

Preparation and Characterization of Semi-Interpenetrating Network Polystyrene/PVDF Cation Exchange Alloy Membranes

Xiaocheng Sun, Fei Chen, Yinlin Lei, Yunjie Luo, Yingxian Zhao

School of Biotechnology and Chemical Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, People's Republic of China

Correspondence to: Y. Lei (E-mail: leiy@nit.net.cn).

ABSTRACT: The polystyrene-DVB/PVDF alloy particles were prepared by pulverizing the polymerization product of styrene/DVB/PVDF in DMF, and then sulfonated with concentrated sulfuric acid to gain the cation exchange alloy powder, which was directly thermoformed by a hot-press machine to form the titled cation exchange alloy membranes with the structure of semi-interpenetrating polymer network. The effects of the polystyrene-DVB to PVDF mass ratio and the DVB content in the monomers on the physical and electrochemical properties of the prepared alloy membranes were investigated. While the Fourier transform infrared spectroscopy (FTIR) confirms the components of membranes, the scanning electron microscopy (SEM) reveals that the alloy membranes possess a uniform distribution of functional groups, and a more dense structure with the increases of DVB content and PVDF content. The optimal prepared membranes have the area electrical resistance values within 3.0–6.6 $\Omega\text{-cm}^2$, obviously superior to the commercial heterogeneous cation exchange membrane, as well as the moderate water contents of 35–40% and the desirable permselectivity with a transport number more than 0.95. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1220–1227, 2013

KEYWORDS: Polystyrene; PVDF; cation exchange; alloy membrane; semi-interpenetrating network

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INTRODUCTION

In the past decades, the electro-driven membrane separation processes have been widely applied to some areas, including food, drug, energy, biotechnology, chemical industry, waste water treatment, as well as the desalination of sea and brackish water, and so forth.^{1–3} Ion exchange membrane is undoubtedly the principal “hardware” pillar supporting the successful application of these processes. According to the connection way of charge groups or their chemical structure, ion exchange membranes can be classified into homogenous and heterogeneous membranes, in which the charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. Compared with homogenous membranes, the heterogeneous membranes can be manufactured by a relatively simple process, in which the ion exchange particles (predominantly the ground resin) are embedded in the matrix material (e.g., polyethylene) through a series of physical operations including milling, blending, open milling, thermoforming with reinforcing fabrics.⁴ Consequently, these two low-price components contribute a very low manufacturing cost to heterogeneous membranes. Moreover, this type of membrane exhibits a favorable oxidative stability owing to its inert matrix.^{5,6} All these advantages make heterogeneous membranes still gain a number of applications,

particularly in the primary electro-driven membrane separation processes such as the brackish water desalination.⁷

However, the inherent structure drawback, principally due to the incompatibility between the hydrophilic ion exchange particles and the inert matrix material, hinders heterogeneous membranes from further applications in other high-demand areas. Further, the dropout of ion exchange particles from the matrix and the formation of cavities will happen almost during the whole separation process. With the increase of the membrane area electrical resistance and the energy consumption, the process has to be interrupted to replace with new membranes. To solve these problems, a great deal of efforts on optimizing the structure of heterogeneous cation exchange membranes have been made. Most of the studies had focused on the design and synthesis of membrane materials or the physical modification technique, for the purpose of developing novel heterogeneous cation exchange membranes by the solution casting method. For instance, Hu et al.⁸ used the poly(ether sulfone) (PES) as binder and the sulfonated poly(phenylene sulfide) (SPPS) powder as polyelectrolyte to prepare cation exchange membranes with an outstanding conductivity. In other study, the slightly sulfonated poly(ether ketone) (SPEKK) was dissolved in NMP to act as the binder, improved the compatibility with the

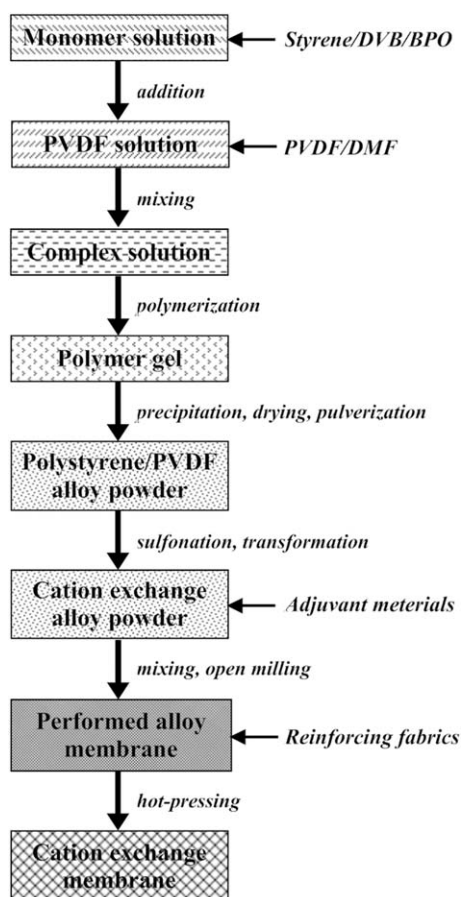


Figure 1. Manufacturing process of polystyrene/PVDF cation exchange alloy membranes.

cation exchange resin powder to a great extent.⁹ Recently, the ultrasonic technology was utilized to promote the distribution of cation exchange particles in polymer binder, and had been found to reduce the aggregation of these particles and the formation of cavities.¹⁰ Besides, the addition of inorganic fillers into the casting solution¹¹ and the surface modification by coating polymer,¹² became the strategic sections on improving the performance of heterogeneous membranes.

