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Non-laminated ion-exchange membranes

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ABSTRACT

Presence of reinforcing fabric noticeably increases mechanical properties of ion-exchange membranes, but at the expense of difficult membrane manufacturing and higher cost. All non-laminated ion-exchange membranes have limited mechanical strength including higher dimension changes during swelling. Heterogeneous ion-exchange membranes are commonly made from low-density polyethylene (LDPE) which is easily processable, but this LDPE cannot be used for non-laminated membranes due to extreme composite brittleness. Replacing LDPE by linear low-density polyethylene (LLDPE) the non-laminated membranes become more elastic, but their mechanical properties are still poor and also their use is limited. Polypropylene (PP) generally has much higher mechanical strength, higher temperature resistance and lower creep behavior in comparison with LDPE or LLDPE. Due to immiscibility of PP with polyethylene (PE), their blends are limited only for composites with lower filler content. For increasing PP flexibility the propylene-based elastomers (PBE) are very good alternative to PP/PE blends. Mechanical and electrochemical properties of anion-exchange non-laminated membranes prepared from LDPE, LLDPE, polypropylene random copolymer (PPR), PBE and blend of PPR with PBE were compared in this article. Due to expected higher mechanical properties of PPR-based composites, the non-laminated membranes were prepared also with increased ion-exchange resin content. It was proved that PPR-based non-laminated membranes have higher tensile strength even for membranes with increased ion-exchange resin content. It was also proved that by increased PBE content, the elongation increases at the expense of decreasing modulus.

Keywords: Non-laminated ion-exchange membrane; Polypropylene composite; Propylene-based elastomer

1. Introduction

Ion-exchange membranes must have good electrochemical properties, sufficient mechanical properties and low cost. The main issue for ion-exchange membranes is the compromise between electrochemical and mechanical properties. Increasing concentration of ion-exchange groups leads to dramatical decrease of mechanical properties for both homogeneous and heterogeneous membranes due to increasing water content. Therefore, in many cases the reinforcing fabric is incorporated, but at the expense of difficult membrane manufacturing and higher cost. But for some application non-laminated ion-exchange membranes are used, for example, electrodeionization or electrodialysis (ED) with bipolar membranes [1]. The lamination is limited for ion-exchange hollow fibers, but for some application, like diffusion dialysis, they could have some benefit in comparison with flat sheet membranes similar as hollow fiber for filtration processes [2].

Heterogeneous ion-exchange membranes are commonly made from low-density polyethylene (LDPE), which is easily

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processable, but this polyethylene (PE) cannot be used for non-laminated membranes due to extreme composite brittleness. Replacing LDPE by linear low-density polyethylene (LLDPE) or metallocene-type linear low-density polyethylene (mLLDPE), the membrane brittleness can be reduced, and therefore, the membranes can be prepared without additional fabric support. However, the mechanical properties of these membranes are still poor, and therefore, their use is limited [3]. The main limitation is low modulus and tensile strength, which causes high-dimensional changes during swelling and cutting, stack building and also ED due to temperature and ion concentration changes.

High-density polyethylene (HDPE) and polypropylene (PP) have much higher mechanical strength and temperature resistance, and especially PP has lower creep behavior [4] in comparison with LDPE or LLDPE. Due to limited miscibility of PP with PE, their blends are limited only for composites with lower filler content [5,6]. For increasing PP flexibility the propylene-based elastomers (PBE) are very good alternative to PP/PE blends. Similarly, the ethylene-based elastomers can be used for increasing flexibility of LDPE, LLDPE or HDPE.

PP has other important advantage. It is not affected by environmental stress cracking [7]. In swollen membrane the polymer binder is continuously tensile stressed, which leads to internal crack in long term. Some solutions may speed up this cracking, which in general decreases membrane life.

Main objective of this work is to prove benefits of using polypropylene random copolymer (PPR) or PPR/PBE blends as a good alternative to PE binders for heterogeneous non-laminated ion-exchange membrane.

2. Experimental setup

2.1. Materials

Electrochemical and mechanical properties of prepared anion-exchange membranes were investigated in this article. Strong anion-exchange resin Suqing 201x4 Cl and several types of polymers were used for this purpose. Table 1 shows typical properties of selected polymers. Producers did not guarantee these values, and therefore, it can be used only for basic selection and classification. Due to random copolymerization of PPR, it generally has lower melting temperature (around 140°C–150°C), tensile modulus and higher elongation at break (more than 200%) in comparison with homopolymer or impact copolymer PP. Higher elasticity and lower melting temperature of PPR seem to be more promising for membrane preparation than for rigid PP homopolymer or impact copolymer. Low melting temperature is necessary to avoid temperature degradation of anion-exchange resin.

