PREPARATION OF TWO-LAYER ANION-EXCHANGE POLY(ETHERSULFONE) BASED MEMBRANE: EFFECT OF SURFACE MODIFICATION

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ABSTRACT

The present work deals with the surface modification of a commercial microfiltration poly(ethersulfone) membrane by graft polymerization technique. Poly(styrene-co-divinylbenzene-co-4-vinylbenzylchloride) surface layer was covalently attached onto the poly(ethersulfone) support layer to improve the membrane electrochemical properties. Followed by amination, a two-layer anion-exchange membrane was prepared. The effect of surface layer treatment using the extraction in various solvents on membrane morphological and electro-chemical characteristics was studied. The membranes were tested from the point of view of water content, ion-exchange capacity, specific resistance, permselectivity, FT-IR spectroscopy and SEM analysis. It was found that the two-layer anion-exchange membranes after the extraction using tetrahydrofurane or toluene exhibited smooth and porous surface layer, which resulted in improved ion-exchange capacity, electrical resistance and permselectivity of the membranes.

Key words: poly(ethersulfone) membrane, surface modification, graft polymerization

INTRODUCTION

Separation membranes have become an important part of chemical technology because of their growing industrial applications in the areas of separation and purification processes, biotechnology, nanotechnology and membrane based energy devices. Ion-exchange membranes (IEMs) are among the most advanced types of separation membranes which are generally utilized as an active separator in diverse electrically driven processes. Energy saving, resource recovery and pollution control are the main reasons for development of IEMs. Increasing the efficiency of a membrane is achieved in practice by an improvement of membrane permeability and selectivity at the same time. These two qualities are contradictory from the physical substance, nevertheless, new types of membranes are still being developed shifting the dependence of the selectivity on permeability (Robeson plot) to the upper right. One possibility is the preparation of a structurally modified multilayer membrane based on commercially available polymers [1,2]. The other way represents the utilization of polymer blends, in particular on the basis of a semi-interpenetrating polymer networks [3–5]. In some cases, organic-inorganic hybrid membranes are reported, exhibiting increased physicochemical and electrochemical properties [6,7].

In a study [8] have been studied organic-inorganic hybrid membrane (CEMS) which have been chemically modified in situ polymerization of aniline in an acidic medium using an oxidizing agent such as $FeCl_3$. The presence of the polyaniline (PANI) on the surface and inside the membrane matrix was confirmed by scanning electron microscopy.

In the case of using the multilayer system, different characteristics of each layer are combined; thereby the desired combination of properties can be easily achieved. In the simplest arrangement, a two-layer system composed of the basic support layer and the highly separating surface layer can be applied. The purpose of the carrier layer is usually to ensure sufficient mechanical properties, minimal porosity and sufficient permselectivity, whereas the surface layer should generally provide the maximum transport of ions from solution into the membrane phase, and vice versa. This layer should therefore have the highest possible conductivity. The surface layer can also be used as a separation means, e.g. for a preferential transport of univalent ions from multivalent, or as a means for reducing the impact of fouling [9].

In recent years, the role of surface characteristics in determining the separation properties of membranes is obvious [10–14]. Different methods such as graft polymerization [15,16], plasma modification [17,18], corona discharge, and flame treatment [19] have been utilized in membrane surface modification to alter the physical and chemical properties of membranes without affecting the bulk properties. Huang *et. al.* [20,21] prepared a positively charged nanofiltration (NF) membrane using the ultrafiltration membrane as a support layer, the quartenized chitosan as an active layer by the method of cross-linking. The obtained membrane showed high rejection of $MgCl_2$ and low rejection of Na_2SO_4, and the positively charged characteristic of the NF membranes was demonstrated. Chung et. al. [22–24] crosslinked polyimide substrate with hyperbranched polyethyleneimine and obtained a stably attached layer on the membrane surface showing positively charged surface properties.

In the current research, the surface modification of a commercial microfiltration membrane was carried out to achieve efficient electrochemical properties useful in electrodialysis processes. Two-layer polymeric membranes were composed of a porous poly(ethersulfone) (PES) support layer, which is a commercially available material commonly used for microfiltration and dialysis membrane production; and an anion-exchange surface polymeric layer based on poly(styrene-co-divinylbenzene-co-4-vinylbenzylchloride). Followed by amination, the two-layer anion-exchange membranes (AEM) were prepared. The effect of surface layer treatment using extraction by commonly utilized solvents on morphological and electro-chemical characteristics of the membranes was studied. The membranes were tested from the point of view of water content, ion-exchange capacity (IEC), specific resistance, permselectivity, FT-IR spectroscopy and SEM analysis.