Though these works had exhibited some properties superior to the traditional heterogeneous membranes, there still was a possibility to increase the manufacturing cost with respect to the solvent consumption and the inconvenient operation, because of the employed solution casting method. In consideration that China has turned to be the world's largest production place for ion exchange resins,¹³ we propose a novel process for manufacturing the polystyrene/PVDF cation exchange alloy membrane, in which polystyrene-DVB/PVDF alloy powder will be sulfonated according to the same method employed in the production of cation exchanger, and then directly thermoformed to form the cation exchange membrane with the semi-interpenetrating polymer network structure. For optimizing the preparation process, the effects of the polystyrene-DVB to PVDF mass ratio and the DVB content in the monomers on the physical and electrochemical properties of the prepared alloy membrane

will be investigated. For the quality control, a commercially available heterogeneous cation exchange membrane is chosen to compare with our custom-made membranes.

EXPERIMENTAL

Materials and Chemicals

Poly(vinylidene fluoride) (PVDF, FR904) powder was purchased from Shanghai Sanaifu Co. Ltd. (China). Styrene was ordered from Beijing J&K Scientific (China). Divinylbenzene (DVB) with a purity of wt. 63.2% and Benzoyl peroxide (BPO) were of technical grade, and provided by Shangyu Pure Resin (Shaoxing, China). The commercial heterogeneous cation exchange membrane (code-named QHC) and nylon reinforcing fabrics were gifts from Qianqiu Water Treatment (Hangzhou, China). Other chemicals were obtained from local suppliers.

Alloy Membrane Preparation

In a typical example, the solution of 28.1 g styrene, 1.9 g DVB and 1.3 g BPO (the monomer solution) was slowly added into a solution of 30.0 g PVDF in 80 mL DMF (*N,N*-dimethylformamide). The mixture was stirred at 60°C for at least 1 h until it formed a homogeneous complex solution. The complex solution was polymerized under nitrogen atmosphere at 85°C for 12 h. The resulting jellylike polymer gel was put into the boiling water where it precipitated into white particles. After being filtered out from water, dried at 105°C for 2 h, and ground to the 50 mesh sieve size, the received polystyrene/PVDF alloy powder (53.2 g) was preswelled in 100 mL DCE (1,2-dichloroethane) in a 1-L flask for 3 h, and then sulfonated for 6 h at 80°C by addition of 300 mL concentrated sulfuric acid (more than 98 wt %). The sulfonated product was thoroughly washed with water, and then immersed into 1 N NaOH solution overnight to transform into Na⁺ form. After being filtered out from NaOH solution, dried at 105°C until the constant weight, the gained cation exchange alloy powder was mixed with small amounts of additives such as methyl red (coloring agent), pentaerythritol tetrastearate (anti-oxidant) and calcium stearate (releasing agent) at 170–180°C for 15 min within a CF-1L mixing machine (Chang Feng Rubber & Plastics Machinery, Dongwan, China). After that, a CF-120 open mill machine (also Chang Feng Rubber & Plastics Machinery) was used to perform the alloy membrane and control its thickness within 0.35–0.40 mm. The operation temperature was also 170–180°C. In some cases, 80-mesh nylon fabric sheets were placed on the bottom and the upper sides of the preformed alloy membrane, and the system was hot pressed at 30 MPa and 170–180°C for 35 min by a column-type plate vulcanizing press machine (Yahua Machinery, Qingdao, China). The whole process is shown in a chart in Figure 1, and the contents of styrene, DVB, and PVDF in each experiment are listed in Table I.

Fourier Transform Infrared, Scanning Electron Microscopy

The components of alloy particles prepared in different stages were confirmed by Fourier transform infrared (FTIR) (Tensor 27, Bruker Optics, Germany). After being fractured, cast into liquid nitrogen and finally sputter-coated with gold, the inner morphologies of alloy membranes were analyzed by scanning electron microscopy (SEM) (Utral 55, Carl Zeiss, Germany).

Table I. Compositions of Cation Exchange Alloy Membranes

Sample no.	DVB content ^a (wt %)	$R_{\text{St-DVB/PVDF}}^{\text{b}}$ (-)
Variation in $R_{\text{St-DVB/PVDF}}$		
Sample 1	5.0	0.6
Sample 2	5.0	0.7
Sample 3	5.0	0.8
Sample 4	5.0	0.9
Sample 5	5.0	1.0
Variation in DVB content		
Sample 6	4.0	0.8
Sample 7	3.0	0.8
Sample 8	2.0	0.8
Sample 9	1.0	0.8

^aThe mass percentage of DVB to the monomer mixture (styrene and DVB).