2.2. Membrane preparation

Anion-exchange resin was washed, dried below 2 wt% of humidity and milled below 50 μm with median at ~15 μm. Then the resin was kneaded with different polymers by twin-screw kneader module PTW24/28 of Thermo Scientific HAAKE PolyLab OS modular system at 160°C and screw speed 60 rpm. Only PPR-1 was kneaded at 180°C due to low melt flow index (MFI) and high melting point, which increased torque and die pressure in comparison with PE and PBE with similar MFI but with much lower melting temperature. The feed rate for polymer was set to 1 kg/h and for anion resin to 1.5 kg/h (60 wt% of anion resin). PPR mixture was also prepared with 65 wt% of anion resin by increasing feed rate of resin up to 1.857 kg/h. Extruded strand was cooled by conveyor belt and cut to 2 mm length granules.

Prepared granulates were extruded by single-screw extruder Rheomex 19/25 module of the same PolyLab OS device. Flexible die with 10 cm width was used for extrusion. The die gap was set to produce membrane foil with thickness around 0.4–0.5 mm. The temperature of extrusion was set to 140°C–160°C in the ramp (for PPR-1 150°C–160°C), and the screw speed was 60 rpm. The membrane foil was extruded between the rolls of three-roll haul-off unit. The rolls were heated up to 80°C. The gap between two rolls and their speed was set to reach final thickness between 0.4 and 0.5 mm.

Finally, the membrane foils were pressed in hydraulic press ZHOT60MT from Presshydraulika (Czech Republic) for 5/2 min (preheating/press) at the temperature 160°C and the pressure 25 kg/cm^2. Samples were cooled below 60°C before removing from the press. Rapid cooling and uncontrollable force between the rolls during extrusion cause uncontrollable crystallization and morphology changes, creating some defects on the foils. Therefore, the heat pressing and cooling at controlled conditions are necessary.

2.3. Membrane characterization

The following basic membrane properties were analyzed: thickness of dry and swelled membrane, dimensional changes during swelling, electrochemical properties (resistance and

Table 1
Typical properties of used polymers (data from product data sheets)

Polymer	Density (g/cm^3)	Melting temperature (°C)	MFI[a] (g/10 min)	Tensile modulus[b] (MPa)	Elongation at break[b] (%)
LDPE	0.924	111	6.5	220	120
LLDPE	0.924	124	20	240	570
mLLDPE	0.918	117	2	160	590
HDPE	0.956	130	20	925	>100
PPR-1	–	–	2	1,050	–
PPR-2	–	–	45	1,100	–
PBE	0.888	107	2	359	680

[a] For PE at 190°C, and for PP or PBE at 230°C.

[b] Different methods and specimen are used for different polymers or grades.

permselectivity) and also mechanical properties of swelled membrane (modulus, ultimate stress and ultimate strain).

Dimensional changes during swelling were analyzed according to own internal methods where sample dimension and weight of dry and swelled membranes were measured.

Both electrochemical resistances (areal R_A and specific R_S) of investigated membranes were determined by a standard potentiometric compensation method [8]. The electrochemical resistance for compensation method was calculated by the following Eqs. (1)–(4):

$$R_j^s(\Omega) = \frac{\left|U^s_{meas.}(1,2) - U^s_{as}(1,2)\right|_j + \left|U^s_{meas.}(2,1) - U^s_{as}(2,1)\right|_j}{2I} \tag{1}$$

$$R_j^{s+m}(\Omega) = \frac{\left|U^{s+m}_{meas.}(1,2) - U^{s+m}_{as}(1,2)\right|_j + \left|U^{s+m}_{meas.}(2,1) - U^{s+m}_{as}(2,1)\right|_j}{2I} \tag{2}$$

$$R_{A,j}\left(\Omega\cdot cm^2\right) = \left(R_j^{s+m}(1) - \bar{R}^s\right)A_m \tag{3}$$

$$R_{S,j}(\Omega.cm) = \frac{R_{Aj}}{Th_j} \tag{4}$$

where R_j^s is resistance without membrane; R_j^{s+m} is resistance with membrane; R_{Aj} is area resistance of membrane; $U_{\text{meas.}}$ is measured potential under the current; U_{as} is asymmetric potential measured without applied current; A_m is active sample area; Th_j is sample thickness; index s is the solution; index m is the membrane; and index j is the solution type. The (1,2) and (2,1) are the mean sequence of saturated calomel electrode. The 0.5 M NaCl was used for measurement. In Fig. 1, there is scheme of measuring cell including real cell with a galvanostat.