EXPERIMENTAL PART

Materials

PES microfiltration membrane MT, (Synder, USA), divinylbenzene (DVB) (Sigma-Aldrich, purity 80%), styrene (St) (Sigma-Aldrich, purity 99.9%), 4-vinylbenzyl chloride (VBC) (Sigma-Aldrich, purity 90%), benzoyl peroxide (BP) (Sigma-Aldrich, 75% remainder water), tetrahydrofurane (THF), chloroform and toluene (Penta Chemicals, Czech Republic, purity 99.8%), trimethylamine (TMA) (Sigma-Aldrich, 45 wt.% in H_2O).

Surface modification

The surface modification of PES membranes consisted in grafting (Fig. 1) a polymeric surface layer of poly(styrene-co-divinylbenzene-co-4-vinylbenzylchloride) onto a commercial PES membrane support layer. In the first step, the PES membrane was cleaned overnight using distilled water and subsequently dried at 50 °C to constant weight. Then the membrane was immersed in the mixture of monomers (St, DVB and VBC) that were copolymerized in the presence of BP initiator. The reaction proceeded at 80 °C for 5 h. The composition of monomer mixture is listed in Table 1. After that, the morphology of the prepared surface modified membrane was tailored by Soxhlet extraction using different extraction media, namely, THF, toluene, chloroform and distilled water. The extraction was terminated after 72 hours and amination of the surface modified PES membrane was performed for introducing anion-exchange functionalities by using 45 wt.% TMA in H_2O (Fig. 2). The amination proceeded at room temperature for 24 h, followed by conditioning in 1 M NaOH for 24 hours, washing with distilled water and subsequent conditioning in 1 M HCl.

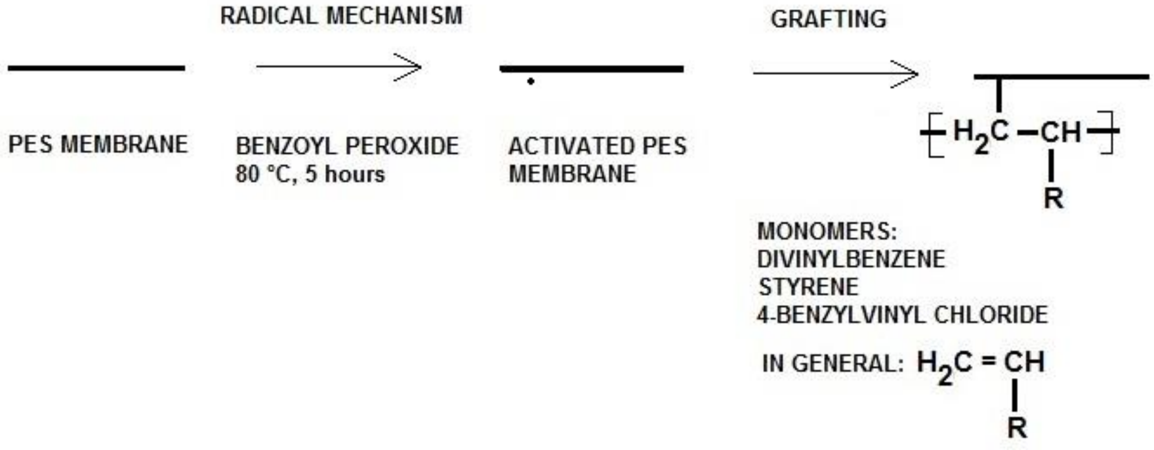

Fig. 1: Radical and grafting mechanism of PES membrane [25].

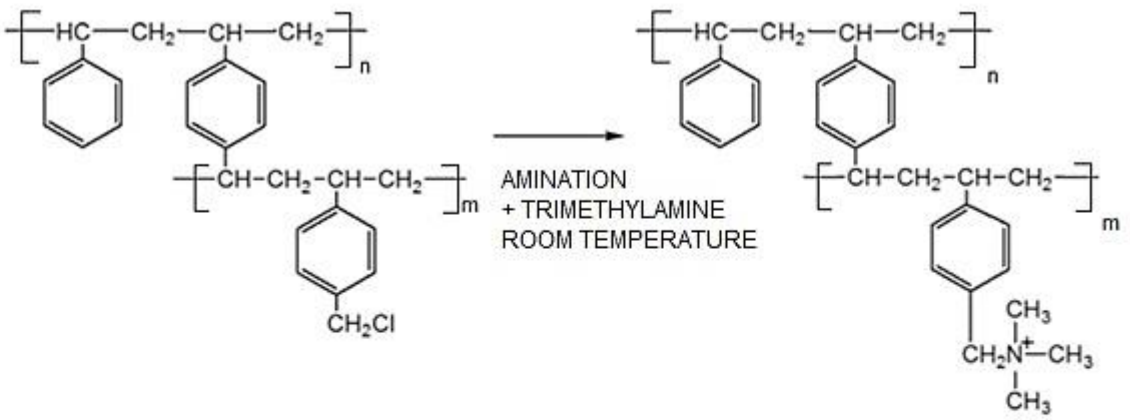

Fig. 2: Amination of poly(styrene-co-divinylbenzene-co-4-vinylbenzylchloride) surface layer using TMA.