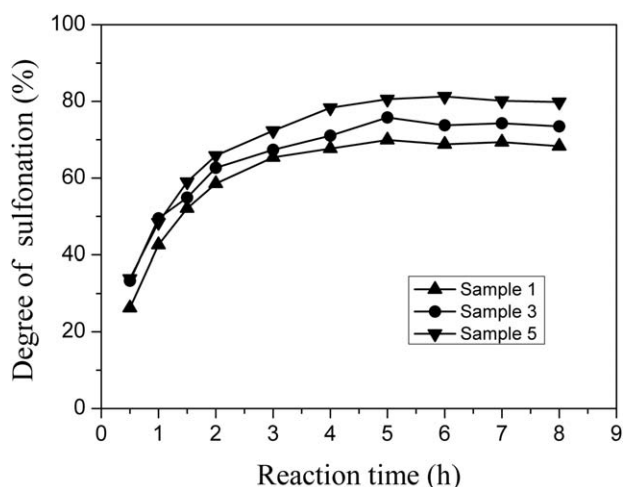
^bThe mass ratio of the monomer mixture (styrene and DVB) to PVDF powder in the styrene/DVB/PVDF/DMF complex solution.

Water Content, Ion Exchange Capacity

To measure the water content, samples were soaked in deionized water for 24 h, removed the surface water with a filter paper, and immediately weighed. The samples were dried under vacuum at 60°C until the constant weight. The water content was defined as the mass percentage of soaked water per gram of dry sample, $W_c = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$, in which W_{wet} and W_{dry} represented the weights of the wet and the dry samples, respectively. The ion exchange capacity (IEC) was determined by the back titration method.¹⁴ From that, the H-form sample (about 0.2 g) was equilibrated with 0.01 N NaOH solution (100 mL) and carried out back titration with 0.01 N HCl solution. The IEC (mmol/g) was equal to the net consumption of NaOH in milliequivalents per gram of the dry sample.

Area Resistance, Apparent Transport Number

According to the classical test method,^{15–17} a two-compartment electrolytic cell system was employed to measure the area resistance (r) and the cation apparent transport number (t^+). In our

**Figure 2.** Sulfonation degree as a function of reaction time.

system, the geometric parameter of cell (κ) was set to be 1.0 cm^{-1} , and the effective surface area of membrane sample (A) was 1.0 cm^2 . The r was therefore simplified to be the difference between $1/\sigma_1$ and $1/\sigma_0$, where σ_0 and σ_1 referred to the conductivities of the blank and the sample-loaded systems, respectively. As far as the cation apparent transport number was concerned, the system was loaded a membrane sample to hold-off 0.1 N KCl and 0.01 N KCl solutions. After the electric potential between two sides was measured by a digital multimeter, the membrane potential and the t^+ value could be estimated by the Nernst equation.

Dimensional Stability¹⁷

For the dimensional stability tests, two 5.0 × 3.0 cm rectangular membrane samples were vertically immersed in 0.5 N and 3.5 N NaCl solutions for 24 h respectively, and then measured their three-dimensional (3D) sizes with a digital micrometer.¹⁷ Although x_0 , y_0 , and z_0 were the dimensions after immersing in 3.5 N NaCl solution, x_1 , y_1 , and z_1 represented the values in the case of 0.5 N NaCl. As a result, 3D changes were calculated from $(x_1 - x_0)/x_0 \times 100\%$, $(y_1 - y_0)/y_0 \times 100\%$ and $(z_1 - z_0)/z_0 \times 100\%$, respectively.

Bursting Pressure Test

Before a test, membranes were cut into the circular shape (5.0-cm diameter), and fixed tightly on the bottom of a stainless steel column filled with glycerol. With the increase of given nitrogen pressure from the column top, the membrane would break suddenly, where the bursting pressure was recorded. Three samples were used in each test, and the average value was reported.

RESULTS AND DISCUSSION

Sulfonation

Sulfonation of the pulverized polystyrene/PVDF alloy powder was carried out with 1,2-dichloroethane as the swelling agent and concentrated sulfuric acid as the sulfonation agent, according to the same method widely employed in the manufacture of strongly acidic polystyrene-based cation exchange resins. From Figure 2, the sulfonation had almost completed after 6 h under given conditions but only having the maximal reaction degree

Table II. Effect of $R_{\text{St-DVB/PVDF}}$ on Sulfonation Degree^a

$R_{\text{St-DVB/PVDF}}$	Theoretical IEC ^b (mequiv./g)	Experimental IEC (mequiv./g)	Degree of sulfonation (%)
0.6	2.63	1.81	68.8
0.7	2.82	1.99	70.6
0.8	2.97	2.19	73.7
0.9	3.11	2.40	77.2
1.0	3.22	2.57	79.8

^aDVB content = 5.0 wt %, 50 g polystyrene/PVDF alloy powder in 100 mL 1,2-dichloroethane and 300 mL concentrated sulfuric acid, sulfonation for 6 h at 80°C.