Permselectivity (or transport number) is determined by using the same cell as for electrochemical resistance but without applied electric current. The principle of this static method is based on Henderson's equation which determines the transport number under diffusion [9]. The experimental cell is separated into two parts by ion-exchange membrane. Every part contains a solution with different concentration. For measurement the 0.1 and 0.5 M KCl solution and silver chloride reference electrode were used at 25°C. Eqs. (5) and (6) were used for permselectivity calculation:

$$E_{M\ theor}(V) = -\frac{RT}{zF}\cdot\ln\left(\frac{\gamma^2_{\pm,1}\cdot m^2_{S,1}}{\gamma^2_{\pm,2}\cdot m^2_{S,2}}\right) \tag{5}$$

$$P(\%) = \frac{E_{M\ meas}}{E_{M\ theor}}\cdot 100\% \tag{6}$$

where $\gamma_\pm$ is activity coefficient; m_s is the molality of solution 1 (0.1 M KCl) and solution 2 (0.5 M KCl); R is the universal gas constant; T is the temperature in K; z is the ion charge number; F is the Faraday constant; E_M is the theoretical or measured membrane potential.

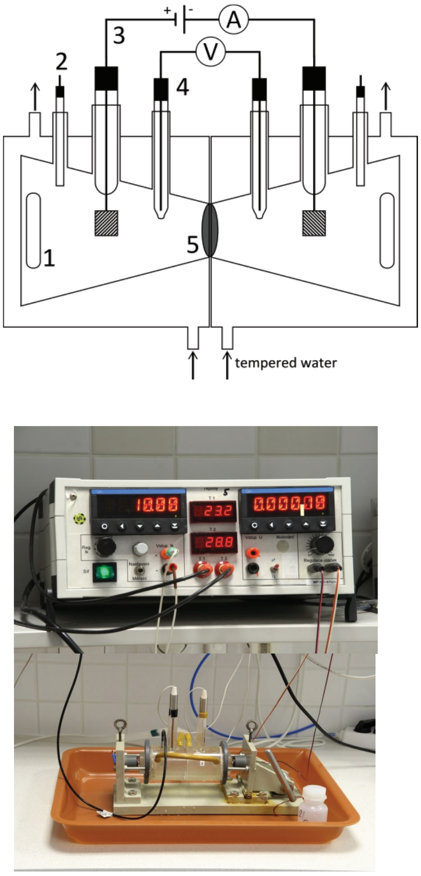

Fig. 1. Scheme of tempered double-walled cell equipped by magnetic stirrer: 1 – temperature probe; 2 – pair of platinum electrodes connected to galvanostat; 3 – pair of saturated calomel electrodes (SCE) connected to voltmeter 4 and sample 5. On the bottom, there is real cell with combined galvanostat with voltmeter.

Mechanical properties were analyzed on tensile benchtop tester Tinius Olsen H5KT according to EN ISO 527-3. The size of samples was 150 × 25 mm, which was suitable for good reproducibility. Average thickness from three measuring points were used for calculation of modulus. According to method minimally five valid measurements were done. The average modulus (MPa), ultimate stress (MPa) and ultimate strain (%) were evaluated for each sample. Due to required sample size and limiting size of prepared membranes, the mechanical properties were measured only in the longitudinal direction.

3. Results and discussion

3.1. Dimensional changes during swelling

Swelling of the membrane in water or other solution is one of important processes. The polymer network is stretched during swelling. Depending on polymer type and its elasticity, different porous structure is created. For brittle polymer, swelling causes polymer network failure, which is indicated by white lines along the membrane surface. The white color is caused by the light scattering by the crazes. In polymer technology, this behavior is known as stress whitening. On the opposite site, elastomers are more resistant to network failure during swelling.

Generally, any cracks lead to increase membrane porosity (free volume) and decrease mechanical properties. Also the size of cracks is generally higher than size of pores in stretched elastomers. Therefore, the porous structure of membrane made from brittle polymer would be more permeable for bigger species than membrane made from elastomers. This behavior influences all membrane properties.

From Figs. 2 and 3 it is evident that PE-based membrane samples swell more than PPR-based samples, especially in length and width direction and weight. Due to high thickness fluctuation over the sample area, the calculated dimensional change in thickness would be misleading. For example, PPR-1 with 65 wt% of resin have to swell more than its 60 wt% analog, but for dimensional change in thickness the 60 wt% sample show higher value.

Although LLDPE and especially HDPE have higher modulus than LDPE or mLLDPE, membranes with LLDPE and HDPE have high degree of swelling due to high brittleness of these selected polymers. Due to high mechanical strength of PPR and high environmental stress cracking resistance (ESCR), both samples PPR-1 and PPR-2 with 65 wt% of resin show similar swelling as PE-based samples with only 60 wt% of resin. It is also clear that with increasing PBE content the swelling increases due to softening ability of PBE, which decreases modulus of membranes. The lowest dimensional changes and weight were measured for PPR-based samples, which means that PPR has better reinforcing capability than PE.

