Preparation of Novel Heterogeneous Cation-Permeable Membranes from Blends of Sulfonated Poly(phenylene sulfide) and Poly(ether sulfone)

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ABSTRACT: Novel heterogeneous cation-exchange membranes using poly (ether sulfone)(PES) as binder and sulfonated poly(phenylene sulfide) (SPPS) powder as polyelectrolyte were prepared by the solution casting-immersion method. Compared with a conventional route for heterogeneous membrane, the steps of milling resin into fine powders and the pressing at high temperature are avoided, and thus permits a simple technique for the preparation of such membrane. The effect of the particle size and loading of SPPS resin on the properties of the membranes such as ion-exchange capacity, water content, electrical resistance, transport number, diffusion coefficient of electrolytes, etc., have been studied. It is shown that the membrane fundamental properties are largely dependent on both the resin loading and the particle size of SPPS resin. By adjusting these two important parameters, one can obtain heterogeneous membrane with both good conductivity, selectivity, and proper water content for different industrial purposes such as electrodialysis, diffusional dialysis, etc. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 167–174, 2004

Key words: ion exchangers; membranes; heterogenous polymers; blends

INTRODUCTION

The development of synthetic ion exchange membrane reported by Juda[1] in 1949 and Juda and McRae[2] in 1950 stimulated both commercial and academic interest in such membranes and the related processes. There are two main classes of ion exchange membrane: one for cations permeability, and another for anions permeability. Today, cation-permeable membranes seem to receive more attention than anion ones, due to their various electrochemical applications such as in fuel cells, proton conductors, in addition to the traditional electrodialysis and diffusional dialysis.[3–8] There are multiroutes for the preparation of such kinds of membranes. The commonly utilized neutral starting material is a styrene–divinylbenzene copolymer, from which a strong acid cation-exchange membrane is usually prepared by sulfonation. A alternative way is directly sulfonated from the aromatic polymers or from the solution blends of sulfonated aromatic polymers and nonfunctional polymers.[3,4] For such preparation, the functional groups, that is, sulfonated groups, have been chemically bonded with the membrane polymer chains and thus called homogenous membranes or interpolymeric ion-exchange membranes. This kind of membrane has good electrochemical properties but they are poor in mechanical strengths.

As a compensation, heterogeneous membranes, in which the functional group is not chemically connected with the membrane polymers, have some characteristics such as possessing good mechanical strengths and good dimensional stability under different ionic forms and in different solutions but are poor in electrochemical properties. Generally, in the different applications, the fundamental requirements for ion-exchange membranes (IEMs) are the same: the selectivity, the permeability, and the stability should be sufficient. Nevertheless, some of these requirements are more important for the function than others when they are used in different processes.[6–8] For example, in electrodialysis, if the selectivity is sufficient, the membrane mechanical stability seems more important than electrochemical properties, and hence, heterogeneous cation-exchange membranes may replace the interpolymer membranes in some of the electrodialysis (E.D.) applications.[9] This is one of the reasons that the development of new or modified cation-exchange materials for heterogeneous cation membranes continues.

For preparation of a heterogeneous membrane, the routes mainly concerns with (1) dispersing the resin

powders with polymer solution and forming the membrane by evaporating the solvents; (2) dispersing the resin powders with polymer binder and then pressing at high temperature; or (3) dispersing the resin powders with monomer and then conducting polymerization.[9–12] A support is usually introduced into the preparation to obtain reinforced membranes. In these routes, the ion-exchange resin made from the styrene–divinylbenzene copolymer is commonly utilized as functional materials. As is well known, the resin is very hard to mill into very fine powders for the convenience of the ion-exchange membrane due to their strong crosslinking structure, and also, it is very expensive. Thus, an incorporation of resin into the available routes will give rise to both complexity and high membrane cost in the manufacturing.

Therefore, in this study, we attempt to develop a new route for preparing a heterogeneous membrane without using any styrene–divinylbenzene copolymer resins. This new heterogeneous membrane is prepared from the blends of sulfonated poly(phenylene sulfide) (SPPS) and nonfunctional poly(ether sulfone) by phase inversion. The sulphonation of poly(phenylene sulfide) (PPS), the membrane preparation processes, as well as their properties such as water content, ion exchange capacity (IEC), membrane area resistance, transport number, etc., will be fully investigated.

EXPERIMENTAL

Materials

Poly(phenylene sulfide) (PPS) and Poly(ether sulfone) (PES) are conventional polymers and purchased from the Chinese commercial market. Concentrated (98 wt %), fuming sulfuric acid (20% SO_3), dimethyl formide (DMF), and other chemicals were obtained commercially and used without further purification. All chemicals used in the experiments were analytical grade.

Sulfonation of PPS

The PPS polymer is dried for more than 6 h in an oven at 100°C. An amount of 50 g polymer powder is dispersed to the proper volume of concentrated sulfuric acid and keep stirred at 60°C for 2 h. Then a suitable quantity of oleum is added five times within 24 h. The reaction mixture is stirred for up to 120 h at acontrolled temperature to achieve the desired sulphonation degree. The final solution was precipitated with iced water and washed until the pH is nearly 7 and then the SPPS resin particles was subsequently dried in an oven at 60°C for at least 20 h to get the sulfonated polymers, and sieved to the desired mesh number.

