

# Preparation of Novel Semihomogeneous Cation-Permeable Membranes from Blends of Sulfonated Poly(phenylene sulfide) and Sulfonated Phenolphthalein Poly(ether ether ketone)

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**ABSTRACT:** A series of semihomogeneous cation-exchange membranes were prepared with binary blend systems, such as sulfonated phenolphthalein poly(ether ether ketone) (SPEEK-C)/sulfonated poly(phenylene sulfide) (SPPS), or ternary blend systems, such as phenolphthalein poly(ether ether ketone) (PEEK-C)/SPEEK-C/SPPS, by solution blending and phase inversion, in which PEEK-C and SPEEK-C acted as binders and SPPS powder acted as a polyelectrolyte. Compared with homogeneous and heterogeneous membranes, the prepared semihomogeneous membranes had good electrochemical properties and mechanical strength as well as good dimensional stability. The fundamental properties of the membranes, such as the ion-ex-

change capacity, water content, electrical resistance, transport number, diffusion coefficient of the electrolytes, and streaming potential, were largely dependent on both the loading of the SPPS resin and the sulfonation degree of PEEK-C. Through the adjustment of these two important parameters, a series of semihomogeneous membranes with the desired conductivity and selectivity and the proper water content for different industrial purposes, such as electrodialysis, diffusional dialysis, and proton exchange, were achieved. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1478–1485, 2004

**Key words:** membranes; ion exchangers; semihomogeneous

## INTRODUCTION

Homogeneous and heterogeneous ion-exchange membranes supercede each other in different ways. Homogeneous membranes, having good electrochemical properties, lack mechanical strength, whereas heterogeneous membranes, having very good mechanical strength, are comparatively poor in their electrochemical performances.

A heterogeneous membrane, in which the functional group is not chemically connected to the membrane polymer chains, can be made through the mechanical incorporation of a powdered ion-exchange resin into sheets of rubber, poly(vinyl chloride) (PVC), acrylonitrile copolymers, or some other extrudable or moldable matrix. Such membranes can be prepared through (1) the calendaring of ion-exchange particles into an inert plastic film, (2) the dry molding of inert film-forming polymers and ion-exchange particles and

the subsequent milling of the mold stock, (3) the dispersion of resin particles in a solution containing a film-forming binder and the subsequent evaporation of the solvent, or (4) the dispersion of a resin powder in a monomer and subsequent polymerization to produce an ion-exchange membrane.<sup>1–6</sup> A support is usually added to the preparation to obtain reinforced membranes. In these routes, the ion-exchange resin made from the styrene–divinylbenzene copolymer is commonly used as a functional material. In addition, the synthesized functional polymeric powder is used instead of ion-exchange particles for the same purpose.<sup>7</sup>

Meanwhile, a homogeneous membrane, in which the functional groups have been chemically bonded with the membrane polymer chains, is often obtained (1) through the functionalization of the styrene–divinylbenzene copolymer, (2) through the functionalization of the aromatic polymers, or (3) from solution blends of the functional aromatic polymers and non-functional polymers.<sup>8–12</sup> In these processes, a cation-exchange membrane is often obtained by sulfonation, whereas an anion-exchange membrane is obtained through chloromethylation and quaternary amination.

To combine the advantages of these two kinds of membranes, that is, to avoid their disadvantages, we need a new kind of membrane with excellent electro-

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chemical properties and mechanical strength. If a polymer with limited functional groups is used as a binder instead of a neutral polymer such as PVC<sup>2,3</sup> or PES<sup>7</sup> in the aforementioned membrane preparation route for heterogeneous membranes, a new kind of membrane, called a semihomogeneous membrane, can be expected, having the features of both homogeneous and heterogeneous membranes. The heterogeneous functional groups provide good mechanical strength, whereas the homogeneous functional groups provide excellent electrochemical properties.

In a previous article, we proposed a new route for a heterogeneous cation-exchange membrane based on solution blends with sulfonated poly(phenylene sulfide) (SPPS) and the neutral polymer PES.<sup>7</sup> Continuing on this topic, here we report studies on the preparation and properties of semihomogeneous cation-exchange membranes based on sulfonated phenolphthalein poly(ether ether ketone) (SPEEK-C), which is used as a binder in which SPPS particles are dispersed. The importance of this investigation lies in an elaborate study of the effect of the sulfonation of phenolphthalein poly(ether ether ketone) (PEEK-C) and the loading of the resin on the different mechanical and electrochemical properties of the membranes.