3.2. Electrochemical properties

Electrochemical resistance or conductivity of ion-exchange membrane strongly depends on ion mobility through membrane. Generally, high ion mobility is for membranes with high swelling degree and high functional group concentration. High porosity or free volume also increases ion mobility and increases membrane ion conductivity, but decreases membrane permselectivity due to increased rate of unselective transport.

From Fig. 4 and Table 2 the lowest electrochemical resistance was measured for LLDPE- and HDPE-based membranes. These membranes have also the lowest permselectivity, which correlate with higher swelling degree and probably high amount of cracks. This can be related to lower ESCR for these PE. During swelling the polymer matrix is continuously stressed, which leads to creation of cracks and their propagation. Both branched LDPE and mLLDPE have higher ESCR, and therefore, these polymers are much more resistant to cracking and creating macropores, which supports unselective ion transport (decrease of both resistance and permselectivity). Be aware that high ESCR does not mean high elongation.

PPR and PBE have extremely high ESCR, and therefore, these membranes seem to create different porous structure than PE. PP is one of the common materials used for ultrafiltration or microfiltration membranes. Porosity of these membranes is created during polymer film stretching. During membrane, swelling the polymer is also stretched, and therefore, it can also create specific porous structure probably very similar to filtration membranes.

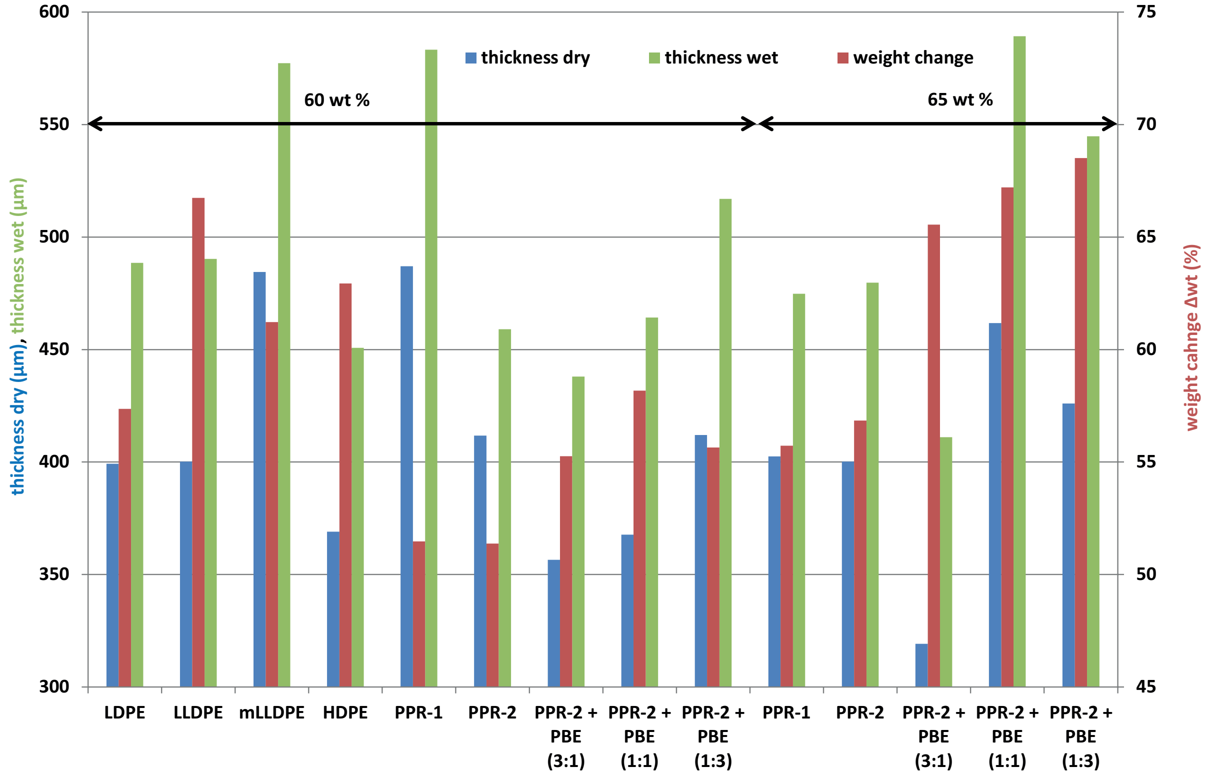

Fig. 2. Thickness of dry and swollen (wet) samples including weight change during swelling.