^bThe theoretical IEC is equal to the maximum value on the assumption that all of polystyrene components in alloy powder are sulfonated entirely.²⁰

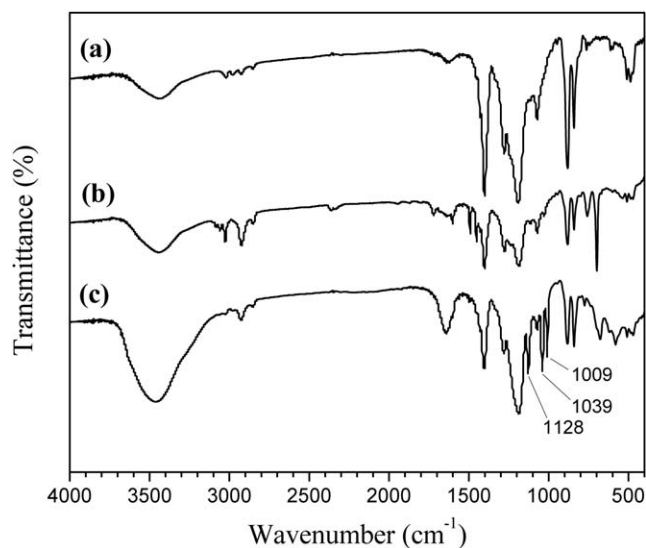


Figure 3. FTIR spectra of (a) PVDF powder, (b) Polystyrene-DVB/PVDF alloy powder, and (c) Sulfonated cation exchange alloy powder.

less than 80% (from 68.8 to 79.8%, listed in Table II). However, the sulfonation degree of the classical strongly acidic polystyrene-based cation exchange resins mostly exceeded 90%. The difference in the two sulfonation degrees indicated that the interpenetration of inert PVDF reduced the reaction accessibility of polystyrene component, leading to the decrease of the sulfonation degree with the increase of PVDF content (corresponding $R_{\text{St-DVB/PVDF}}$ from 1.0 to 0.6). Finally, the introduction of sulfonic acid groups into the polystyrene/PVDF alloy powder was confirmed by the FTIR spectra (Figure 3). From the spectra 3(c), two sharp peaks respectively at 1128 and 1009 cm^{-1} , as well as the S=O stretching vibration at 1039 cm^{-1} , were observed, all attributing to the SO_3^- group features.

Membrane Morphologies

Morphologies of the prepared cation exchange alloy membranes were exhibited by SEM. Figure 4 showed their images in the cross-section at various DVB contents and $R_{\text{St-DVB/PVDF}}$ values. The white regions emerged in these images were most likely to represent the $\text{C}_6\text{H}_5\text{SO}_3^-$ functional clusters, which had been embedded in the PVDF matrix. Compare with (a), (b), and (c), an obvious fact that more functional clusters appeared with the increase of $R_{\text{St-DVB/PVDF}}$ from 0.6, 0.8 to 1.0 will be observed. Consequently, a uniform distribution of functional clusters has been proved to exist in all samples, particularly in Sample 5 [Figure 4(c)].

As Liu et al.¹⁸ had pointed out, the solvent played an important role in determining the ultimate morphology of PVDF membrane. When DMF used as the PVDF solvent and water as the coagulant, a uniform porous structure could form, due to the high mobility of PVDF chains in DMF and the relatively strong affinity between DMF and water.¹⁹ However, the crosslinking by DVB in polystyrene/PVDF alloy powder or membrane would limit the moving of PVDF. As a result, with increasing DVB content from 1.0% (Sample 9), 3.0% (Sample 7), to 5.0% (Sample 3), the alloy membrane structure transformed into the semi-

interpenetrating network feature [Figure 4(b,c)] from the honeycomb-like feature (see 4(e)).

Effects of DVB Content on Membrane Properties

For a practical viewpoint, the prepared alloy membranes should have the proper physical and electrochemical properties, such as water content (W_c), IEC, area resistance (r), apparent transport number (t^+) and dimensional stability. We first focused on the effects of DVB content on these properties, by fixing $R_{\text{St-DVB/PVDF}}$ value equal to 0.8. As we know, the increase of DVB content in the polystyrene/PVDF alloy polymer would produce a more dense structure. Therefore, the water content decreased rapidly from 49.2 to 35.5% [shown in Figure 5(a)], and the apparent transport number increased accordingly from 0.84 to 0.96 [Figure 5(d)]. Based on the result discussed by Choi et al.,²⁰ the crosslinking polymer network could prevent the sulfonation agent from penetrating into polystyrene/PVDF alloy powder, which led to the decrease of IEC. But from Figure 5(b), the effect of DVB content on IEC was negligible. This phenomenon might be attributed to the preswelling of the alloy powder in 1,2-dichloroethane before sulfonation, which could facilitate the penetrating of concentrated sulfuric acid into the alloy powder, to obtain an approximately equal IEC at serial DVB contents.

The area electrical resistance of ion exchange membrane was closely related to the ionic conduction, which mainly depended on the water content and the quantity of functional groups (IEC). In detail, the conduction of counter-ions in an ion exchange membrane was accomplished mainly through the behavior of adsorption and dissociation between fixed functional groups, whereas the migration of co-ions took advantage of the hydrated channels formed by free water molecules in the interstitial regions. Therefore, more fixed functional groups could promote the conduction of counter-ions, and the water molecules would facilitate the migrations of both co-ions and counter-ions. Consequently, the area electrical resistance had a small amplitude increase with increasing DVB content by possessing relatively less hydrated channels, as shown in Figure 5(c). Fortunately, the area resistances of all samples were noticeably lower about 50–60% than the commercial heterogeneous membrane QHC (10.12 $\Omega\cdot\text{cm}^2$). Similar to the area electrical resistance, the transport number was also affected by IEC and water content. As DVB content increased, a more dense structure, an obvious decrease in water content, and an approximately equal IEC, had synthetically resulted in a favorable improvement in the transport number. Moreover, the samples at 1.0 and 2.0% DVB content exhibited the inferior transport number compared with the control membrane QHC, indicating that the adequate DVB content was essential to obtain a desirable permselectivity for the present alloy membrane.