## EXPERIMENTAL

### Materials

Poly(phenylene sulfide) (PPS) and PEEK-C were conventional polymers purchased on the Chinese commercial market. Concentrated (98 wt %) fuming sulfuric acid (20% SO<sub>3</sub>), dimethylformamide (DMF), and other chemicals were obtained commercially and were used without further purification. All chemicals used in the experiments were analytical-grade.

### Sulfonation of PPS and PEEK-C

The sulfonation method for PPS was the same as that used in our previous studies.<sup>7</sup> In this study, SPPS with an ion-exchange capacity (IEC) of 2.6 mequiv/g (sulfonation degree = 0.35) was used for the preparation of the semihomogeneous membranes. The particle size of the resins was about 200 mesh, corresponding to an average particle size of 60 μm.

The sulfonation of PEEK-C has been reported in the literature<sup>10–12</sup> and can be described as follows. The polymer was dried for more than 6 h in an oven at 100°C, and 500 mL of concentrated sulfuric acid was heated to 60°C; then, 60 g of the polymer powder was dispersed in the concentrated sulfuric acid. The reaction mixture was stirred for a certain time to achieve a certain sulfonation degree. The final solution was precipitated with iced water and washed until the pH was nearly 7, and the obtained SPEEK-C was subse-

quently dried in an oven at 60°C for at least 20 h to produce the sulfonated polymers. The degree of sulfonation was determined via a combination of acid–base titration and gravimetry and was controlled by the reaction time. Preliminary tests showed that SPEEK-C of a higher sulfonation degree was not suitable for a binder and was even water-soluble. Therefore, three kinds of SPEEK-C were used for the later membrane preparation; the sulfonation times were 0, 1.5, and 3 h, which corresponded to IEC values of approximately 0, 0.35, and 0.55 mequiv/g, respectively, at the experimental temperature.

### Membrane preparation

The membrane preparation followed a route analogous to one reported in a previous article.<sup>7</sup> Binary solutions were prepared through the dissolution of PEEK-C or SPEEK-C of different sulfonation degrees in DMF overnight at room temperature so that PES could dissolve sufficiently. SPPS resins of different loadings were then dispersed in the binary solutions to form ternary dispersions. The mixtures were stirred for 3 min, and air bubbles were extracted through vacuumizing to form casting solutions.

At room temperature, these viscous solutions were cast onto glass plates with a proper glass knife to form thin films. They were immediately immersed in iced water to precipitate the polymer and form membranes. Then, the membranes were pretreated with 1M HCl and 1M NaOH solutions four times and washed with deionized water for a further evaluation of the membrane properties.

For comparison, ternary polymer systems were obtained from solution blends of PEEK-C, SPEEK-C, and SPPS, and corresponding supported and nonsupported membranes with different blend ratios were prepared with an analogous casting procedure.

### Evaluation of the membrane properties

The characteristic properties of the investigated membranes included the IEC, water uptake ( $C_R$ ), wet thickness ( $d$ ), area resistance ( $R_m$ ), diffusion coefficient ( $D$ ), membrane potential ( $E$ ), streaming potential, and flux. The methods were completely the same as those described in our previous articles,<sup>7,13–15</sup> except that the streaming potential and flux could be described as follows.

The unit used for the simultaneous determination of the streaming potential and flux is shown in Figure 1. It was constructed from two sections made of a poly(methyl methacrylate) resin, and specially designed Ag/AgCl electrodes were connected to each section. Each membrane (effective area = 3.94 cm<sup>2</sup>), preconditioned with a 1M KCl solution, was mounted between the half-cells. Before the experiment was begun, the

