly recovered and concentrated in the retentate stream.

According to the results obtained in this study it can be concluded that by adding Praestol 859 to the coagulation bath, an increase in both ThMP process water filtration fluxes as well as membrane flux recovery without diminishing the retention values of hemicellulose and lignin can be achieved.

Acknowledgements

The presented extended abstract is a manuscript elaborated from the work developed during this master thesis. The master thesis was part of a joint project of the Membrane Group from the Department of Chemical Engineering, Lund University and the Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus. The project was supported by Belarusian Republican Foundation for Fundamental Research, grant No. X18MC-018.

Literature:

- Alsari, A.M., Khulbe, K.C., Matsuura, T., 2001. The effect of sodium dodecyl sulfate solutions as gelation media on the formation of PES membrane. *J. Memb. Sci.* 188, 279-293.
- Bacchin, P., Aimar, P., Field, R., 2006. Critical and sustainable fluxes: theory, experiments and applications. *J. Memb. Sci.* 281, 42-69.
- Bildyukevich, A.V., Plisko, T.V., Liubimova, A.S., Volkov, V.V., Usosky, V.V., 2017. Hydrophilization of polysulfone hollow fiber membranes via addition of polyvinylpyrrolidone to the bore fluid. *J. Memb. Sci.* 524, 537-49.
- Bokhary, A., Cui, L., Lin, H. J., Liao, B. Q., 2017. A Review of Membrane Technologies for Integrated Forest Biorefinery. *Journal of Membrane Science and Research*, 3, 120-141.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., 2008a. Effect of molecular weight of PEG on membrane morphology and transport properties. *J. Memb. Sci.* 309, 209-221.
- Chakrabarty, B., Ghoshal, A. K., Purkait, M. K., 2008b. SEM analysis and gas permeability test to characterize polysulfone membrane prepared with polyethylene glycol as additive. *J. Memb. Sci.* 320, 245-253.
- Chen, W., Peng, J., Su, Y., Zheng, L., Wang, L., Jiang, Z., 2009. Separation of oil/water emulsion using Pluronic F127 modified polyethersulfone ultrafiltration membranes. *Separation and Purification Technology*, 66, 591-597.
- Deng, B., Li, J., Hou, Z., Yao, S., Shi, L., Liang, G., Sheng, K., 2008. Microfiltration membranes prepared from polyethersulfone powder grafted