In the practical applications, the dimensional stability in various electrolyte solutions is the most desirable criteria for any commercially successful ion exchange membrane products. For roundly estimating to this property, the membranes both covered and uncovered the nylon reinforcing fabrics were prepared and tested. The results were displayed in Figure 6. From that, an obvious decreasing tendency could be observed with the

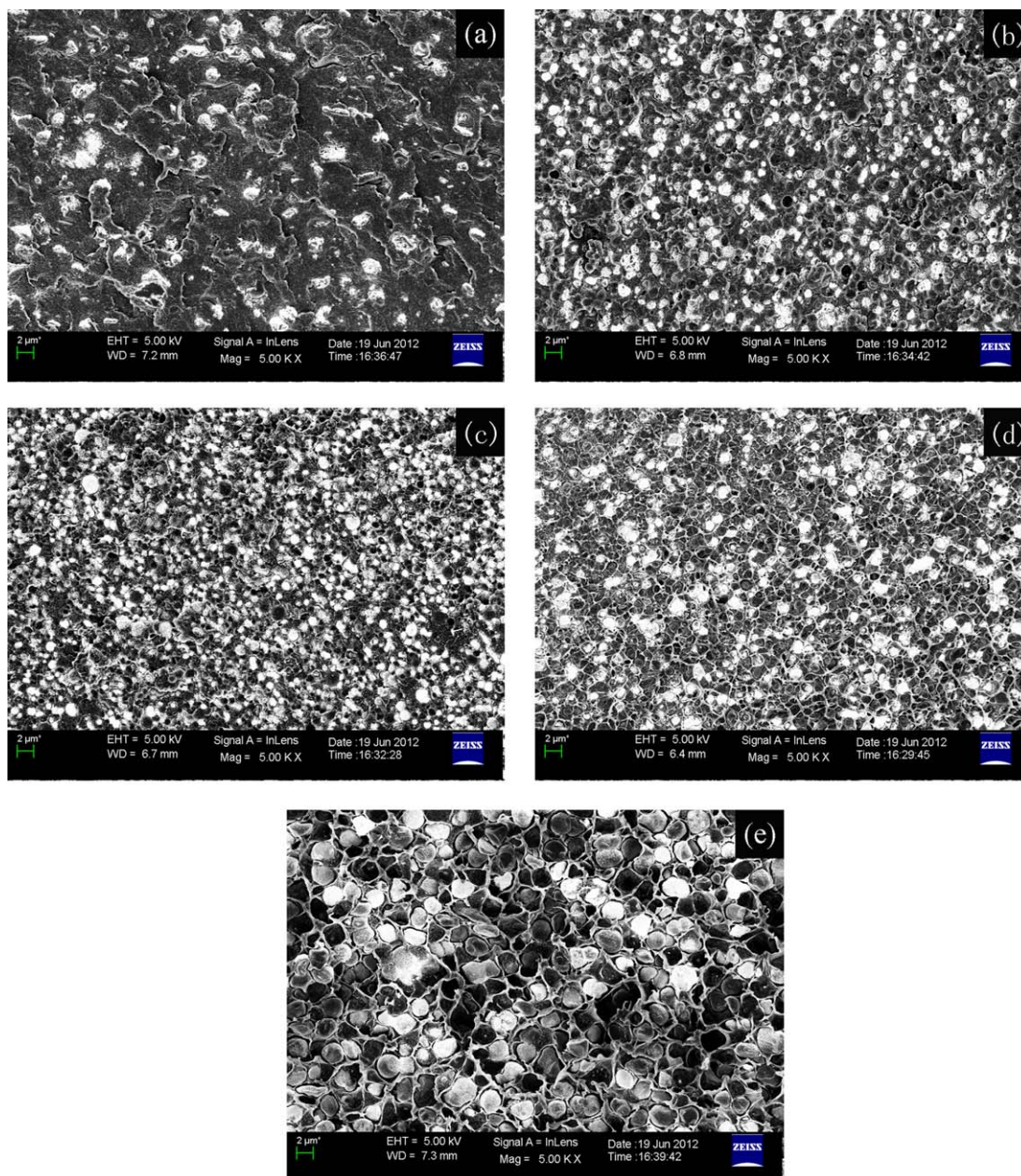


Figure 4. SEM images of prepared cation exchange alloy membranes: (a) Sample 1, (b) Sample 3, (c) Sample 5, (d) Sample 7, and (e) Sample 9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase of DVB content, indicating that the denser alloy structure had generated and thus limited alloy membranes' swelling in NaCl solutions. With respect to the reinforcing fabrics, the prepared alloy membranes at low DVB contents, as well as the commercial heterogeneous membrane QHC, had been remarkably improved on the 3D stability. But in the case of samples at high DVB contents (4.0 and 5.0%), the nylon reinforcing fabrics only could improve this property to a little extent. It was worthwhile to mention that the dimensional stabilities of these two alloy membranes were better than that of the reference QHC, which demonstrated that our unreinforced alloy membranes had the potential for direct applications. In addition, the almost identical 3D changes (calculated from Figure 6, not

shown) for all alloy membranes corroborated once again the uniform distribution of functional groups.