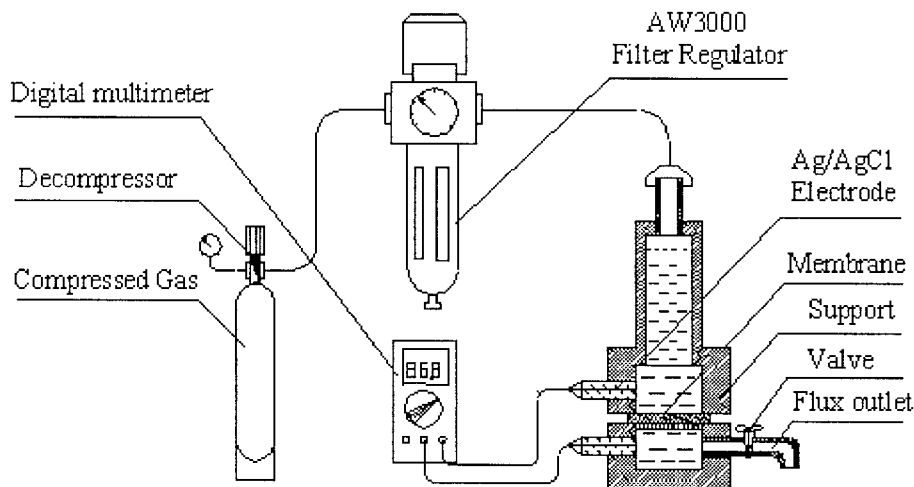


Figure 1 Schematic drawing for the simultaneous determination of the streaming potential and flux.

compartments were filled with a 0.1M potassium chloride solution. The potential drop between the two electrodes was recorded with a digital multimeter (DT9205, Zhangzhou Mater Electronics Co., Ltd.) at given pressure intervals. At least 8–10 different pressure differences ( $\Delta P$ ) were applied, and the electrical potential difference ( $\Delta E$ ) was measured. Then, the streaming potential was calculated as the ratio of the measured electric potential drop over the applied pressure difference, that is,  $\Delta E/\Delta P$ .

The flux was determined in the same unit at a fixed  $\Delta P$  value of 0.3 MPa. Fluxes (corresponding to a 0.1M KCl solution) were determined through the measurement of the time taken to collect a given volume of the permeate mass and were calculated as follows: flux =  $V/(At\Delta P)$ , where  $V$  is the total volume of the solution permeated during the experiment,  $A$  is the membrane area,  $t$  is the operation time, and  $\Delta P$  is the pressure difference across the membranes.

All these properties were evaluated at room temperature (20–22°C).

## RESULTS AND DISCUSSIONS

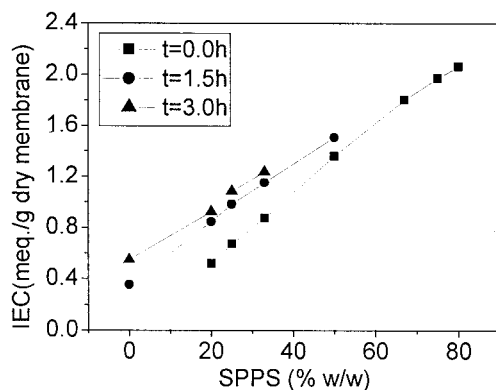
### Physical appearance of the membranes

Because the apparent properties of the membranes, such as the homogeneity, the compatibility of the SPPS resin and PEEK-C or SPEEK-C binder, and the mechanical strength could be preliminarily evaluated from the physical appearance of the prepared membranes, the physical appearances of the cation-exchange membranes prepared from PEEK-C or SPEEK-C and SPPS resins of different loadings are presented in Table I. For both kinds of binders (PEEK-C and SPEEK-C), with an increase in the resin loading, the membranes changed from flexibility to brittleness; this suggested that the compatibility of the resin binders

decreased as the SPPS loading increased. The physical appearance also could change with the sulfonation degree of SPEEK-C. For example, the resin loading for PEEK-C could be as high as 75% without any brittleness, whereas for SPEEK-C with IEC = 0.35 mequiv  $g^{-1}$  (sulfonation time = 1.5 h), the membranes became brittle at a loading greater than 50%, and for SPEEK-C with IEC = 0.55 mequiv  $g^{-1}$  (sulfonation time = 3 h), the membranes became brittle at a loading greater than 33%; this indicated that the longer the sulfonation time was (corresponding to a higher degree of sulfonation), the lower the resin loading was. This may be explained by the membrane formation process and the interactions between the solvent, nonsolvent, and polymers. As reported in the Experimental section, the

TABLE I  
Physical Appearance of Membranes 0.5 mm Thick (wet)  
with Different Sulfonation times of PEEK-C and  
Loadings of the SPPS Resin

| Sulfonation time of PEEK-C (h)            | SPPS (wt %) | Physical appearance |
|---|-------------|---------------------|
| 0 (IEC = 0 mequiv. of dry membrane)       | 20          | Fine                |
|   | 25          | Fine                |
|   | 33          | Fine                |
|   | 50          | Fine                |
|   | 67          | Fine                |
|   | 75          | Fine                |
| 1.5 (IEC = 0.35 mequiv/g of dry membrane) | 80          | Brittle             |
|   | 0           | Fine                |
|   | 20          | Fine                |
|   | 25          | Fine                |
|   | 33          | Fine                |
| 3 (IEC = 0.55 mequiv/g of dry membrane)   | 50          | Brittle             |
|   | 0           | Fine                |
|   | 20          | Fine                |
|   | 25          | Fine                |
|   | 33          | Brittle             |