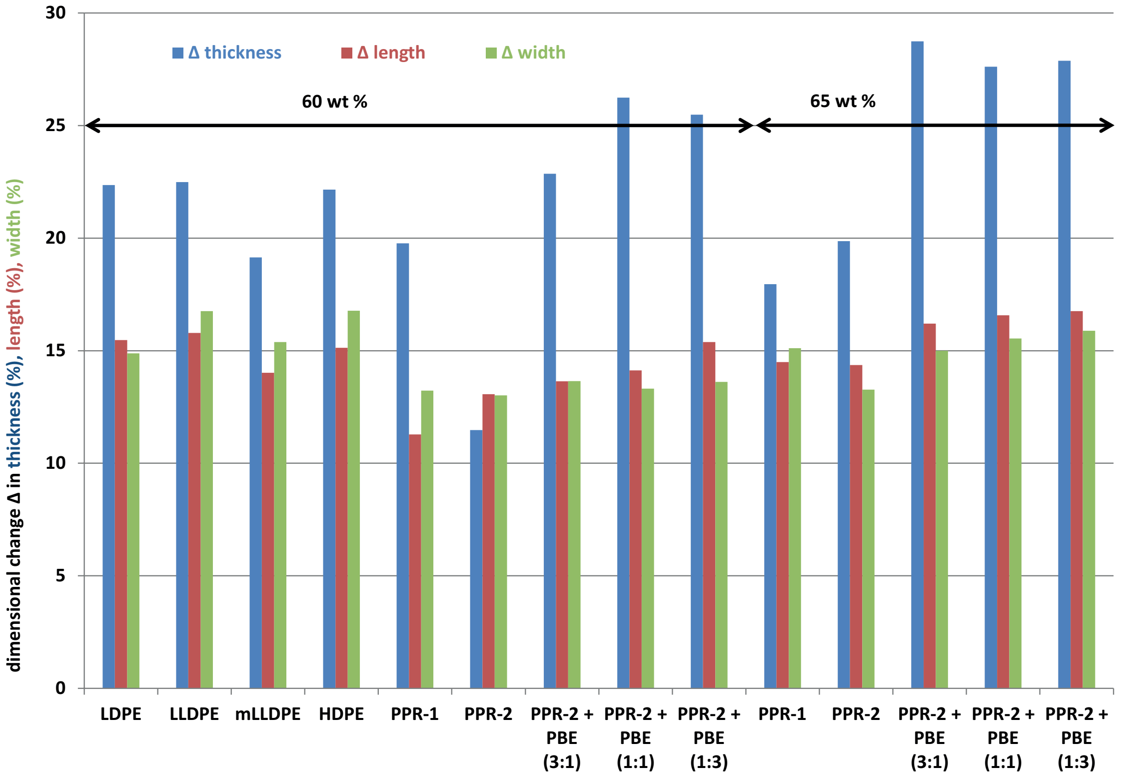

Fig. 3. Dimensional changes for different samples.