Table 1: Composition of reaction mixture for surface modification of PES membrane.

Surface layer	Reaction mixture (wt. %)			
	VBC	DVB	BP	St
1	48.7	16.2	2.6	32.5
2	55.9	4.4	2.9	36.8

Membrane characterization

Morphological studies

The surface morphologies of prepared membranes were examined by scanning electron microscope QUANTA FEG 450 using ESEM mode. The samples were chrome plating.

FT-IR spectroscopy

The membranes were characterized by infrared spectroscopy on a modular instrument IS50 FT-IR (Nicolet companies). The reflective technology ATR (IS50 ATR) equipped with diamond crystal, KBr beam splitter, InGaAs detector 2.6 μm, IR radiation source, HeNe reference laser and linear scan Vectra™ interferometer was used. The resolution was 2 cm^{-1} and the spectrum was integrated from 64 scans. The measurements were performed in the range from 4000 cm^{-1} to 400 cm^{-1}. The resulting spectra were processed using a conversion algorithm ATR correction on the transmission spectrum based on the input data: the angle of incidence of 45°.

Water content and ion-exchange capacity (IEC)

Before measuring the water content, a membrane sample was vacuum-dried at 100 °C until the constant weight was obtained. Then the membrane was left to swell in demineralised water for 12 hours and after wiping the free water with filter paper rapidly and carefully, the membrane was weighed immediately. After conditioning in Cl^- cycles, IEC of an IEM was determined in the following manner: 1 g of the membrane sample was treated with 50 mL of 4% $NaNO_3$ then the sample was left on a shaker for 1 hour at room temperature. Thereafter, for the actual determination, 10 mL of the solution was pipetted and diluted to 30 mL with demineralized water and the sample was titrated with 0.1 M $AgNO_3$ and the equivalence point was determined using K_2CrO_4 indicator. *IEC* of the IEM per gram of dry matter was calculated using the relation (1):

$$\mathrm{IEC} = \frac{\left(\frac{C_{AgNO3} \times V_{AgNO3}}{V^{l}_{NaNO3}}\right) \times V_{NaNO3}}{M} \qquad (1)$$

where V_{AgNO3} is the volume of $AgNO_3$ solution, c_{AgNO3} is the concentration of $AgNO_3$ solution, V^{l}_{NaNO3} is the consumed amount of the solution for titration (10 mL), V_{NaNO3} is the added amount of 0.1 M $NaNO_3$ (50 mL) and m is the weight of dried membrane sample.

Electrical resistance and permselectivity

The electrical resistance is practically important due to its relation with energy consumption in the process. Before the measurement of the specific resistance (R_s) and the areal resistance (R_A) of a membrane, a membrane sample was equilibrated in a solution of 0.5 M NaCl for 24 hours. The resistance was measured at room temperature in 0.5 M NaCl in the test cell using a compensation method. The test cell consisted of two parts which are separated from one another by the IEM sample. Constant direct current of 10 mA was set between interposed platinum electrodes and voltage was measured between reference calomel electrodes at 25 °C. The specific resistance was determined according to the relationship (2):

$$R_s = \frac{\left(U_{IM+sol} - U_{sol}\right)}{I} \cdot \frac{S}{th} \qquad (2)$$

where R_s is the specific resistance of IEM, U_{IM+sol} is the potential of a solution with the embedded IEM sample, U_{sol} is the potential of a solution without inserting IEM sample, I is the direct current, S is the active area of IEM sample of 0.785 cm^2 and th is the thickness of IEM sample.

The areal resistance was determined using the relationships (3,4):

$$R_A = (R_j^{r+r} - R^r)A \qquad (3)$$

$$R_r = \frac{\left|U_{meas}(1,2) - U^r_{as}(2,2)\right|_j + \left|U_{meas}(2,1) - U^r_{as}(2,1)\right|_j}{2I} \qquad (4)$$

where U_{as} is the asymetric voltage and U_{meas} is the measured voltage.