**Figure 2** Effect of the SPPS resin loading and sulfonation time of PEEK-C on the IEC of the membranes.

membranes were prepared by a phase-inversion method. Therefore, the membrane structure largely depended on the polymer-solvent-gelatin medium (nonsolvent) system. For a membrane prepared from PEEK-C or SPEEK-C of low sulfonation, the interaction between the polymer and the solvent (DMF) was less than that between the solvent and the gelatin medium (water); therefore, the speed of the solvent diffusing out of the membrane was greater than that of the nonsolvent diffusing into the membrane. On the basis of the phase-inversion mechanism,<sup>16,17</sup> the final membranes prepared from PEEK-C or SPEEK-C of low sulfonation could be denser and stronger in their mechanical properties. For a membrane prepared from SPEEK-C of a high sulfonation degree, the situation was the opposite, and so the loading was reduced to achieve the proper mechanical strength. In addition, with an increase in the sulfonation degree of SPEEK-C, the polymer chain of a membrane was easily hydrated, and the mechanical strength decreased correspondingly.

The morphological behavior of the membranes prepared in this study was similar to that of our previous system, SPPS/PES;<sup>7</sup> it is not the focus of this article and is not, therefore, shown here.

### IEC and the water content

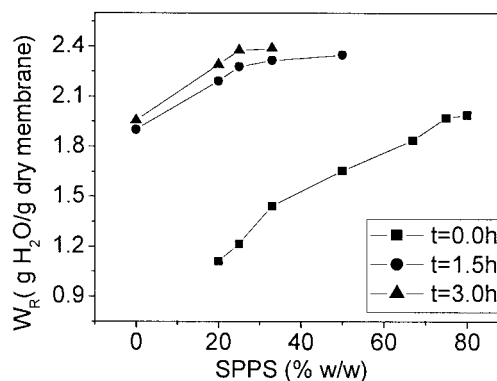
For practical purposes, a sufficient IEC and a proper moisture content are expected for such membranes. As shown in Figure 2, the IEC of membranes prepared from the SPPS resin and SPEEK-C of different sulfonation times (and, therefore, different sulfonation degrees) linearly increased with an increase in the resin loading and conformed approximately to the theoretically calculated curves. However, the slopes of the curves differed slightly: the higher the sulfonation degree of SPEEK-C, the smaller the slope of the curve. This occurred because the functional groups came from two parts: SPPS and SPEEK-C. When the total

weight of a membrane was fixed, an increase in the resin loading meant a decrease in SPEEK-C. Therefore, the net increase in IEC was equal to the IEC difference between increased SPPS and decreased SPEEK-C. It is not hard to understand why the slope decreased with an increase in IEC of SPEEK-C.

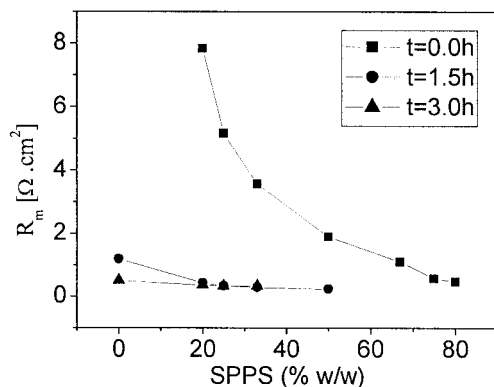
The water content increased with an increase in the SPPS resin loading (Fig. 3). This may have happened because, as for most charged membranes, the water content increased in the order of IEC on account of the strong hydration effect of the functional groups. For a given quantity of the SPPS resin, the membrane water content dramatically increased with the sulfonation time of PEEK-C in comparison with unsulfonated PEEK-C. Of course, an increase in IEC due to the sulfonation of PEEK-C contributed to the water content. Another possible reason was that, for a membrane prepared from the SPEEK-C binder with a higher sulfonation degree, the resin particles were loosely wrapped in the binder, and the membrane was more hydrated during the immersion by water, as mentioned previously; therefore, a substantial increase was observed when SPEEK-C was used as a binder. This provided a convenient way of controlling both the water content and IEC, except through controlling the mesh size of the resin, as described in our previous article;<sup>7</sup> that is, through the adjustment of the loading of SPPS and the sulfonation time of PEEK-C, a series of membranes with desired IECs and water contents can be reasonably acquired to satisfy different industrial demands.