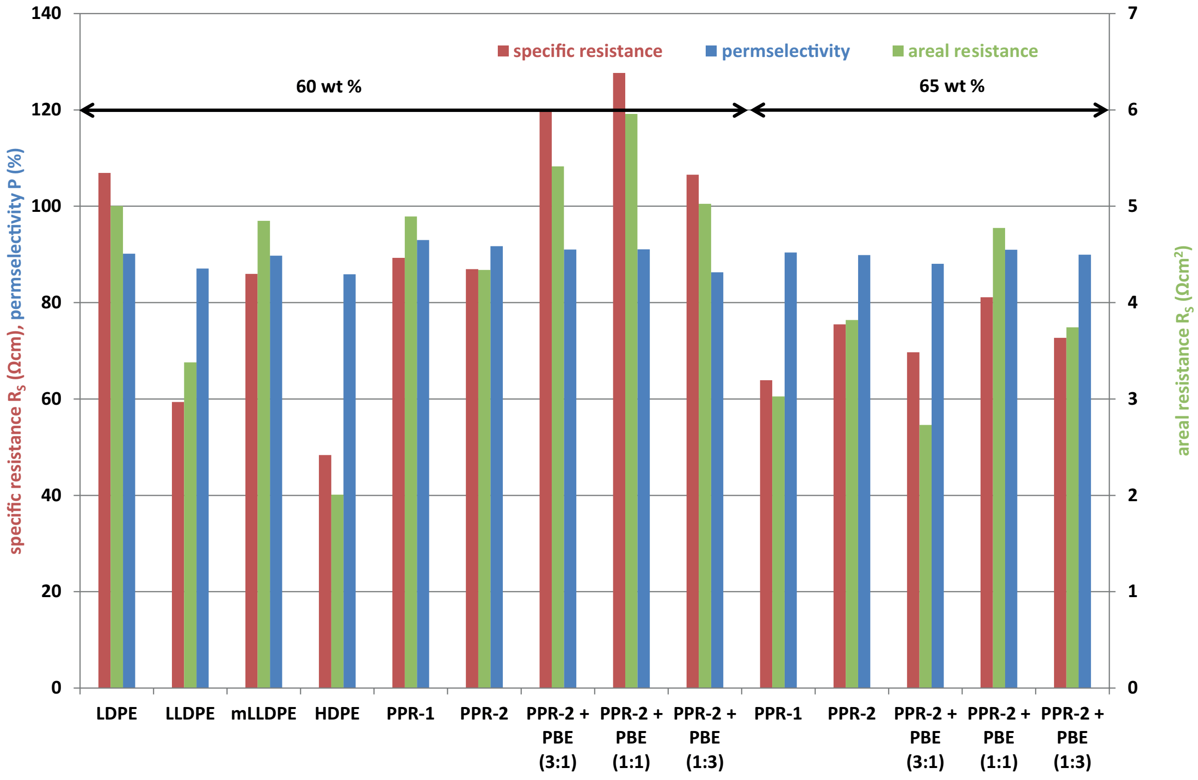

Fig. 4. Areal and specific resistance including permselectivity for different samples.

Table 2
Basic physical and electrochemical properties of membranes

Samples		Th_d (μm)	Th_w (μm)	Change in thickness (%)	Change in length (%)	Change in width (%)	Change in weight (%)	R_A (Ω cm^2)	R_S (Ω cm)	P (%)
60 wt% of anion resin	LDPE	399	489	22.4	15.47	14.88	57.4	5.00	106.9	90.16
	LLDPE	400	490	22.5	15.79	16.75	66.7	3.38	59.4	87.09
	mLLDPE	485	577	19.1	14.02	15.38	61.2	4.85	86.0	89.76
	HDPE	369	451	22.2	15.12	16.77	62.9	2.01	48.4	85.88
	PPR-1	487	583	19.8	11.28	13.22	51.5	4.89	89.3	92.99
	PPR-2	412	459	11.5	13.07	13.02	51.4	4.34	87.0	91.70
	PPR-2 + PBE (3:1)	357	438	22.9	13.64	13.65	55.3	5.41	120.2	91.02
	PPR-2 + PBE (1:1)	368	464	26.2	14.12	13.31	58.2	5.96	127.7	91.05
	PPR-2 + PBE (1:3)	412	517	25.5	15.38	13.61	55.6	5.03	106.6	86.31
65 wt% of anion resin	PPR-1	403	475	18.0	14.50	15.11	55.7	3.03	63.9	90.42
	PPR-2	400	480	19.9	14.36	13.27	56.8	3.82	75.5	89.87
	PPR-2 + PBE (3:1)	319	411	28.7	16.20	15.00	65.6	2.73	69.7	88.06
	PPR-2 + PBE (1:1)	462	589	27.6	16.57	15.54	67.2	4.77	81.1	90.97
	PPR-2 + PBE (1:3)	426	545	27.9	16.76	15.88	68.5	3.74	72.7	89.96

Due to resistance of PP to cracking, there would be fewer cracks, which can dramatically decrease membrane permselectivity and its mechanical strength. Also due to high mechanical strength of PP, the membrane swells less than PE which also decreases membrane porosity (free volume) and therefore increases both resistance and permselectivity. A little bit different situation occurs for PBE.

All elastomers have extremely high elasticity, and therefore, the cracks are created only at extremely high elongation. Addition of PBE to membrane matrix leads to increased membrane elasticity, but at the expense of reducing formation of open porous structure. Low mechanical strength of elastomers leads to increased water content and total porosity, which decreases membrane permselectivity. Probably due to low open porosity (low amount of cracks), the ion pathways are reduced, which leads to increased membrane resistance. Therefore, PBE need to be used only in a small amount.

3.3. Mechanical properties

In the end the mechanical properties of membranes correlate to behavior of polymers in highly filled composites. Branched LDPE, low molecular weight LLDPE and HDPE makes the membrane composite too brittle even when the ultimate elongation of swelled membrane is similar to PPR (Fig. 5). The reason could be the different mechanism of cracking where mentioned PE probably creates large cracks while PPR creates small cracks that cause the PPR membrane much more elastic and resistant to break. It seems this behavior also relates to higher ESCR for PPR. Therefore, these PEs are not suitable for non-laminated membranes. The highest ultimate elongation was measured for mLLDPE composite (more than 200%) but at the expense of lowest modulus. Therefore, this membrane is too elastic, and its use in non-laminating form is also limited. There would be some possibility of blending mLLDPE with HDPE to obtain optimal combinations of elasticity and toughness similar to tested blend of PPR and PBE.

All swelled PPR- and PBE-modified membrane samples are elastic. The samples with pure PPR have highest modulus and ultimate stress, which makes the membrane tough. The lower ultimate strain for PPR-2 correlates with its lower molecular weight. Higher PBE content, which acts as impact modifier, increases ultimate strain, but at the expense of decreasing both modulus and ultimate stress. The PBE makes the membrane softer, which correlates to higher swelling degree.