The permselectivity (P) was determined using method of Henderson [26]. Membrane samples were equilibrated in 0.5 M KCl for 24 hours before the measurement. 0.1 and 0.5 M KCl solution were poured into separate parts of the test cell. Permselectivity was subsequently determined according to the relationship (5):

$$P = \frac{U_{meas}}{U_{teor}} \times 100\ (\%) \qquad (5)$$

where U_{meas} is the measured voltage and U_{teor} is the theoretical voltage based on Nernst's law expressed by the relationship (6), with regard to the activity of cations a_{K1}, a_{K2} and anions a_{A1}, a_{A2} in KCl solution presen in separate parts of the test.

$$U_{teor} = -\frac{RT}{2F} \times \ln \frac{a_{K1} \times a_{A1}}{a_{K2} \times a_{A2}} \qquad (6)$$

where R is the universal gas constant = 8.3145 J/mol K,T is temperature (K) and F is the Faraday constant = 96 485 C mol^{-1}.

RESULTS AND DISCUSSION

Surface morphology of two-layer membranes

Two polymeric systems were used as surface modifiers of the commercial microfiltration PES membrane resulting in the preparation of two-layer polymeric membranes. The polymeric systems differed especially in crosslinking density due to different amounts of DVB. The purpose of the support layer formed by PES microfiltration membrane is to ensure mechanical properties as well as good transport properties due to increased porosity, whereas the grafted surface layer should serve mainly as a separation means, providing transport of ions into the membrane phase and ensuring the selectivity of the resulting membrane as well.

To remove unreacted compounds and to tailor the porosity and surface morphology of the grafted copolymer separation layer, the extraction of surface modified two-layer membranes was carried out using different solvents, namely THF, toluene, chloroform and water. It was found that PES membrane integrity remained unaffected after carrying out the extraction in THF, toluene and water, but not all unreacted compounds are supposed to be removed, especially in the case of water extraction, which was demonstrated by gravimetrical measurements (see Table 2). In the case of using chloroform as the extraction media, both the surface layer and the PES support layer were damaged during the extraction process, which was manifested clearly by SEM measurements (Fig. 3, 4).

It is well known that the membrane performance is strongly dependent on its surface and morphology. The effect of extraction treatment on AEMs surface morphology is shown in Fig. 3 and Fig. 4. It is evident that the surfaces of the membranes were changed by extraction treatment. The membranes after the extraction using chloroform exhibited rough and damaged surface (see Fig. 3), whereas the surface structure of AEMs tailored with water, toluene and THF extraction exhibited relatively smooth and uniform character with regularly distributed pores. Thus, assuming that the pores generate easy flow channels for the counter-ion transportation, the two-layer AEM treated particularly by toluene or THF extraction may provide favorable ionic conducting performance with improved electrochemical characteristics and decreased impact on the polarization phenomenon.

Table 2: Effect of extraction treatment using various solvents on the amount of extracted compounds.

Surface on membrane	Extracting solvent	Surface on AEM PES membrane after extraction (wt. %)
1	chloroform	32.99
	water	72.18
	tetrahydrofurane	63.32
	toluene	64.05