### $R_m$

Besides sufficient IECs and proper water contents, membranes should have good electrical resistance. As expected, the area membrane resistance decreased with an increase in the SPPS loading for all the considered systems (Fig. 4). In the membranes prepared

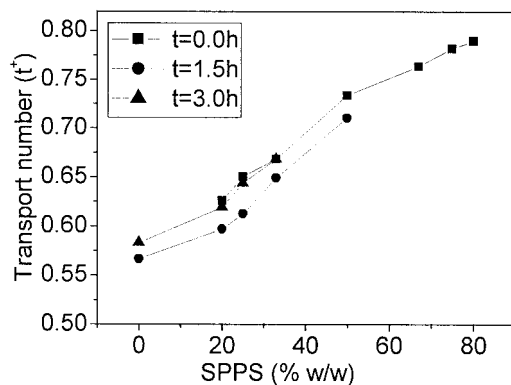


**Figure 3** Effect of the SPPS resin loading and sulfonation time of PEEK-C on the water content ( $W_R$ ) of the membranes.



**Figure 4** Effect of the SPPS resin loading and sulfonation time of PEEK-C on  $R_m$  of the membranes.

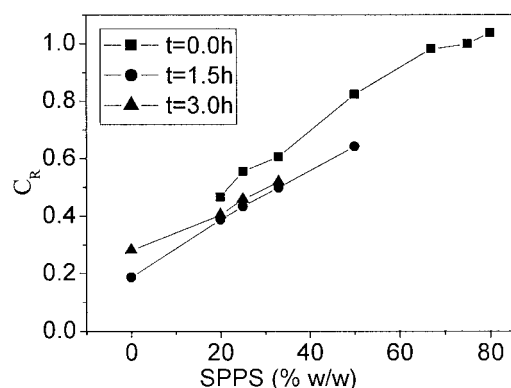
from blends of SPPS and PEEK-C, the electrical resistance decreased dramatically with the resin loading, whereas for the membranes prepared from SPEEK-C, the change in the electrical resistance was very small. This trend is related to the ionic conductivity mechanism in a charged membrane and follows an analogous explanation in our previous articles.<sup>7,18,19</sup> Ionic conduction in a charged membrane depends mainly on two factors: the water content and the active point (IEC). An-exchange membrane has been considered from the viewpoint of a three-phase membrane model, in which the membrane consists of a hydrophobic polymer, an active exchange zone, and an interstitial zone.<sup>18,20</sup> Counterion transport occurs mainly through the active region, in which it moves by a hopping mechanism, and co-ion transport occurs mainly through an interstitial region because of the minimal repulsive force caused by ion-exchange sites. Thus, both the interstitial region and active exchange zone contribute to the conductance. The necessity of an insulator transition for a conductor requires at least one infinite cluster composed of these two regions. The more active points there are, the more clusters are formed and the more conductive the membrane is. For a membrane prepared from SPPS/PEEK-C, that is, a heterogeneous membrane, SPPS, having an exchange point, corresponds to the active point, whereas PEEK-C corresponds to the hydrophobic polymer. Therefore, as the resin loading in the membrane increases, the active exchange zone dramatically increases, producing an abrupt decrease in the membrane  $R_m$  value. For a membrane prepared from SPPS/SPEEK-C, that is, a semihomogeneous membrane, both SPPS and SPEEK-C contribute to the active point. Before the addition of SPPS, the active points from SPEEK-C reach the conductive threshold, and an increase in the SPPS loading only increases the total active point, so the electrical conductance is only slightly increased and an abrupt change is not observed unless the IEC of SPEEK-C is much lower.



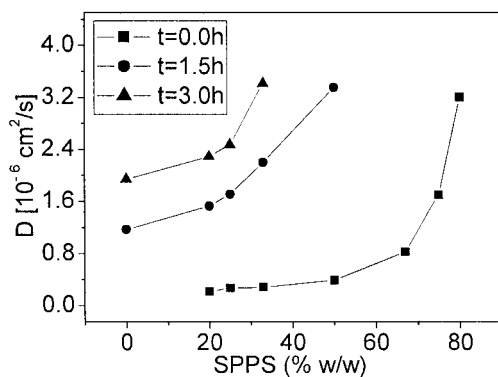
**Figure 5** Transport number versus the SPPS resin loading and sulfonation time of PEEK-C.