- with acrylic acid by simultaneous irradiation and their pH dependence. *Radiation Physics and Chemistry*, 77, 898-906.
- Ghiggi, F.F., Pollo, L.D., Cardozo, N.S., Tessaro, I.C., 2017. Preparation and characterization of polyethersulfone/N-phthaloyl-chitosan ultrafiltration membrane with antifouling property. *European Polymer Journal*, 92, 61-70.
- Guillen, G., Pan, Y., Li, M., Hoek, E., 2011. Preparation and Characterization of Membranes Formed by Nonsolvent Induced Phase Separation: A Review. *Ind. Eng. Chem. Res.* 50, 3798–3817.
- Han, M.-J., Nam, S.-T., 2002. Thermodynamic and rheological variation in polysulfone solution by PVP and its effect on the preparation of phase inversion membrane. *J. Memb. Sci.* 202, 55–61.
- Hansen, N.M.L., Plackett, D., 2008. Sustainable Films and Coatings from Hemicelluloses: A Review. *Biomacromolecules*, 9 (6), 1493-150537.
- Holda, A.K., Vankelecom, I.F.J., 2015. Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes. *J. Appl. Polym. Sci.* 132, 42130.
- Howe, K.J., Clark, M.M., 2002. Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environ. Sci. Technol.* 36, 3571–3576.
- Kängsepp, P., Sjölin, M., Mutlu, A. G., Teil, B., Pellicer-Nàcher, C. First full-scale combined MBBR, coagulation, flocculation, Discfilter plant with phosphorus removal in France. *Water Practice and Technology wpt2019081*.
- Lang, W., Chu, L., Guo, Y., 2011. Evolution of the precipitation kinetics, morphology, and permeation performance of phenolphthalein poly (ether sulfone) hollow-fiber membranes with polyvinylpyrrolidones of different molecular weights as additives. *J. of Appl. Polym. Sci.* 121, 1961-1971.
- Li, L., Yin, Z., Li, F., Xiang, T., Chen, Y., Zhao, C., 2010. Preparation and characterization of poly (acrylonitrile-acrylic acid-N-vinyl pyrrolidone) terpolymer blended polyethersulfone membranes. *J. Memb. Sci.* 349, 56-64.
- Liu, Y., Koops, G.H., Strathmann, H., 2003. Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution. *J. Memb. Sci.* 223, 187-199.
- Luo, M.-L., Zhao, J.-Q., Tang, W., Pu C.-S., 2005. Hydrophilic modification of poly(ether sulfone) ultrafiltration membrane surface by self-assembly of TiO₂ nanoparticles. *Appl. Surf. Sci.* 249, 76 – 84.
- Miller, D.J., Dreyer, D.J., Bielawski, C.W., Paul, D.R., Freeman, B.D., 2017. Surface modification of water purification membranes: a review. *Angewandte Chem.* 56, 4662-4711.
- Örså, F., Holmbom, B., Thornton J., 1997. Dissolution and dispersion of spruce wood components into hot water. *Wood Sci. and Tech.* 31, 279-290.
- Plisko, T.V., Liubimova, A.S., Bilyukovich, A.V., Penkova, A.V., Dmitrenko, M.E., Mikhailovskii, V.Y., Melnikova, G.B., Semenov, K.N., Doroshkevich, N.V., Kuzminova, A.I., 2018. Fabrication and characterization of polyamide-fullerenol thin film nanocomposite hollow fiber membranes with enhanced antifouling performance. *J. Memb. Sci.* 551, 20–36.
- Radovanovic, P., Thiel, S., Hwang, S.-T., 1992. Formation of asymmetric polysulfone membranes by immersion precipitation. Part II. The effects of casting solution and gelation bath compositions on membrane structure and skin formation. *J. Memb. Sci.* 65, 231-246.
- Rahimpour, A., Madaeni, S.S., Mansourpanah, Y., 2010. Nanoporous polyethersulfone (PES) membranes modified by acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA) as additives in the gelation media. *J. Memb. Sci.* 364, 380-388.
- Rahman, N.A., Maruyama, T., Matsuyama, H., 2008. Performance of polyethersulfone/Tetronic 1307 hollow fiber membrane for drinking water production. *Journal of Applied Sciences in Environmental Sanitation*, 3, 1–7.
- Rattanapan, C., Sawain, A., Suksaroj, T., 2011. Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes. *Desalination* 280 (1 - 3), 370-377.
- Sawada, I., Fachrul, R., Ito, T., Ohmukai, Y., Maruyama, T., Matsuyama, H., 2012. Development of a hydrophilic polymer membrane containing silver nanoparticles with both organic antifouling and antibacterial properties. *J. Memb. Sci.* 387, 1–6.
- Shockravi, A., Vatanpour, V., Najjar, Z., Bahadori, S., Javadi, A., 2017. A new high performance polyamide as an effective additive for modification of antifouling properties and morphology of asymmetric PES blend ultrafiltration membranes. *Microporous and Mesoporous Materials*, 246, 24-36.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., and Templeton, D. Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples, Laboratory Analytical Procedure (LAP), Revised January 2008 (2006).
- Susanto, H., Stahra, N., Ulbricht, M., 2009. High performance polyethersulfone microfiltration membranes having high flux and stable hydrophilic property. *J. Memb. Sci.* 342, 153-164.
- Tarleton, E.S., 2007. *Solid/Liquid Separation. Equipment Selection and Process Design*, Elsevier Science.
- Thuvander, J., Arkell, A., Jönsson, A.-S., 2018a. Reduction of energy demand by use of air sparging during ultrafiltration of alkali-extracted wheat bran hemicelluloses. *Chemical Engineering Research and Design*, 138, 43-50.
- Thuvander, J., Zarebska, A., Hélix-Nielsen, C., Jönsson, A.-S., 2018b. Characterization of irreversible fouling after ultrafiltration of thermomechanical pulp mill process water. *Journal of Wood Chemistry and Technology*, 38, 276-285.
- Van Tuil, R., Fowler, P., Laher, M., Weber, C. J., 2000. Properties of biobased packaging materials' in Weber CJ (Ed.), *Biobased Packaging Materials for the Food Industry – Status and Perspectives*, Copenhagen, The Royal Veterinary and Agricultural University, Department of Dairy and Food Science, 13–44.
- Wang, Y. Q., Su, Y. L., Ma, X. L., Sun, Q., Jiang, Z. Y., 2006. Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance. *J. Memb. Sci.* 283, 440–447.
- Xu, C., Liu, X., Xie, B., Yao, C., Hu, W., Li, Y., Li, X., 2016. Preparation of PES ultrafiltration membranes with natural amino acids based zwitterionic antifouling surfaces. *Appl. Surf. Sci.* 385, 130-138.
- Zhao, C., Xue, J., Ran, F., Sun, S., 2013. Modification of polyethersulfone membranes—a review of methods. *Progress in Materials Science*, 58, 76-150.
- Zhu, L., Song, H., Wang, G., Zeng, Z., Xue, Q., 2018. Symmetrical polysulfone/poly (acrylic acid) porous membranes with uniform wormlike morphology and pH responsibility: Preparation, characterization and application in water purification. *J. Memb. Sci.* 549, 515-522.
- Zou, W., Huang, Y., Luo, J., Liu, J., Zhao, C., 2010. Poly (methylmethacrylate–acrylic acid–vinyl pyrrolidone) terpolymer modified polyethersulfone hollow fiber membrane with pH sensitivity and protein antifouling property. *J. Memb. Sci.* 358, 76-84.