2	chloroform	28.16
	water	73.94
	tetrahydrofurane	56.75
	toluene	46.17

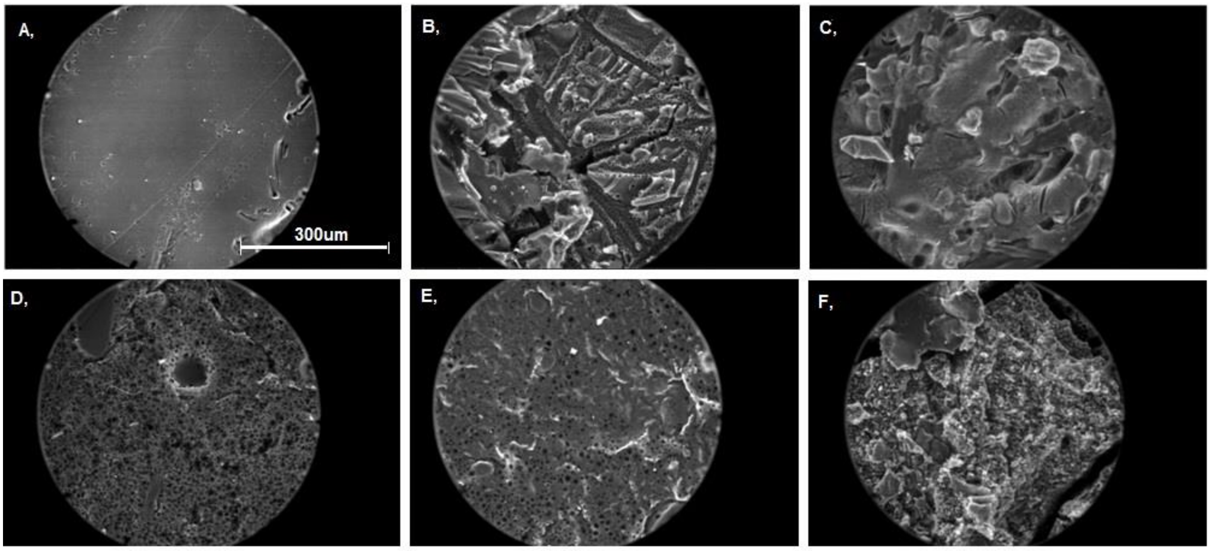

Fig. 3: The SEM surface images (500x magnification) of treated membranes using different extraction solvents: A − PES membrane without modification and extraction treatment, B – AEM coated with surface on membrane 1 after the extraction in chloroform, C - AEM coated with surface on membrane 2 after the extraction in chloroform, D − AEM coated with surface on membrane 1 after the extraction in toluene, E – AEM coated with surface on membrane 2 after the extraction in toluene, F − AEM coated with surface on membrane 1 after the extraction in THF.

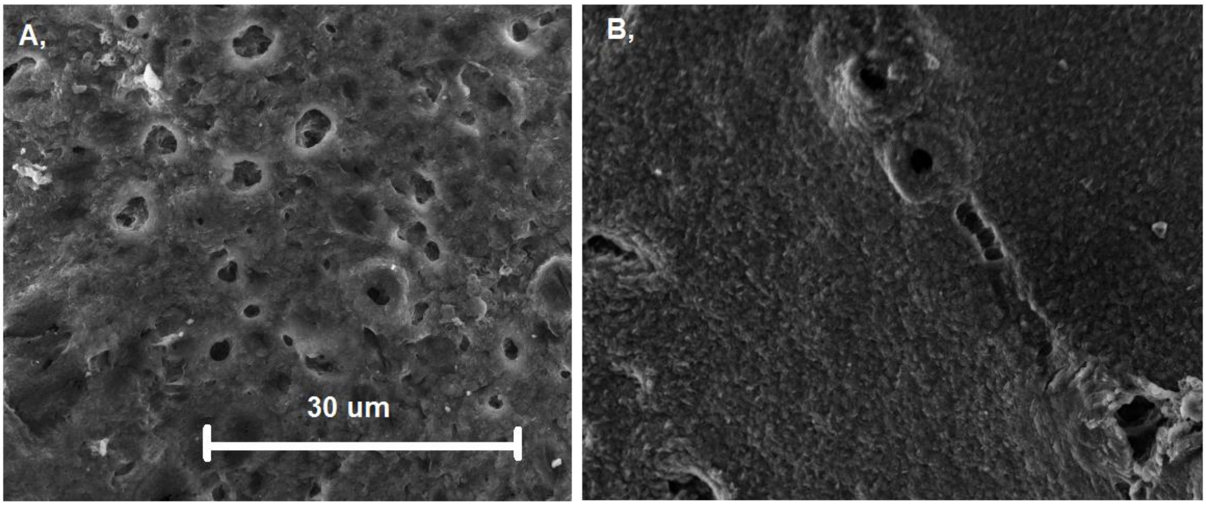

Fig. 4: The SEM surface images (5000x magnification) of treated membranes using different extraction solvents A - AEM coated with surface on membrane 1 after the extraction in THF, B - AEM coated with surface on membrane . after the extraction in THF.

FT-IR spectroscopy was carried out for comparing the PES membrane without modification, the surface modified membrane without amino functionalities and the AEM, the latter two membranes coated with surface on membrane 2 and treated using THF extraction (see Fig. 5). The peaks assigned to aromatic groups were shown at 1630 cm^{-1} and 1490 cm^{-1} and those of quaternary ammonium group at 980, 898 and 812 cm^{-1}. It is evident from the curve corresponding to the AEM that the surface layer containing ion-exchange amino functionalities was covalently grafted on the support PES membrane even after performing THF extraction.