### Static transport number

The permselectivity of membranes prepared at different loadings and different sulfonation times of PEEK-C was characterized through the measurement of the concentration membrane potential between 0.2M and 0.1M KCl solutions. The transport numbers of cations (potassium ions) were calculated on the basis of these potentials and are given in Figure 5. Obviously, the transport number increased with the resin loading. However, in comparison with heterogeneous membranes prepared from blends of SPPS and PEEK-C, the semihomogeneous membranes, prepared from blends of SPPS and PEEK-C, showed relatively low transport numbers. Theoretically, the transport number or selectivity is related to the ratio of the IEC to the water content, that is, the fixed group concentration, and is not directly related to the water content or IEC. The fixed group concentration calculated from the IEC and water content at different resin loadings and sulfonation degrees of SPEEK-C is shown in Figure 6. Obviously, the fixed group concentration increased with the resin loading, and this permitted the same order for selectivity. However, the membranes were pre-



**Figure 6** Fixed group concentration ( $C_R$ ) versus the SPPS resin loading and sulfonation time of PEEK-C.



**Figure 7**  $D$  versus the SPPS resin loading and sulfonation time of PEEK-C.

pared by phase inversion. It is common knowledge that membranes are at least two-layered structures with a denser skin layer and a looser sublayer. Thus, the structure and thickness of the skin layer may affect the transport properties. For a membrane prepared from PEEK-C as a binder, the skin layer might be thicker and denser because of the weak reaction between the solvent and polymer (the solvent diffuses out of the membrane), and as a result, the corresponding membrane may behave as if having a higher transport number. This might explain the experimental fact that the transport numbers of the poly(ether ether ketone) (PEEK)/SPPS membranes were higher than those of the sulfonated membrane, as shown in Figure 5. It was deduced that the skin layer became thinner as the sulfonation degree of SPEEK increased, and so the transport number for membranes prepared from SPEEK-C was largely dependent on the fixed group concentration and followed a slightly increasing trend with the sulfonation degree.

## $D$

The  $D$  values of the membranes prepared from resins of different loadings and PEEK-C of different sulfonation times are shown in Figure 7.  $D$  increased with the resin loading and sulfonation time of PEEK-C. Theoretically, electrolyte transport in an ion-exchange membrane is related to two important factors: (1) the active point, which can attract counterions of the electrolyte and thus speed the diffusion, and (2) the homogeneity of the active point distribution, which provides a channel for ionic transport. Therefore, the increase in  $D$  with the resin loading and the sulfonation time of PEEK-C shown in Figure 7 agrees with the trend of the intrinsic parameters of the membranes, such as the IEC and water content, which have been discussed in detail already.

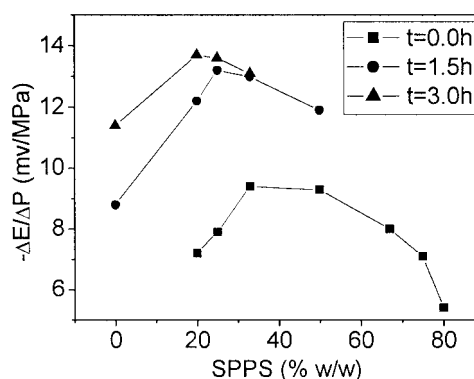
In addition,  $D$  was somehow affected by the physical structure of the membranes. As discussed previ-

ously, the membranes behaved as two-layered structures, and both the thickness and denseness of the skin layer decreased with the sulfonation degree of the binder polymer PEEK-C; therefore, at the same resin loading,  $D$  of a membrane prepared with PEEK-C as a binder was much lower than  $D$  of a membrane prepared with SPEEK-C as a binder. Moreover, there was an abrupt change in  $D$ , as shown in Figure 7. At a high resin loading, the membranes tended to be loose and even brittle, as shown in Table I; this permitted conventional flow and diffusional flow and greatly increased  $D$ .

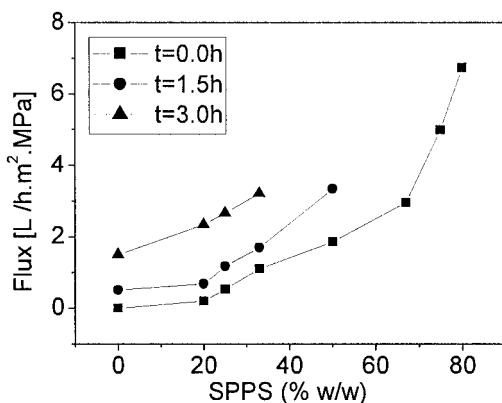
## Streaming potential

To further examine the electrical properties of the prepared membranes, we examined their streaming potentials. The results are shown in Figure 8. For the membranes prepared with different resin loadings, the streaming potential first increased with an increase in the SPPS resin loading and then decreased, whereas for the membranes prepared from SPEEK-C of different sulfonation degrees at the same loading, the streaming potential increased with the sulfonation degree.

