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Cation-exchange membrane modified by inorganic short fibres

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ABSTRACT

Ion-exchange membranes have been used in separation processes, for example, electrodialysis, electrodeionisation and electrophoresis. Preparation of a new type of heterogeneous ion-exchange membrane with improved mechanical properties is described in the paper. Heterogeneous cation-exchange membranes reinforced by short carbon fibres (1 mm) were prepared with different amount of the fibres and ion-exchange resin. Fibres and ion-exchange resin were compounded with polyethylene matrix in two steps. Membrane foil was formed by extrusion. Electrochemical properties of the membranes like electric resistance, permselectivity and counterion-transfer number were measured. Microstructure and morphology of the membranes were assessed by light microscopy. Properties of reinforced membranes were compared with unreinforced membrane in all cases. Results clearly show that electrochemical properties depend on amount of the ion-exchange resins and are not negatively affected by presence of carbon fibres. Light microscopy has provided evidence of absence of large fibre clusters. Fibres are uniformly distributed throughout the volume of the membrane.

Keywords: Cation-exchange membrane; Reinforced membranes; Carbon fibres

1. Introduction

Electrodialysis (ED) belongs to the electromembrane separation processes that are characterised by the following common features:

(1) They proceed in solutions of salt that can be dissociated down to cations and anions.
(2) They employ a membrane that divides working chamber into separate areas. The membrane used is a special case of a permselective membrane, so called ion-exchange membrane. It can contain either positive (anion-exchange membrane) or negative (cation-exchange membrane) functional groups, thus allowing permeation of the respective counterions.
(3) As the main driving force for streamlining ionic flow gradient of electrical potential is applied in normal direction to the membrane surface, hence the +/− ions move to the −/+ electrode, bringing about their separation.

ED is used for increasing/decreasing salt concentration in the solution. For that purpose, a membrane

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stack is created by alternating arrangement of cation-exchange membranes, spacers with channels, anion-exchange membranes, producing two separate solution streams—concentrate and diluate. The third stream runs alongside electrodes, helping eliminate excess ions from the electrode area, thus preventing their corrosion, and deposit creation [1].

In practice, desalination of sea/brackish water to produce potable water is one of the most important application of ED. Among further technologies, e.g. salt production, whey desalination or deacidification of fruit juices, and many others can be listed.

Heterogeneous ion-exchange membranes for ED are produced out of film-forming polymers, either by dry-moulding or melt-forming (calendering, extrusion) techniques. As one of those polymers, polyethylene (PE) is fairly permeable, harmless, chemically resistant, easily processed and cost-effective material; however, it shows quite disadvantageous mechanical properties (low tensile strength, and creep resistance). Usually, very high content of the ion-exchange resin (up to 65 wt%) causes further drop in membrane performance. To improve mechanical properties of the membrane, proper reinforcement is necessary, e.g. reinforcing fabric, non-woven or fibres.

The motivation for the use of inorganic fibres in ion-exchange membrane is to improve the mechanical properties.

2. Experimental

2.1. Materials

Two types of PE have been used for membrane matrix: low flow PE [MFI (2.16 kg; 190˚C) = 3.5 cm^3/10 min] and high flow [MFI (2.16 kg; 190˚C) = 50 cm^3/10 min]. Mixture of strong acid cation-exchange resin types has been used to prepare heterogeneous cation-exchange membrane, blend was called DPI. Chopped carbon fibres SIGRAFIL® C30 supplied by SGL Group with uniform length of 1 mm and diameter of 7 μm have been used for reinforcing of the cation-exchange membrane. Fibres have got modulus 240 GPa and single filament resistivity 0.0022 Ω cm; surface of carbon fibres was coated by the manufacturer for better adhesion to an epoxy matrix.

