THE EFFECT OF REINFORCING FABRIC ON ION EXCHANGE MEMBRANE PROPERTIES UNDER CYCLIC pH CHANGES

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Abstract: The article deals with comparison of the influence of ion exchange membranes (IMs) composition on their dimensional changes and electrochemical properties. Mainly the influence of chemical stability of polyester (PES) or poly(phenylene sulfide) (PPS) reinforcing fabric was investigated. These fabrics were made from fibers of the same thickness and had the same construction of warp and weft. IMs were exposed to cyclic pH changes which were realized by alternately soaking in HCl and NaOH solutions of concentration 1 mol.L⁻¹ for 24 hours. Overall, IMs spent 9 days in each solution. Dimensions, weight, ion exchange capacity and area resistance of IMs were continuously evaluated. Reinforcing with PPS fabric led to length and height stabilization of IMs as compared with reinforcing by PES fabric. Moreover membranes reinforced with PPS fabric showed the highest ion exchange capacity and stable area resistance (7.4±0.5 Ω .cm² or 6.3±0.1 Ω .cm² for anion or cation exchange membrane, respectively) during the testing period. Contrary, IMs reinforced with PES fabric showed gradual decrease of area resistance corresponding to increased swelling. The sharpest decrease in area resistance was observed for IM(H)-PES Ralex, from 11.6 Ω .cm² to 3.5 Ω .cm² for anion exchange membrane and from 6.1 Ω .cm² to 3.5 Ω .cm² for cation exchange membrane. It was proved that by minimizing the dimensional changes of IMs longer stability of area resistance and ion exchange capacity was obtained.

Keywords: reinforcing fabric, degradation, pH, polyester, poly(phenylene sulfide)

1 INTRODUCTION

Membrane processes are being used for drinking and industrial water treatment. The processes find their application more and more in chemical, automotive and food industry or energetics. Membranes used in processes in which the gradient of electric field is the moving force are classified as ion exchange membranes (IMs). They are mainly used in electrodialysis, electrodeionization, diffusion dialysis or cataphoresis [1-3].

IMs are preferentially made from polymer materials called heterogeneous [4]. So IM belona to the polymer composites as is demonstrated from the structure of its fracture on Figure 1. Basic heterogeneous IM is component of resin functionalized with ion exchange groups. Particles of the resin are dispersed in thermoplastic matrix, so the IM can be produced via extrusion in a form of sheet, hollow fiber or tubular membrane [2, 5, 6].

Flat sheet membranes use to be reinforced with polymer fabric which significantly improves their mechanical properties [7, 8]. Under working conditions IMs contain usually tens of weight percent of water which enables the swelling of resin particles and fills pores and voids present in membrane structure. Water acts as a plasticizer and medium for transport of ionic species. Based on the type of resin functional groups, two kinds of IMs are distinguished. Anion exchange membranes (AMs) transport preferentially anions and reject cations and cation exchange membranes (CMs) transport cations and reject anions [1].



Figure 1 Fracture of ion exchange membrane obtained by scanning electron microscopy

Before use, IMs need to be swollen which is usually realized by soaking them in demineralized water for several hours. Membrane swelling is strongly affected by the properties of reinforcing fabric. In general, dimensional changes of IMs caused

by swelling are not isotropic. Also membrane tensile dependent on the properties are direction of measurement, thus IMs represent orthotropic structure. Properties of IMs gradually change under the operational conditions of individual technologies. These changes are referred to the changes in membrane microstructure. Some producers recommend activation of membranes in various chemical solutions prior to their use. Some types of activation are also usually done before membrane characterization and quality control. The main objective of the activation is to make the resin particles available in a matrix. As a consequence of volumetric changes of the resin caused by hydration pressure and changes of ionic form of functional groups membrane matrix become more open and a network of conductive channels through IM is generated [9]. Usually acid or base solutions are used for IMs activation or clean in place [10].