It is well known that the magnitude of the streaming potential is dependent on two main factors, the membrane charge density and the pore structure of the membrane integrity, if the other conditions, such as the temperature and the tested electrolyte solution, are kept fixed. From the Helmholtz–Smoluchowski equation, the magnitude of the charge density reflects qualitatively the corresponding magnitudes of the streaming potential if the membranes have a unique structure; that is, the larger the membrane charge density is, the higher the streaming potential values are. However, the pore size of the membrane integrity reflects the opposite magnitudes of the streaming potential if the membranes have the approximate charge density; that is, the larger the membrane pore size is, the lower



**Figure 8** Streaming potential ( $\Delta E/\Delta P$ ) versus the SPPS resin loading and sulfonation time of PEEK-C.



**Figure 9** Flux versus the SPPS resin loading and sulfonation time of PEEK-C.

the streaming potential values are. As discussed previously, the membranes were at least two-layered structures with a denser skin layer and a looser sublayer. The flux of the membranes may be dependent on the skin layer (also reflected by the flux, which is shown in Fig. 9), but the streaming potential is largely dependent on the integrity structure or the sublayer structure because the skin layer is much thinner than the sublayer. For the membranes prepared from SPEEK-C of different sulfonation degrees at the same resin loading, the charge density was the dominant factor, and so the streaming potential increased with the sulfonation degree of SPEEK-C. For the membranes prepared with different resin loadings, both the charge density and the pore size of the membrane integrity increased with the loading, and the situation became complicated. At a low resin loading, an increase in the charged density was the dominant factor responsible for the corresponding increase in the streaming potential, whereas at a high resin loading,

the increase in the pore size of the membrane integrity (reflected by the flux, as shown in Fig. 9) became the dominant factor responsible for the corresponding decrease in the streaming potential.

The sign of the streaming potential indicated the sign of the electrical charges of the membranes; obviously, all the membranes behaved as if having negative streaming potential values. This indicated that the membranes were cation-exchanged.

### Properties of the ternary polymer blend membranes and the woven-fiber-supported membranes

As an experiment, the properties of the membranes prepared from ternary polymer blends (PEEK-C/SPEEK-C/SPPS) were also investigated. The results are shown in Table II with the different blend ratios. Obviously, the main characteristics, such as the IEC, water content,  $R_m$ , and streaming potential, followed the same trends as those of the binary polymer blends, and the magnitudes of the properties were between those of the SPPS/PEEK-C and SPPS/SPEEK-C binary blend membranes at a given SPPS resin loading. As a member of the PEEK family, PEEK-C exhibits excellent mechanical properties at room temperature similar to those of PEEK, but this polymer is amorphous and shows better solubility in certain polar solvents such as DMF because of its large phenolphthalein group in the chain, as shown in Figure 10.<sup>10</sup> After a sulfonic group is introduced into the benzene ring, the solubility of the sulfonated polymer in strong polar aprotic solvents such as DMF and *N,N*-dimethylacetamide increases a lot, and this produces greater convenience in preparing a ternary polymer system from solution blends.

To increase the mechanical strength, we also prepared some supported membranes from woven fiber.

**TABLE II**  
Main Characteristics of Various Blend Ratios of Unsupported and Supported Membranes with Ternary Polymer Systems