2.2. Membrane preparation

Preparation of the heterogeneous cation-exchange membrane took place in several subsequent steps. First, the organic treatment of carbon fibres was removed by heating in laboratory oven at 500˚C for 2 h. Subsequently, bald carbon fibres were compounded into high-flow PE matrix on two-screw mixer (D = 27 mm; L = 40D). High flow PE does have inferior mechanical properties, but has very low viscosity, which is advantageous for the formation of the composite blend. The produced masterbatch with content of carbon fibres 20 wt% was granulated. Predefined percentage of the carbon fibre master batch has been mixed up with a virgin low-flow resin and/or a virgin high-flow resin, respectively. The mixed product has been filled into the hopper to feed it to the Buss compounding line. Homogenisation has been carried up according to the processing standard, including feeding milled cation-exchange resin into the polymer melt via two-side dosing units. Subsequently, extrusion of the membrane sheet reinforced with carbon fibres has been performed at UTB in Zlin, using small extruder with a head width of 30 cm, leading extruded polymer melt through a heated three-roll-calender.

2.3. Membrane testing

2.3.1. Microstructure

Light microscopy in transmitted light was used for assessment and documentation of the membrane microstructure. Length of fibres and their orientation were measured with aid of image analysis software. Printed picture of the membrane with fibres was inserted into transparent foil and fibres were redrawn before determining the length of fibres automatically. This step is necessary because there is a poor contrast between fibres and background. Foil with redrawn fibres and scale was scanned into computer like 1-bit image and analysed by Image J software; more than 250 individual fibres were analysed and resulting distribution of length of the fibres plotted.

2.3.2. Membrane resistance

The membrane specific and areal resistance was measured in a tempered cell of our own design. Conditioning (alternating exposure in 1 M HCl and 1 M NaOH) and equilibration (0.5 M NaCl, 24 h) took place prior the measurements of the membrane resistivity. Electric resistance of the membrane was measured in 0.5 M NaCl solution at laboratory temperature by compensation method; the measuring was carried out at constant 10 mA DC.

2.3.3. Desalination tests

Series of salt test was conducted on laboratory electrodialyser unit P EDR-Z/10-0.8. Cation-exchange

membrane reinforced by carbon fibre was tested in stack together with standard anion-exchange membrane Ralex®. Each test was performed four times, 2× in positive and 2× in negative mode with 2 wt% Na_2SO_4 solution.

2.3.4. Mechanical properties

Tensile experiment was performed with tensile tester LabTest 2.010 at crosshead speed of 5 mm/min in conformity with standard EN ISO 527-3. Two types of stripe specimen (20 × 150 mm) were cut out of the extruded membrane belt, longitudinal with the extrusion direction and transverse to this direction. Five test specimens were measured for each type of membrane.

3. Results and discussion

3.1. Microstructure

The microstructure of the membrane is shown in Fig. 1. Short side of picture corresponds with the extrusion direction.

Optical microscopy brought conclusive evidence that carbon fibres were uniformly dispersed in membrane (Fig. 1) and fibres did not create clusters.

The fibres in the membrane have a median length of 0.12 mm and lengths of fibres correspond to the log-normal distribution (Fig. 2). Result of the microstructure analysis suggests that an intensive fibre fracture occurs during the preparation of the membrane. Fibres breakage is associated with three thermo-mechanical cycles that fibres are subjected to, during the membrane preparation: compounding fibres with PE, compounding ion-exchange resin with PE and PE/C—fibres and extrusion of membrane.

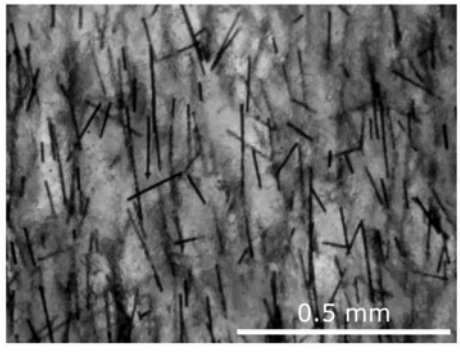

Fig. 1. Micrograph of carbon fibres in cation-exchange membrane.