Effects of $R_{St-DVB/PVDF}$ Values on Membrane Properties

With the increase of $R_{St-DVB/PVDF}$ value, the polystyrene-DVB/PVDF alloy particles would supply more polystyrene component for sulfonation, and therefore produced higher IEC and water content, as shown in Figure 7(a,b). As a result, an overall decreasing tendency in the area electrical resistance appeared [Figure 7(c)]. A noticeable high r value ($6.63 \Omega \cdot \text{cm}^2$) at $R_{St-DVB/PVDF}$ of 0.6 could be attributed to the diffusion limitation of ionic conduction, caused by the segregation of ionic domains due to the lack of functional groups. However, the conduction

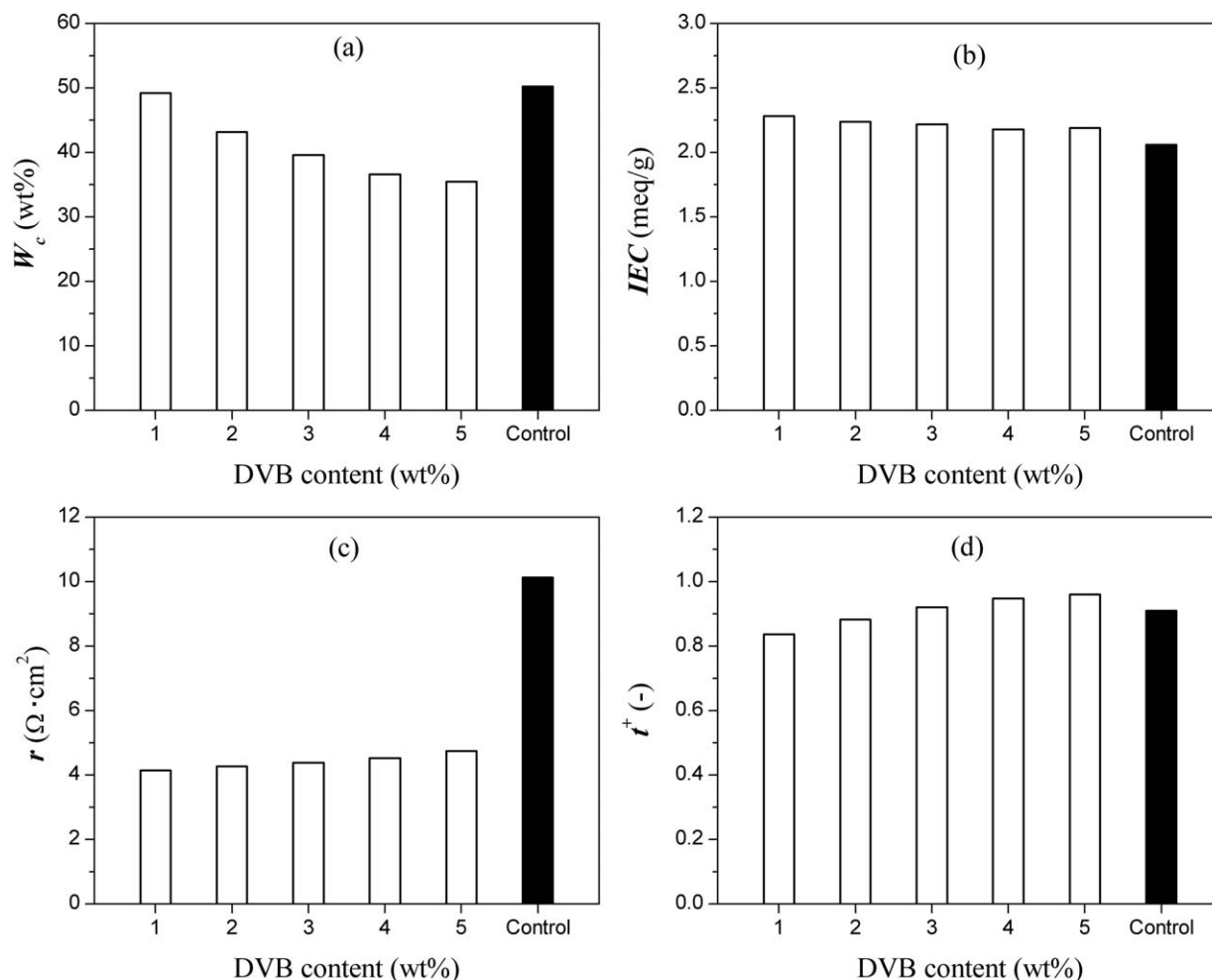


Figure 5. Effect of DVB content on: (a) Water content; (b) IEC; (c) Area resistance; (d) Apparent transport number.

of counter-ions had been facilitated to a larger degree by supplying more fixed functional groups, though both counter-ions' and co-ions' migration processes were enhanced due to the increase of water content. Finally, the transport number rose slowly, as shown in Figure 7(d). Conversely, the transport number at $R_{\text{St-DVB/PVDF}}$ of 1.0 decreased slightly (from 0.96 to 0.95), which could be explained for the existence of incompatibility domains between the hydrophobic PVDF matrix and the aggregation of excessive hydrophilic SO_3^- groups, and the partially broken semi-interpenetrating network structure provided some additional channels for the co-ions' migration, and consequently caused a slight decrease of the transport number.