This work deals with repeated applying of HCI and NaOH solutions to the IMs. The objective was to evaluate the effect of cyclic pH changes on the geometry and functional properties of IMs. The purpose of examining IMs reinforced with poly(phenylene sulfide) (PPS) fabric was its enhanced chemical stability against polyester (PES) fabric.

2 EXPERIMENTAL

2.1 Ion exchange membranes

Three IMs were characterized, commercially available IM(H)-PES Ralex (MEGA a.s., Czech Republic) and two development samples IM-PES and IM-PPS. IMs had the same type and filling of the resin. The development membranes differed from the commercial one in the thermoplastic matrix. Matrix of IM-PES and IM-PPS was based on different types of linear low density polyethylene (LLDPE) whereas IM(H)-PES Ralex was made from low density polyethylene (LDPE) matrix. Membranes differed also in their reinforcing fabric which was made from polyester (PES), specifically poly(ethylene terephthalate), or poly(phenylene sulfide) (PPS). Both fabrics were made from monofilament of a diameter 55 µm and had identical construction of warp and weft (32/35 threads Size of per 1 cm). link was approximately 260/230 µm in the direction of warp and weft. Free area of used fabrics was 67%. Ultimate force and ultimate strain in the warp direction were higher for PES fabric (220 N, 31%) than for PPS fabric (140 N, 25%). Figure 2 illustrates the construction of used PES fabric. Dry IMs had thickness in the range 350-450 µm.

2.2 Membrane activation

First, IMs were swelled 24 h under room temperature in demineralized water. Individual membranes were soaked in 0.5 L of appropriate solution, AMs in NaOH (1 mol.L⁻¹), CMs in HCl (1 mol.L⁻¹). After 24 h solutions were poured out and IMs were rinsed with demineralized water till the neutral pH. Then, AMs were soaked in HCl solution and CMs in NaOH solution for 24 h and after that rinsed again with demineralized water till neutral pH. This procedure represented one activation cycle. During this cycle the change of ionic form of AMs is represented as $CI^- \rightarrow OH^- \rightarrow CI^-$, for CMs as $Na^+ \rightarrow H^+ \rightarrow Na^+$. Membranes underwent totally nine activation cycles.



Figure 2 Scanning electron microscopy scan of PES fabric used for membranes reinforcement

2.3 Dimensional and weight changes

After each activation cycle, dimensional and weight changes (Δx , %) of IMs were determined according to (1).

$$\Delta x = 100\% (x_{\rm s} - x_{\rm d}) / x_{\rm d} \tag{1}$$

The symbols in (1) represent the values of parameters (mass *m*, length *l*, width *w* or thickness *h*) in swelled (x_s) or dry (x_d) state.

2.4 Electrochemical properties

Ion exchange capacity (IEC, $\text{mmol.g}_{\text{dry}}^{-1}$) was determined after each activation cycle by titration procedure described in [4, 11] using Metrohm 682 Titroprocessor (Gemini BV). The uncertainty of IEC determination was below 1%.

After 3rd, 6th and 9th cycle area resistance (R_A , Ω .cm²) (2) was measured. Membranes were equilibrated in NaCl solution (0.5 mol.L⁻¹) previous the measurement. Resistance was determined by potentiometric compensation method at 25°C. The scheme of electrochemical cell of self-made construction is mentioned in [4].

$$R_A = S(U_{IM+sol} - U_{sol})/I$$
⁽²⁾

The symbols in (2) represent effective membrane area (S, cm²), potential of measuring cell filled with NaCl solution (0.5 mol.L⁻¹) and membrane (U_{IM+sol} , mV) or electrolyte itself (U_{sol} , mV), and applied direct current (I, mA).

3 RESULTS AND DISCUSSION

Dimensional changes of IMs connected to swelling or change of ionic form are fundamentally affected by the presence of reinforcing fabric. Generally, reinforced IMs swelled preferentially in the direction of their thickness contrary to the width and length.