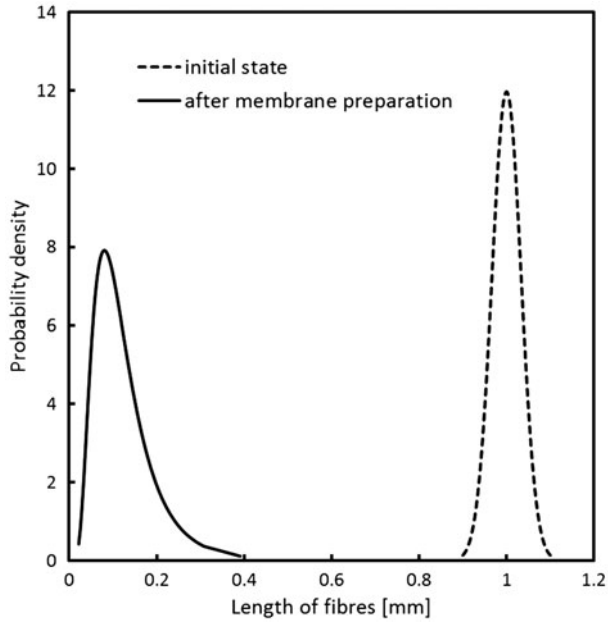

Fig. 2. The distribution of carbon fibres length in initial state and in the membrane.

Fibres orientation caused by the flow of the polymer melt was also analysed by digital image analysis. The fibres are not randomly distributed in plane of the membrane, but are preferentially oriented in the melt flow direction (Fig. 3).

3.2. Membrane properties

The physical and electrochemical properties are listed in Table 1. Membrane filled by carbon fibre with amount above percolation threshold exhibits electron conductivity [2], but carbon fibres should not affect the ionic conductivity. Filling ratio of ion-exchange resin influences membrane resistivity primarily. Results of ionic resistivity measurement of the membranes, filled by carbon fibres, show that reality is more difficult. Membrane with 58 wt% ion-exchange resin and 7 wt% carbon fibres (DPI 58/7) exhibits lower value of resistivity in comparison with membrane filled 62 wt% ion-exchange resin (DPI 62/0). This result suggests the formation of conductive channels alongside fibres, which facilitate the movement of ions [3]. Generally, the heterogeneity of the membrane influences its transport properties [4,5].

Mass difference between dry and wet membranes shows that swelling is determined only by the ion-exchange resin content in membrane (Table 1). However, different ratio of the membrane dimensional changes in longitudinal/perpendicular direction to the

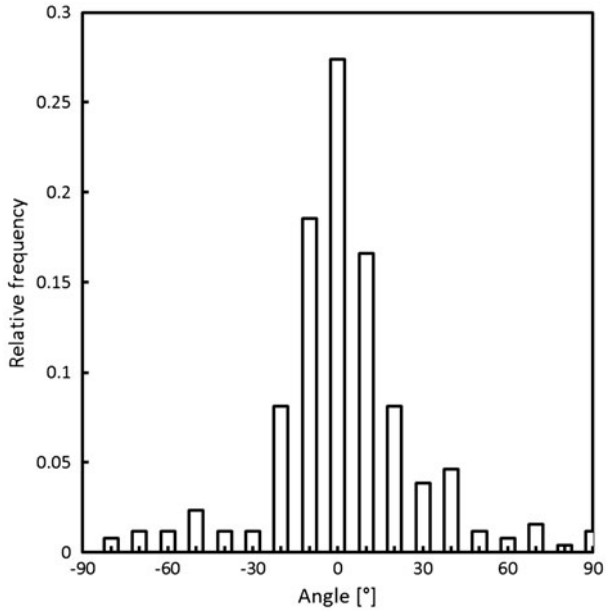

Fig. 3. Distribution of angles between fibres and direction of membrane extrusion.

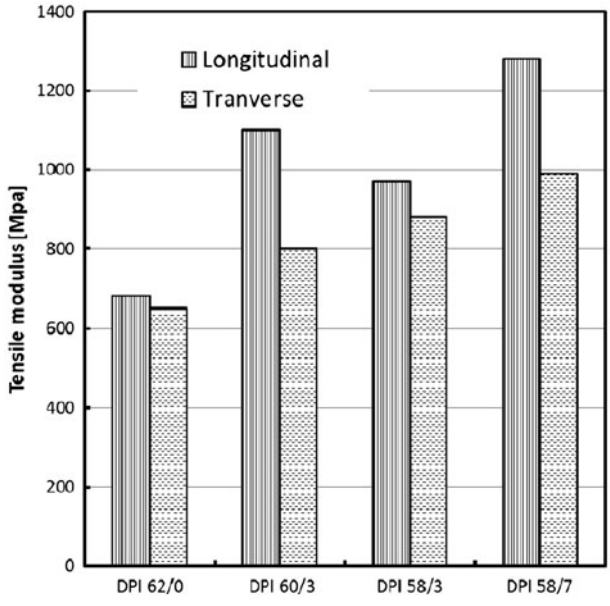

Fig. 4. Tensile modulus of membranes.