For real application the modulus is more important than ultimate stress or strain. There is comparison of stress–strain curves for laminated (anion exchange membrane Ralex; AM-PES) and non-laminated membranes in Fig. 6. For membrane manipulation, ED stack building and ED process itself, the membrane could not be stretched so much. In the area of very low strain up to 0.2%, the PPR-based membranes have very similar tensile stress as laminated membrane based on LDPE. Therefore, PPR-based non-laminated membranes seem to be very good alternative to standard laminated membranes but with respect to higher swelling degree. There is also possibility of laminating PPR-based membrane, which further increases mechanical strength and decreases swelling degree.

4. Conclusions

Most of prepared non-laminated anion-exchange membranes have sufficient electrochemical properties suitable for ED. LLDPE- and HDPE-based membranes show lowest resistance, but at the expense of lowest permselectivity. All tested PE-based anion-exchange non-laminated membranes have poor mechanical properties, and most of them are too brittle. Only mLLDPE-based membrane is elastic, but its elasticity is too high and this membrane is also too soft for use in non-laminated form.

PPR-based anion-exchange non-laminated membranes have highest modulus and ultimate stress including sufficient ultimate strain. This makes these membranes tough even for membranes with increased resin content in comparison with PE-based membranes. Addition of PBE to membrane matrix

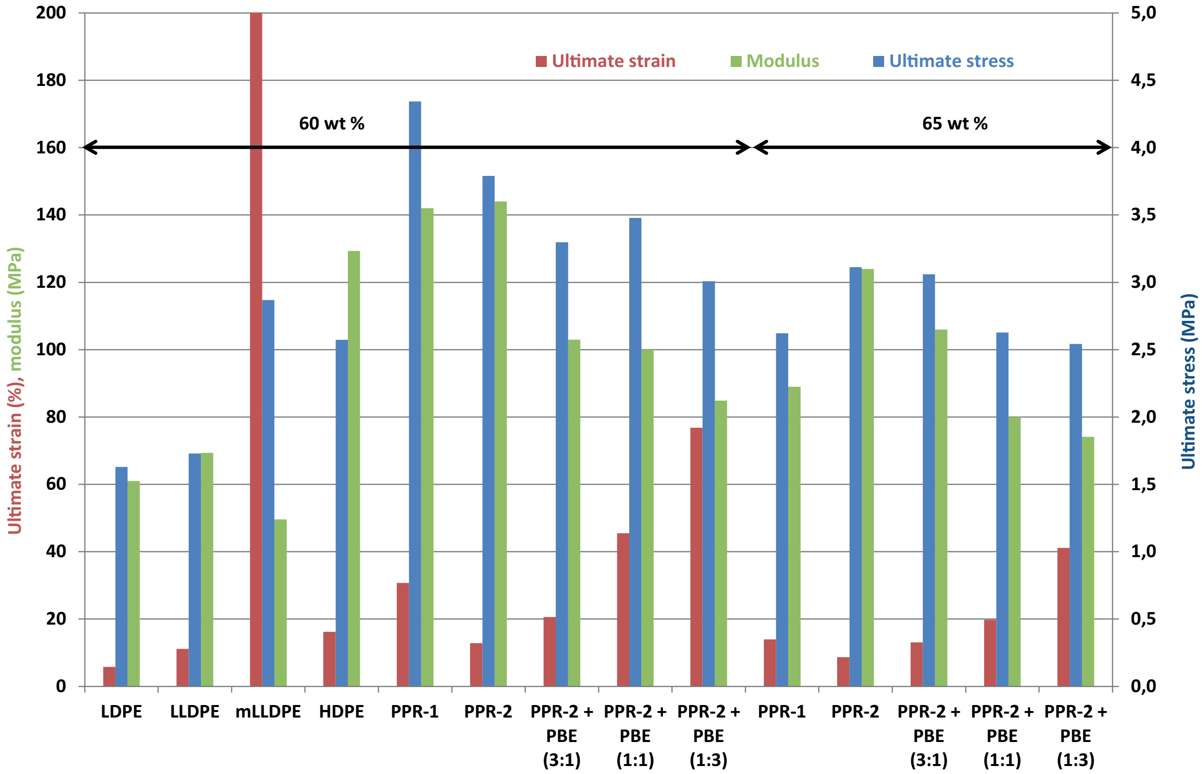

Fig. 5. Mechanical properties for different samples.