Figure 8 shows the 3D changes of the alloy membranes at serial $R_{\text{St-DVB/PVDF}}$ values. The result indicated that the values increased regularly, which arose from the higher water content and more functional groups because of the increased $R_{\text{St-DVB/PVDF}}$. Further, the fact that the nylon reinforcing fabrics had only slightly improved the 3D stability of our alloy membranes, had been confirmed again by Figure 8, as done by Figure 6.

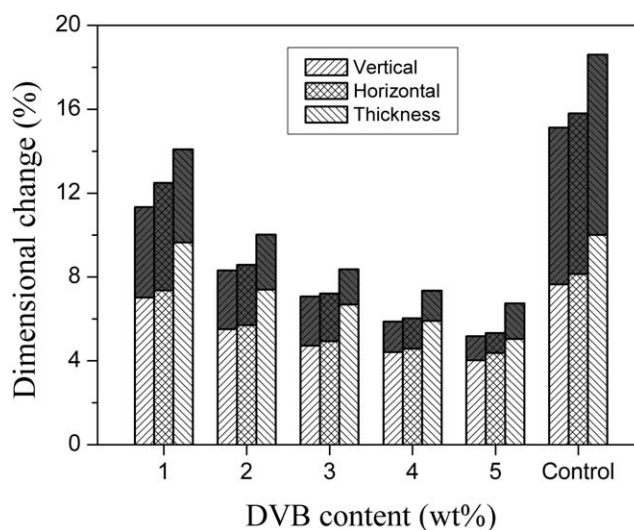


Figure 6. 3D changes at serial DVB contents. The upper legends refer to the samples without reinforcing fabrics, and the lower legends refer to the samples with nylon reinforcing fabrics.