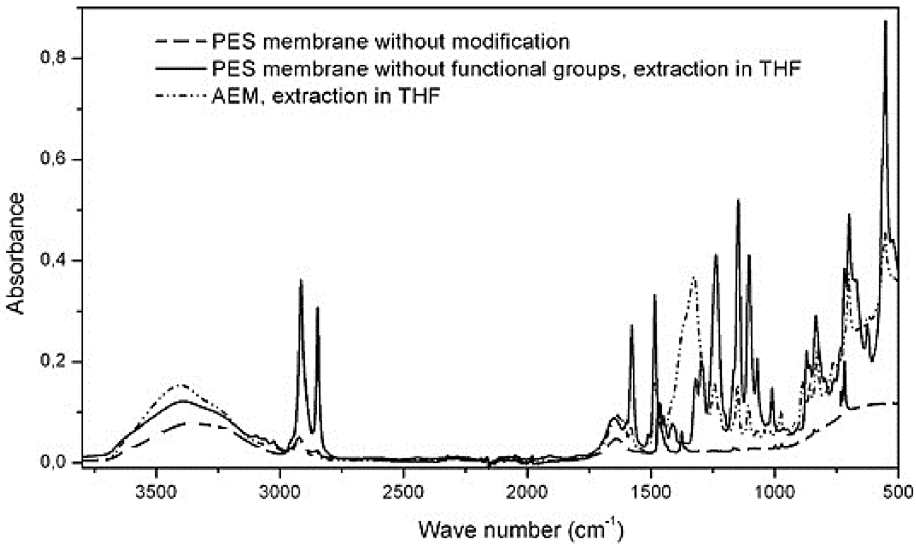

Fig. 5: FT-IR spectra of PES membrane without modification, surface modified PES membrane without amino functionalities and the surface PES AEM, the latter two types of membranes coated with surface layer 2 and treated with THF extraction.

Water content and electro-chemical properties

Determination of water content is of great importance in terms of applicability of the ion-exchange resin. Water assists the transportation of ions from the anode to the cathode. Hence, IEMs should absorb sufficient water, whereas excessive water absorption will induce the loss of dimensional stability and mechanical properties [27]. With a higher water content value, increased conductivity can be expected, which is connected with higher affinity to ions [28].

Table 3 summarizes the results of water content measurements. The lowest values of water content were found in the case of samples extracted with chloroform. As mentioned above, these samples exhibited damaged surface layer as well as the support layer after the extraction in chloroform. When comparing both types of surface layers, the surface layer 1 modified AEMs absorbed lower amounts of water.

The possible explanation of this behavior is the increased crosslinking density of the surface layer 1 copolymer comprising higher amount of DVB units.

To evaluate the functionality of AEMs, IEC was chosen as an evaluative property. The ion-exchange capacity refers to a number of ions that the system is able to bind and it is known to have the profound effects on many important properties of ion-exchange membranes, such as the water swellability [29]. The results of IEC are shown in Table 3. It can be seen that the surface modified AEMs coated with the polymeric layer 1 possessed the highest value of IEC of 1.60 meq/g in the case of performing the extraction in toluene, whereas the lowest value of IEC of 0.79 meq/g was achieved after the extraction using chloroform. For AEMs modified by the polymeric system 2, the maximum value of the IEC of 2.10 meq/g was maintained after the extraction with toluene as well. This fact can be attributed to the presence of pores in the toluene-treated surface layer structure which act as flow channels for the counter-ion transportation. The lowest IEC of 0.80 meq/g was observed in the case of chloroform extraction, which corresponds to the loss of ion-exchange surface layer by chloroform extraction.

Table 3: The results of water content and IEC of anion-exchange hybrid PES membranes.

Surface on membrane	Extracting solvent	Water content (wt.%)	IEC (meq/g dry matter)
1	chloroform	2.4	0.79
	water	9.4	1.59
	tetrahydrofurane	5.1	1.22
	toluene	5.0	1.60

2	chloroform	4.6	0.80
	water	7.4	1.84
	tetrahydrofurane	13.2	1.63
	toluene	11.2	2.10

The electric resistance for surface modified PES membranes without amination and for AEMs (after introducing functional amino groups) was examined (see Table 4). It was shown that all surface modified two-layer membranes without amination exhibited extremely high values of areal and specific resistance (R_A and R_S) in contrast to AEMs, which indicates that the porous PES support layer (exhibiting relatively low electric resistance owing to the porous character) was sufficiently coated with a compact insulating polymer surface layer. After introducing polar amino functionalities, the conductivity of the two-layer modified membranes increased significantly. According to results of electric resistance, the most convenient electric properties were found for the surface modified AEMs coated with the surface layer 2 and treated with THF or toluene extraction. The improved electric properties are probably connected both by the porous character and the increased mobility of the covalently grafted surface layer copolymer (due to lower network density), both phenomena leading to improved ion transport.

Table 4: Ion exchange capacity, areal resistance, specific resistance and membrane thickness averages for the prepared surface modified PES membranes before and after amination.

Surface on	Two-layer membrane without	AEM membrane

membrane	Extracting solvent	amination					
		thickness (μm)	R_A (Ω.cm^2)	R_S (Ω.cm)	thickness (μm)	$R_{A,}$ (Ω.cm^2)	R_S (Ω.cm)
1	chloroform	306	143.93	3378.70	337	2.43	90.00
	water	283	144.39	5102.20	366	13.48	368.20
	THF	284	144.38	5083.90	386	5.20	179.00
	toluene	307	51.04	1254.00	575	11.69	346.90
2	chloroform	307	25.87	842.80	338	0.88	53.00
	water	307	143.78	4683.50	443	3.53	79.60
	THF	325	24.92	797.80	436	1.92	49.00
	toluene	306	144.05	4707.70	445	1.66	38.10
	PES membrane without modification	196	2.53	129.10			

Permselectivity for the two-layer AEMs was investigated as well. Permselectivity indicates the proportion of the charge transferred from the counter ions to the total transferred charge [30]. The results reveal (see Table 5) that after performing chloroform extraction, the membranes exhibited low permselectivity, whereas the surface layer treatment by toluene extraction or THF extraction provided high permselectivity. Low values of permselectivity in the case of AEMs treated with chloroform extraction suggest a significant surface layer removal.