| SPPS/PEEK-C/SPEEK-C (1.5 h) |       | IEC (mequiv/g) | Water content (g · H <sub>2</sub> O/g of dry membrane) | Static transport number ( $t^+$ ) | $D$ (cm <sup>2</sup> s <sup>-1</sup> ) | ( $\Omega$ cm <sup>2</sup> ) | $-\Delta E/\Delta P$ (mV/MPa) |
|-----------------------------|-------|----------------|--|-----------------------------------|--|------------------------------|-------------------------------|
| Unsupported                 | 0:1:1 | 0.19           | 1.71   | 0.54                              | 0.16                                   | 4.01                         | 6.6                           |
|                             | 1:2:2 | 0.67           | 1.98   | 0.58                              | 0.30                                   | 1.03                         | 10.8                          |
|                             | 2:3:3 | 0.81           | 2.05   | 0.59                              | 0.41                                   | 0.72                         | 12.0                          |
|                             | 1:1:1 | 1.02           | 2.17   | 0.61                              | 0.56                                   | 0.47                         | 12.8                          |
|                             | 2:1:1 | 1.45           | 2.33   | 0.68                              | 0.83                                   | 0.34                         | 11.6                          |
|                             | 4:1:1 | 1.86           | 2.40   | 0.72                              | 1.20                                   | 0.33                         | 10.4                          |
| Woven-fiber-supported       | 0:1:1 | 0.16           | 1.51   | 0.53                              | 0.17                                   | 4.60                         | 6.8                           |
|                             | 1:2:2 | 0.50           | 1.78   | 0.56                              | 0.47                                   | 1.51                         | 11.2                          |
|                             | 2:3:3 | 0.53           | 1.90   | 0.58                              | 0.51                                   | 1.00                         | 12.2                          |
|                             | 1:1:1 | 0.70           | 1.97   | 0.59                              | 0.71                                   | 0.86                         | 12.9                          |
|                             | 2:1:1 | 1.07           | 2.13   | 0.65                              | 0.95                                   | 0.77                         | 11.7                          |
|                             | 4:1:1 | 1.56           | 2.20   | 0.69                              | 1.60                                   | 0.76                         | 10.8                          |

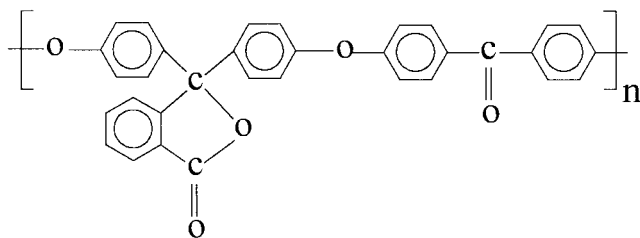


Figure 10 Repeat units of PEEK-C.

Because the fiber had a burst strength about 0.8 MPa, the supported membranes had corresponding strength. The fundamental properties of supported membranes prepared at different resins loadings are also shown in Table II. The changes in the properties with the resin loading followed a reasonable trend, as previously analyzed. With the introduction of the inert substrate, the IEC and water content decreased slightly, whereas the transport number and streaming potential remained approximately unchanged and  $R_m$  increased to some extent.  $D$  also should have decreased slightly because of the introduction of the support, but it did not. This was due to the phase-inversion process. A supported membrane cast solution provided a larger contact region (two sides surface) for the exchange of the solvent-relation medium and formed a membrane with a sandwich structure (two skin layers plus a sublayer), whereas a nonsupported membrane cast solution only provided the top surface for the solvent-relation medium exchange and formed a membrane with a two-layered structure (one skin layer plus one sublayer). This phenomenon was also observed in the SPPS/PES system and was discussed in detail previously.<sup>7</sup>

In summary, a semihomogeneous membrane can be prepared from both binary and ternary polymer blends, and its intrinsic parameters are dependent on the blend ratio and the sulfonation degree of the binder polymers. Through the adjustment of the blend ratio of the ternary system, the choice of the proper sulfonation degree of the binder, and a support, membranes with excellent mechanical and electrochemical properties can be achieved.

## CONCLUSIONS

Following our previous article on heterogeneous cation-exchange membranes, we have reported in this article a new route for semihomogeneous cation-exchange membranes. The membranes can be prepared with a binary blend system such as SPEEK-C/SPPS or

a ternary blend system such as PEEK-C/SPEEK-C/SPPS by solution blending and phase inversion. This new method does not require multiple stages, such as the milling of the ion-exchange resin into fine particles and pressing at high temperatures, and so proves to be simple, economical, and convenient.

As expected, the fundamental properties of the membranes, such as the IEC, water content, electrical resistance, transport number,  $D$  value of the electrolytes, and streaming potential, are largely dependent on the SPPS loading and sulfonation degree of PEEK-C. The mechanical strength of the membranes can be improved with a suitable reinforcing material. In such a case, the resin loading and sulfonation of SPEEK-C must be adjusted so that both have acceptable electrical resistance, selectivity, and water content to comply with different industrial requirements, such as the replacement of homogeneous membranes (interpolymer membranes) for diffusional dialysis and heterogeneous membranes for electro dialysis applications, proton-exchange membranes for fuel cells, and even cation-exchange layers for bipolar membranes.

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