3.1 Dimensional and weight changes

Figures 3 and 4 show the impact of cyclic pH changes on the length of AMs and CMs. It is clearly visible that CMs resistance against cyclic pH changes is higher than the resistance of AMs. The resistance of CMs is given by different mechanism of exposure in alkaline solution towards AMs. As CMs reject anions. OH cannot penetrate into their structure and attack PES fabric [9, 12]. The alkali solution acts predominantly on the CMs surface whereas the fabric is during the extrusion lamination pressed between two heated rolls underneath the membrane surface. As AMs enables the transport of anions, presence of OH⁻ can cause the alkali hydrolysis. In this reaction carbonyl oxygen is attacked by OH, the scission of an ester bond occurs and equivalent amount of hydroxyl and carboxyl end groups is produced [13]. Alkaline hydrolysis is catalyzed by quaternary ammonium chloride present in the anion exchange resin [14]. Generally, it is accepted, that PES fibers are attacked by alkaline solutions from their surface, thus their diameter decreases. Moreover cracks which significantly reduce the strength of fiber can be indicated when the fibers are stressed in alkaline solution [15]. Fabric made of PES loses its strength and is not able to limit the swelling in the direction of length and width. This is obvious from the significant enlargement of the length on Figure 3. After the 3rd activation cycle, AM-PES showed steep increase of its length whereas for AM(H)-PES Ralex the length increased significantly after the 5th cycle. Using the same resin type and filling and the same PES fabric, AM(H)-PES Ralex seemed to be loosely two times more resistant against the beginning of fabric degradation towards AM-PES.

The dimensional stability of IMs is very important during the operation in membrane units. Taking this in mind, PPS fabric is suitable alternative to PES fabric for operations in alkali environment. Even the construction of both fabrics was virtually the same, PPS fabric enables higher increase in length for AMs and CMs immediately after the swelling in demineralized water (0th cycle). However, change in length for IMs reinforced with PPS fabric was below 4%.

The changes in length and width of IMs depend on the number of threads in warp and weft and also on the fixation method. Both PES and PPS fabrics had the same construction but differed in their mechanical properties. Changes in width reflected trends observed for change in length. Moderate anisotropy was observed, which can be associated with different tensile stress of warp and weft threads during the weaving [16]. Fabric from PPS enabled higher increase in width than PES fabric, for AM and CM below 9%.



Figure 3 Dependence of length change of AMs according to the number of activation cycles



Figure 4 Dependence of length change of CMs according to the number of activation cycles

The increase in thickness of IMs after the swelling (0^{th} cycle) was in the range 40-45% for AMs and 59-68% for CMs. The course of thickness changes according to the number of activation cycles for AM(H)-PES Ralex and AM-PES depicted in Figure 5 shows the mutual relationship of dimensional changes. Whereas the length (Figure 3) and width of these AMs increased with the number of cycles, thickness had decreasing trend. The least affected were IMs reinforced with PPS fabric. For CM(H)-PES Ralex and CM-PES (Figure 6) a decline in thickness

change after 5^{th} cycle was observed. This behavior did not correspond to the stable length (Figure 4) and width.



Figure 5 Dependence of height change of AMs according to the number of activation cycles



Figure 6 Dependence of height change of CMs according to the number of activation cycles

The increase in thickness was higher for CMs than for AMs which is the result of lower IEC of anion exchange resins. Therefore, by intensive swelling in the direction of thickness the matrix of CMs is more stressed than in AMs. The increase of swelling tends to rise membrane porosity. At high water content the resin particles could be washed out of the matrix to the surrounding solution. Lower content of resin thus could cause the decrease of swelling in the direction of thickness without significant influence on length and width. Weight changes of AMs and CMs are shown in Figures 7 and 8.