Table 5: Results of permselectivity for two-layer AEMs differing in surface layer type and extraction treatment.

Surface on membrane	Extracting solvent	Permselectivity (%)
1	chloroform	2.4
	water	66.3
	tetrahydrofurane	73.2
	toluene	80.4
2	chloroform	1.1
	water	67.4
	tetrahydrofurane	84.5
	toluene	76.9

CONCLUSION

Two-layer AEMs based on a commercial PES microfiltration membrane were successfully prepared by grafting a polymeric surface layer of poly(styrene-co-divinylbenzene-co-4-vinylbenzylchloride) onto the PES membrane support layer.

The surface morphology of the grafted copolymer separation layer was affected by the extraction using different solvents, namely THF, toluene, chloroform and water. It was shown that the membranes after the extraction using chloroform exhibited rough and damaged surface layer, whereas the surface layer of AEMs treated with THF or toluene extraction was relatively smooth with regularly distributed pores. In contrast to chloroform-treated AEMs, the AEMs comprising THF or toluene-treated surface layer showed improved ion-exchange capacity, electrical resistance and permselectivity, which can be attributed mainly to the presence of pores acting as flow channels for the counter-ion transportation. Thus, the surface layer treatment producing different surface morphology and porosity was shown to play a crucial role in membrane performance and two-layer membranes exhibiting both high permeability and permselectivity, can be successfully prepared by tailoring the surface layer porosity. These membranes can find their application in electrodialytic processes.

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REFERENCES

[1] Meng Wang, Xun-liang Wang, Yu-xiang Jia, Xu Liu, An Attempt for improving electrodialytic transport properties of a heterogeneous anion exchange membrane, Desalination, **2014**, 351, 163–170.

[2] Xun-liang Wang, Meng Wang, Yu-xiang Jia, Bei-bei Wang, Surface modification of anion exchange membrane by covalent grafting for imparting permselectivity between specific anions. Electrochimica Acta, **2015**, 174, 1113–1121.

[3] Y. Mizutani, Structure of ion exchange mebranes, J. Membr. Sci., **1990**, 49, 121–144.

[4] G. Pozniak, W. Trochimczuk, Tubular interpolymer ion exchange membranes, Angew. Makromol. Chem., **1984**, 127, 171–186.

[5] S. S. Madaeni, S. Amirinejad, M. Amirinejad. Phosphotungstic acid doped poly(vinyl alcohol)/poly(ethersulfone) blend composite membranes for direct methanol fuel cells. *Journal of Membrane Science*, **2011**, 380(1–2), 132–137.

[6] Y. Song, X. Cao, Q. Liang. Sulfonated polyimides and their polysilsesquioxane hybrid membranes for fuel cells. *Solid State Ionics*, **2014**, 258(5), 92–100.

[7] H. Beydaghi, M. Javabakht, A. BadieiI. Cross-linked poly(vinyl alcohol)/sulfonated nanoporous silica hybrid membranes for proton exchange membrane fuel cell. Journal of Nanostructure in Chemistry. **2014**, 4(2), 4:97.

[8] M. Kumar, M.A. Khan, Z.A. Alothman. Polyaniline modified organic–inorganic hybrid cation-exchange membranes for the separation of monovalent and multivalent ions. Desalination, **2013**, 325(16), 95–103.

[9] Z. Yong, Y. Sanchuan, G. Congjie, F. Xianshe, Surface modification on thin film composite polyamide membranes by electrostatic self deposition of polycations for improved fouling resistance. Sep. Purif. Technol, **2009**, 66, 287–294.

[10] Z. Xu, J. Wang, L. Shen, D. Men, Y. Xu, Micro porous polypropylene hollow fiber membrane. Part 1. Surface modification by the graft polymerization of acrylic acid. J. Membr. Sci, **2002**, 196, 221–229.

[11] D.R. Lloyd (Ed.), Material Science of Synthetic Membranes, ACS Symposium Series 269, American Chemical Society, Washington, DC, **1985**, (Chapter 1).

[12] W.R. Bowen, N. Hilal, R.W. Lovitt, C.J. Wright, Characterization of membrane surfaces: direct measurement of biological adhesion using an atomic force microscope, J. Membr. Sci., **1999**, 154, 205–209.