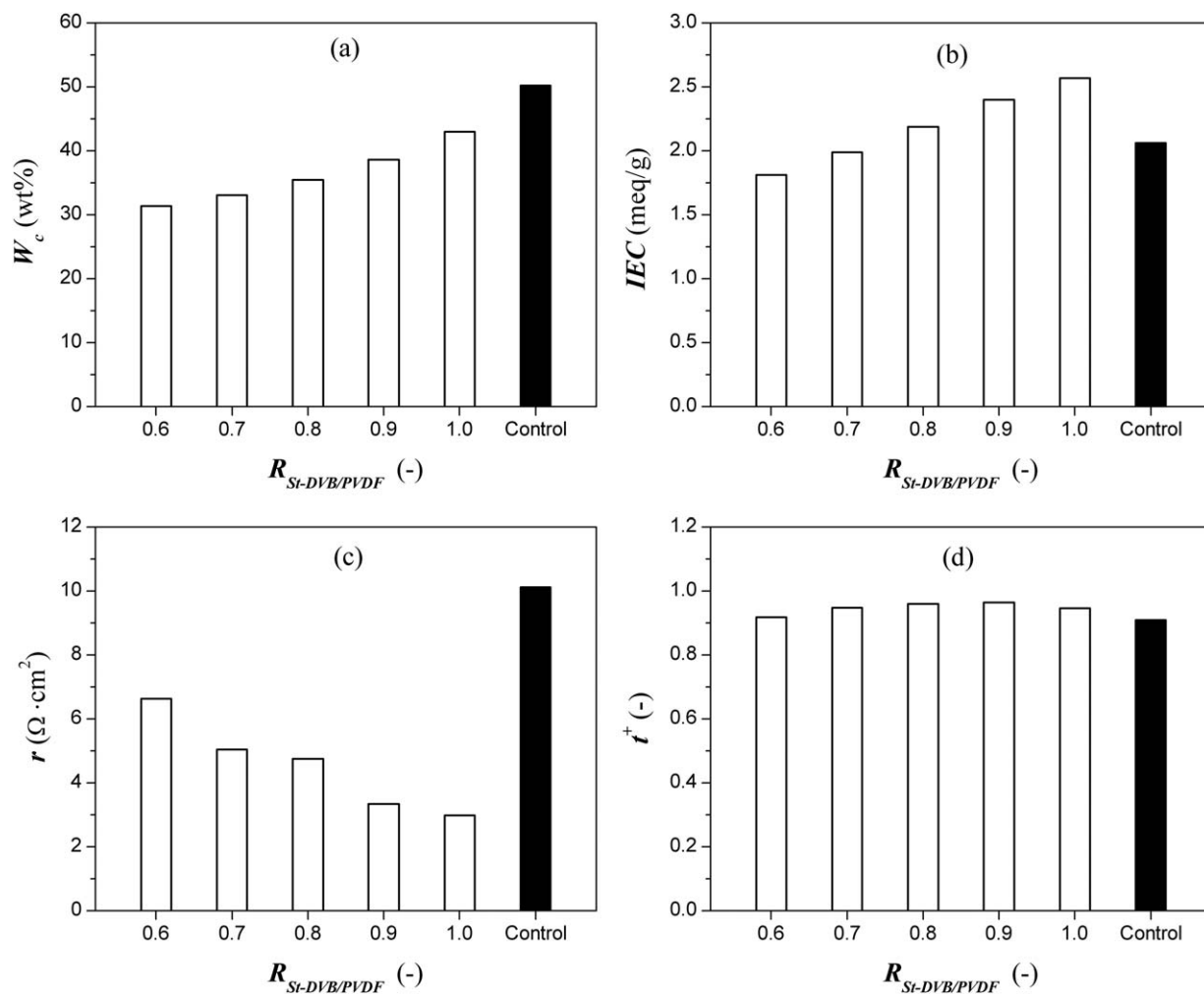


Figure 7. Effect of $R_{St-DVB/PVDF}$ value on: (a) Water content; (b) IEC; (c) Area resistance; (d) Apparent transport number.

Bursting Pressure

There was no doubt that the mechanical strength of a membrane determined the success or failure of its practical application. For the commercial heterogeneous membrane QHC, the nylon reinforcing fabric was absolutely necessary, by preventing from the dropout of ion exchange resin particles and strikingly improving the bursting pressure from 0.15 to 0.65 Mpa (shown in Figure 9). But in the case of our alloy membranes, only no more than 40% improvements from 0.5 to 0.7 Mpa (Samples 8 and 9) were obtained by the nylon reinforcing fabric. In practice, the bursting pressure up to 0.5 Mpa has already met most of industrial applications. It further illustrated that the custom-made alloy cation exchange membrane with the semi-interpenetrating polymer network structure showed the great potential for the future applications.

CONCLUSIONS

By combining the manufacturing method of cation exchange resins with the thermoforming process of heterogeneous ion exchange membranes, the polystyrene-DVB/PVDF cation

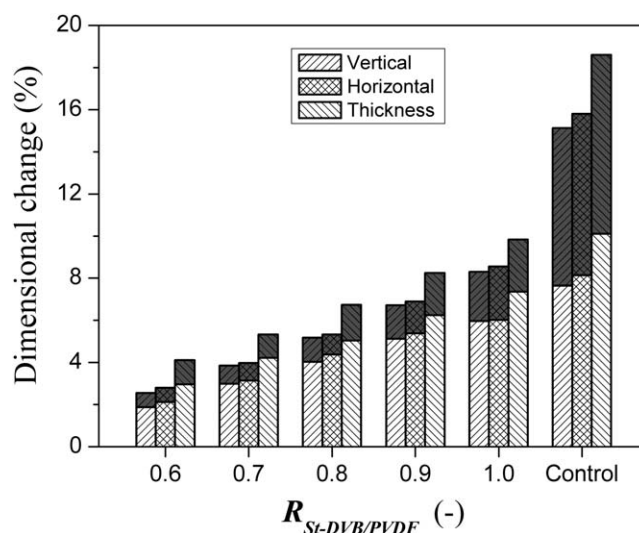


Figure 8. 3D changes at serial $R_{St-DVB/PVDF}$ values. The upper legends refer to the samples without reinforcing fabrics, and the lower legends refer to the samples with nylon reinforcing fabrics.

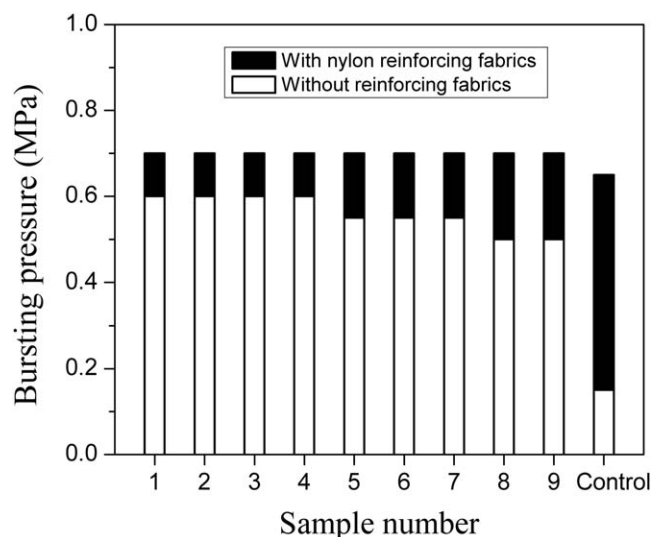


Figure 9. Effect of nylon reinforcing fabrics on bursting pressure. The sample numbers (from 1 to 9) refer to those listed in Table I.

exchange particles and the alloy membranes were prepared. The present membranes have a structure of semi-interpenetrating polymer network, and exhibit the excellent physical and electrochemical properties obviously superior to the commercial heterogeneous cation exchange membrane. The result encourages the further development of the custom-made alloy membrane products and their electro-driven applications in some specific areas. Up to now, these works are under the way.

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