Table 1
Properties of cation-exchange membranes

Membrane	Ionex content (wt%)	CF content (wt%)	Swelling $l/w/t$ (%)	Swelling (wt%)	R_A (Ω cm^2)	R_S (Ω cm)	P (%)
DPI 62/0	62	0	19.6/19.8/27.9	72.0	4.11	86.2	91.3
DPI 58/3	58	3	8.0/20.6/33.7	64.5	4.68	88.8	92.5
DPI 60/3	60	3	9.0/22.1/35.6	68.5	3.97	76.3	93.3
DPI 58/7	58	7	4.0/22.6/37.3	64.3	4.03	73.6	92.5

main fibres orientation during swelling evidenced significant effect of the fibres content. Reinforced membrane showed reduced lengthwise swelling. Oriented fibres apparently hindered deformation of PE associated with swelling of the resin. On the other hand, this is offset by higher swelling of the reinforced membranes in width and thickness that is greater than the unreinforced MF. It also illustrates the fact that only a minimum of fibres is oriented in the direction of width and thickness of the membrane.

Mechanical properties were tested on membranes and results are presented in Fig. 4. All membranes were tested only in dry condition. Higher tensile modules of membranes in the longitudinal direction to the extrusion direction than in the transverse direction were observed in all cases. It corresponds to the microstructural analysis results, which confirmed preferential fibres orientation in the extrusion direction (Fig. 4). Stiffness of the membrane reinforced with 7 wt% CF is about 88% higher in comparison with unreinforced membrane (DPI 62/0). C-fibres content of 3 wt% resulted in stiffness increase of about 40–60% in dry membrane. The result shows that a small amount of well-dispersed carbon fibres can significantly increase the rigidity of the membrane.

3.3. Desalination tests

A series of desalination tests was carried out with all types of membranes. Results show that all the membranes exhibit similar response in desalination test. No distinctive difference was observed during tests, e.g. time dependence of diluate conductivity is similar for all types reinforced membranes (Fig. 5), as curves overlap each other. Time to 95% desalting do not differ statistically, as evidenced by analysis of variance.

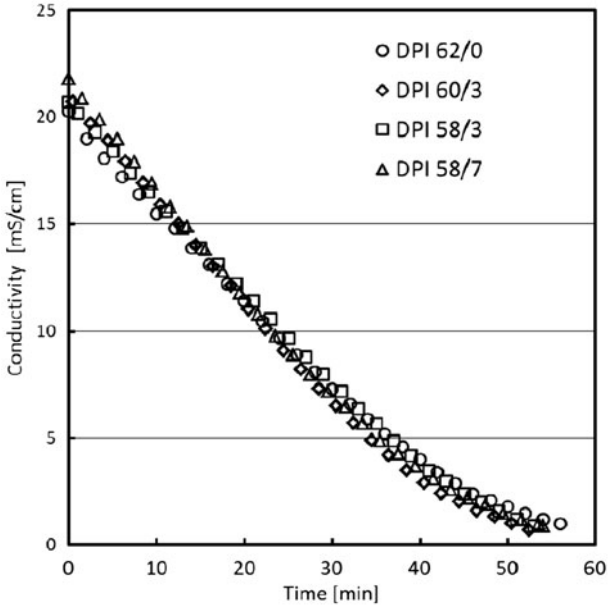

Fig. 5. Time dependence of diluate conductivity.

4. Conclusions

In the present work, the preparation and properties of membrane reinforced by carbon fibres were described. The following results were obtained:

(1) The presence of carbon fibres in membrane resulted in improvement of mechanical properties.
(2) Intensive breakage of fibres was associated to the production of reinforced membranes.
(3) Fibres were uniformly distributed in the ion-exchange membrane.
(4) The presence of fibres positively affected the resistance of the membrane with a lower content of the ion-exchange resin.
(5) The presence of fibres in the membrane has no negative effect on the ED test.

Acknowledgement

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