[13] S.M. Hosseini, B. Rahzani, H. Asiani, A.R. Khodabakhshi, A.R. Hamidi, S.S. Madaeni, A.R. Moghadassi, A. Seidypoor, Surface modification of heterogeneous cation exchange membranes by simultaneous using polymerization of (acrylic acid-

co-methyl methacrylate): Membrane characterization in desalination process, Desalination, **2014**, 345, 13–20.

[14] R. Ibanez, D.F. Stamatialis, M. Wessling, Role of membrane surface in concentration polarization at cation exchange membranes, J. Membr. Sci., **2004**, 239,119–128.

[15] S.S. Madaeni, S. Zinadini, V. Vatanpour, A new approach to improve antifouling property of PVDF membrane using in situ polymerization of PAA functionalized TiO_2 nanoparticles, J. Membr. Sci., **2011**, 380, 155–162.

[16] P. Daraei, S.S. Madaeni, N. Ghaemi, H. Ahmadi Monfared, M.A. Khadivi, Fabrication of PES nanofiltration membrane by simultaneous use of multi-walled carbon nanotube and surface graft polymerization method: comparison of MWCNT and PAA modified MWCNT, Sep. Purif. Technol., **2013**, 104, 32–44.

[17] S.M. Hosseini, S.S. Madaeni, A.R. Khodabakhshi, Preparation and surface modification of PVC/SBR heterogeneous cation exchange membrane with silver nanoparticles by plasma treatment, J. Membr. Sci., **2010**, 365, 438–446.

[18] S.M. Hosseini, S.S. Madaeni, A. Zendehnam, A.R. Moghadassi, A.R. Khodabakhshi, H. Sanaeepur, Preparation and characterization of PVC based heterogeneous ion exchange membrane coated with Ag nanoparticles by (thermal-plasma) treatment assisted surface modification, Journal of Industrial and Engineering Chemistry, **2013**, 19, 854–862.

[19] C.M. Chan, Polymer Surface modification and Characterization, Hanser (Carl), Munich, **1994**.

[20] S.U. Hong, R. Malaisarny, M.L. Bruening, Optimization of flux and selectivity in Cl^-/SO_4^{2-} separations with multilayer polyelectrolyte membranes. J. Membr. Sci., **2006**, 283, 366–372.

[21] M.C. Martí-Calatayud, D.C. Buzzi, M. García-Gabaldón, A.M. Bernardes, J.A.S. Tenório, V. Pérez-Herranz, Ion transport through homogeneous and heterogeneous ion-exchange membranes in single salt and multicomponent electrolyte solutions, J. Membr. Sci., **2014**, 466, 45–57.

[22] T. Kikhavani, S.N. Ashrafizadeh, B. van der Bruggen, Nitrate selectivity and transport properties of a novel anion exchange membrane in electrodialysis, Electrochim. Acta, **2014**, 144, 341–351.

[23] M. wang, Y.X. Jia, T.T. Yao, K.K. Wang, The endowment of monovalent selectivity to cation exchange mebrane by photo-induced covalent immobilization and self-crosslinking of chitosan, J. membr. Sci., **2013**, 442, 39–47.

[24] W.J. Tong, Y.Ch. Gao, H. Mohwald, Poly(ethyleneimine) macrocapsules: glutaraldehyde-mediated assembly and the influence of molecular weight on their properties. Adv. Polym. Technol., **2008**, 19, 817–823.

[25] M. M. Nasef, E. S. Hegazy, Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films, Prog. Polym. Sci. **2004**, 29 (4), 499–561.

[26] Cui W., Kerres J., Eigenberger G. Development and characterization of ion-exchange polymer blend membranes. Sep. Purif. Technol., **1998**, 14, 145–154.

[27] Shuangling Zhong, Xuejun Cui, Sen Dou, Wuncong Liu. Preparation and characterization of self-crosslinked organic/inorganic proton exchange membranes. Journal of Power Sources, **2010**, 195, 3990–3995.

[28] H. Strathmann. Electrodialysis and related processes, in: R.D.Nobe, S.A. Stern (Eds.), Membrane Separation Technology-Principles and Applications, Elesevier Science B.V., **1995**, 214–278.

[29] A. Navarro, C. Rio, J.L. Acosta. Pore-Filling Electrolyte Membranes Based on Microporous Polyethylene Matrices Activated with Plasma and Sulfonated Hydrogenated Styrene Butadiene Block Copolymer. Synthesis, Microstructural and Electrical Characterization. Journal of Polymer Science Part B: Polymer Physics, **2008**, 46(16), 1684–1695.

[30] T. S. Sørensen, M. Dekker, Surface Chemistry and Electrochemistry of Membranes, New York, **1999.**