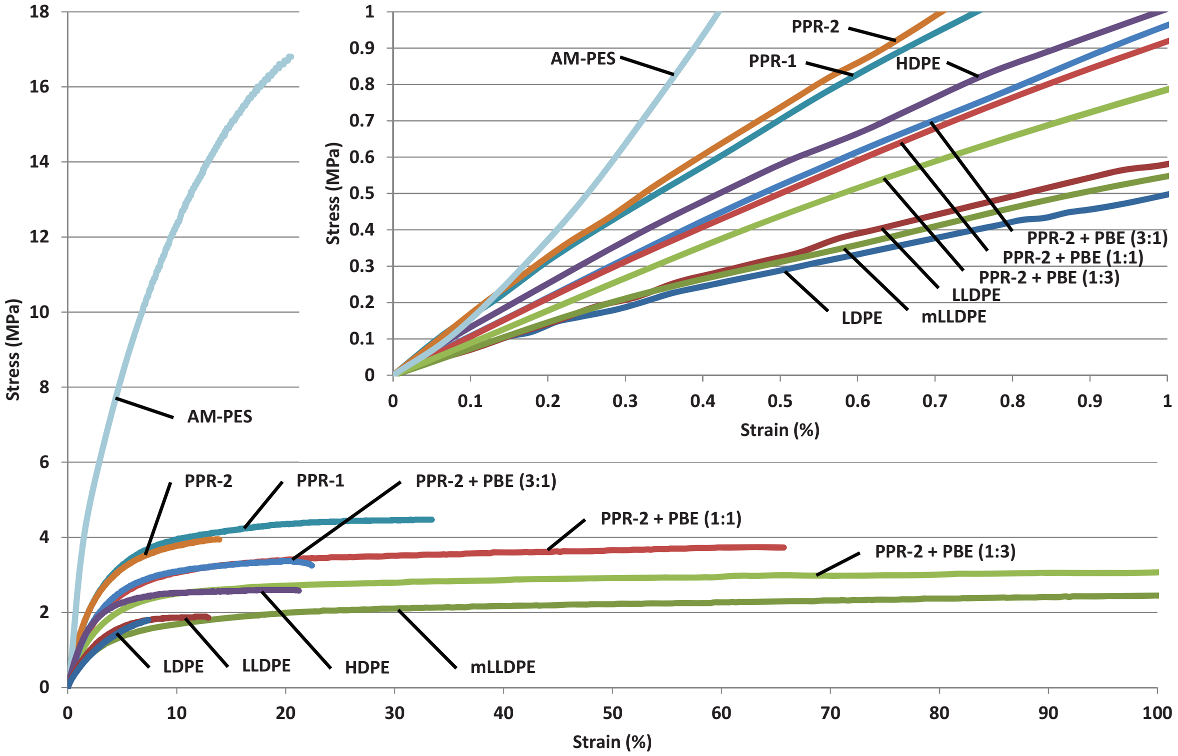

Fig. 6. Stress strain curves for samples with 60 wt% of ion-exchange resin.

leads to increased membrane elasticity, but at the expense of increasing resistance and slight permselectivity reduction. It seems the elastic property of PBE reduces formation of open pore structure, which decreases membrane resistance. Low modulus of PBE leads to increased water content and also total free volume, which makes the membrane less permselective than dense membrane.

In the end ion-exchange membrane composite based on PPR or with combination of PPR with slight amount of PBE has good potential for increasing both mechanical and temperature stability of all ion-exchange membrane type. This allows increasing operating temperature of ED and makes the desalination process more effective in comparison with low temperature process. High mechanical strength of PPR-based membrane composites allows preparing membrane also in hollow fibers, which can be used for diffusion dialysis.

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Abbreviations and symbols

PE	—	Polyethylene
LDPE	—	Low-density polyethylene
LLDPE	—	Linear low-density polyethylene
mLLDPE	—	Metallocene-type linear low-density polyethylene
HDPE	—	High-density polyethylene
PP	—	Polypropylene
PPR	—	Polypropylene random copolymer
PBE	—	Propylene-based elastomer
MFI	—	Melt flow index, g/10 min
R_A	—	Areal resistance of membrane, Ω cm^2
R_S	—	Specific resistance of membrane, Ω cm
P	—	Membrane permselectivity, %
Th_d	—	Thickness of dry membrane, μm
Th_w	—	Thickness of swollen membrane, μm
ESCR	—	Environmental stress crack resistance
ED	—	Electrodialysis
R_j^s	—	Resistance without membrane, Ω cm^2
R_j^{s+m}	—	Resistance with membrane, Ω cm^2
R_{Aj}	—	Areal resistance of membrane, Ω cm^2
$U_{\text{meas.}}$	—	Measured potential under the current, V
U_{as}	—	Asymmetric potential measured without applied current, V
A_m	—	Active sample area, cm^2
Th_j	—	Sample thickness, cm
index *s*	—	Solution phase
index *m*	—	Membrane phase
Index *j*	—	Solution type
R	—	Universal gas constant, J/K mol
T	—	Temperature, K
z	—	Ion charge number
F	—	Faraday constant, A/mol
$E_{M\text{ theor}}$	—	Theoretical membrane potential, V
$E_{M\text{ meas.}}$	—	Measured membrane potential, V

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