Figure 7 Dependence of weight change of AMs according to the number of activation cycles



Figure 8 Dependence of weight change of CMs according to the number of activation cycles

The course of weight changes essential is for understanding the evolution of porositv in membrane structure under the effect of cyclic pH changes. After the swelling (0th cycle) the network of ion conductive channels is being formed which is further developing during membrane operation or also static exposition to the aqueous solutions. The more aggressive is the surrounding environment, the faster is the development in IM porosity, the coherence of thermoplastic matrix decreases and resin particles are more prone to be washed out [9]. Porous structure is filled with surrounding solution and the increase in weight of IM is usually observed [17] as in the case of AM(H)-PES Ralex and AM-PES. For this couple of AMs the presumption of alkali hydrolysis of PES fabric was the highest. With gradual degradation of PES threads, the resulting porosity was filled with HCI or NaOH solutions or demineralized water.

3.2 Electrochemical properties

Area resistance is a measure of membrane process power requirements. Ideal IM has as low area resistance as possible and thus intensive ionic transport enabling to increase the capacity of given technology. Prior to area resistance determination it is usual to use membrane pre-conditioning ranging 1-2 activation cycles described in the article. Results of membranes characterized without pre-conditioning (0th cycle) show the importance of the activation on membrane properties. As mentioned previously, activation is important for development of ion conductive channels throughout the IM resistance As a consequence, is decreasing as is shown for most of the IMs in Figures 9 and 10.



Figure 9 Dependence of area resistance of AMs according to the number of activation cycles



Figure 10 Dependence of area resistance of CMs according to the number of activation cycles

The method of area resistance determination is destructive; each measurement was thus done for a different piece of IM. The decrease of resistance is not caused only by accessibility of larger amount of resin particles. As a side effect of porosity increasing cracks and voids in thermoplastic matrix arise, which generally increase the permeability of IM for both anions and cations regardless the ionic charge of functional groups attached to the resin. As a consequence, IM loses its permselectivity, i.e. preferential selectivity of AM towards anions or CM towards cations.

The ability of ionic transport of IM can be quantified via ion exchange capacity (IEC). This parameter was evaluated after each activation cycle. The results of IEC need to be interpreted with respect to microstructure development. Only resin particles enabling interaction with solution or electrolyte can contribute to the final IEC value. If there are particles which are fully wrapped with polymer matrix they cannot contribute to the resulting IEC. With ongoing activation of IM structure larger amount of resin particles is accessible, thus IEC should increase. At the same time with increasing porosity finer particles could be washed out resulting in decrease of IEC. Final IEC reflects all mentioned effects. The values of IEC found during cyclic pH changes for all IMs were nearly constant. The highest value for AMs was found for AM-PPS and was constant during all measurements $(1.9\pm0.0 \text{ mmol.g}_{drv}^{-1})$. Ion exchange capacity of AM(H)-PES Ralex and AM-PES matched 1.7 \pm 0.2 mmol.g_{dry}⁻¹. All CMs had IEC the range 2.3 ± 0.2 mmol.g_{dry}⁻¹, specifically in 2.5±0.0 mmol.g_{drv} for CM-PPS. Article [12] evaluated long-term influence of NaOH solution (5-15 wt.%) on heterogeneous IMs. The authors did not observe any changes of IEC during IM exposition but they reported the decrease in resistance. The cause was degradation of PES fabric and related dimensional changes of IMs leading to the increase in membrane porosity.

4 CONCLUSION

Three types of AMs and CMs were compared. Based on the obtained results it was shown that chemical composition of reinforcing fabric is very important for dimensional stability of membranes as well as for their electrochemical properties. Reinforcing with PPS fabric contrary to PES fabric which is used in commercially available IM(H)-PES Ralex membranes had positive impact for dimensional changes minimization. The more IM is resistant to dimensional changes connected to the swelling and ionic form changes, the slower the porosity develops. As a consequence lower amount of ion exchange resin particles is washed out of membrane matrix and fewer pores and voids developed thanks to PES fabric degradation in alkaline environment are filled with solution which surrounds IM. Fabric made positive of PPS significantly impact had on stabilization of IMs electrochemical properties.

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