Membrane preparation

Binary solutions were prepared by dissolving poly-(ether sulfone) (PES) in dimethyl formide (DMF) over-
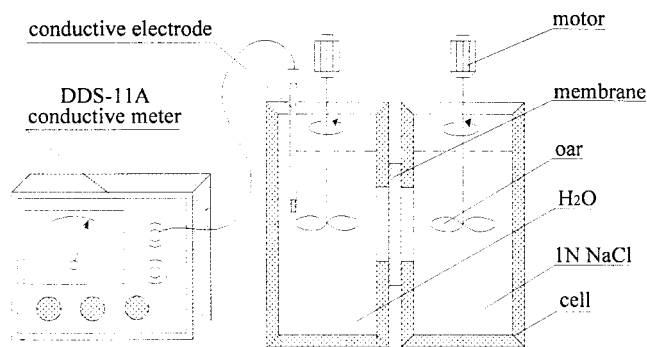
Figure 1 Schematic diagram for determination of a diffusional coefficient.

night at room temperature to let the PES dissolved sufficiently. SPPS resin of different particle sizes and quantity was then dispersed in the binary solutions to form ternary dispersions. The mixture is stirred for 3 min, extracting the air bubble by vacuumizing to form casting solution in use.

At room temperature, the above viscous solution is cast on a glass plate by means of a proper glass knife to form thin films. Then they were immersed in iced water immediately to precipitate the polymer and form membranes. Then, the membrane was pretreated in turn by 1 M HCl and 1 M NaOH solutions four times and finally wash with deionized water for further evaluation of membrane properties.

Supported membranes were prepared by using the same procedure as described above, except that slurry is cast on an inert porous polyvinyl chloride fiber, instead of a glass plate.

Microscopic observation of the membrane

The morphological behaviors of different heterogeneous membranes were studied by an optical microscope (Olympus BX51) at a magnification of five times, and the photographs were taken by a Panasonic colour CCTV camera.

Evaluation of membrane properties

The characteristic properties of the membranes investigated include: ion exchange capacity (IEC), water uptake (C_R), wet thickness (d), area resistance (R_m), diffusion coefficient (D), and membrane potential (E). The methods are completely the same as our previous articles[13–15] except that the diffusion coefficient is described as follows.

As shown in Figure 1, the evaluation of diffusional coefficient was conducted in a batchwise Donnan dialyzer, consisting of a tested membrane, two compartments made of acrylic resin and glass stirrers. The membrane is fastened between the compartments

with silicon rubber gaskets and has an effective area of 4.8×10^{-4} m^2. Before starting an experiment, the right compartment was filled with 1 M, 100 mL the sodium chloride solution, and the left compartment with the equal volume of deionized water. The transport of NaCl through the membrane was recorded with a conductive meter (DDS11A, Shanghai Leici, China) connected to the left compartment at given time intervals. The diffusional coefficient can be calculated from the slope of a curve regression by conductivity–time data and the instrumental constant as follows: [16]

$$D = KLd \qquad (1)$$

where D is the diffusional coefficient in cm^2/s; K is the instrumental constant determined from a standard concentration of NaCl–conductivity relation, membrane effective area, and the unit conversion, and equal to 2.73×10^{-6} in this test; L is the slope of conductivity (μs)–time (min) curves; and d the thickness (cm) of the wet membranes.[16]

All the above properties were evaluated at room temperature of 8–10°C.

RESULTS AND DISCUSSION

Sulfonation of PPS

Unlike PPO (poly phenylene oxide), which is soluble in nonpole solvents and the solphonation can be conducted in a homogeneous way,[17] PPS is sulphonated in a heterogeneous way due to its limit solubility in any solvents. Thus, such sulfonation is restricted to the interface between the solphonation agents and PPS powders, that is, the reaction mainly occur in an amorphous area. Because the first substituted functional group influences the ring system such that only one fixed charge can be introduced in each monomer repeat unit in the condition,[18] there exists a maximum sulfonation degree. In our experiments, fuming acid 20% is used as the sulphonation agent. We found that
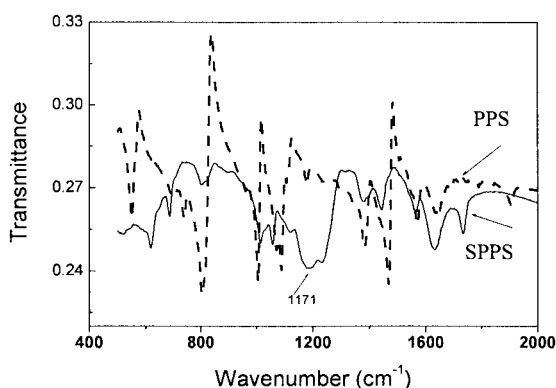

Figure 2 Spectra of the PPS and SPPS.

| Mesh size of SPPS (MS)	PES : SPPS	Physical appearance
100–200	1 : 4	Brittle
	1 : 3	Brittle
	1 : 2	Flexible
	1 : 1	Flexible
	2 : 1	Flexible
200–300	1 : 4	Brittle
	1 : 3	Flexible
	1 : 2	Flexible
	1 : 1	Flexible
	2 : 1	Flexible
>300	1 : 4	Brittle
	1 : 3	Flexible
	1 : 2	Flexible
	1 : 1	Flexible
	2 : 1	Flexible

the suphonation degree follows the common rule: increase with temperature, time, and quantity of fuming acid. The maximum sulfonation degree can be attained as high as 0.54, that is, the Ion Exchange capacity (IEC) 3.60 mEq/g , which can comply with the request of the preparation of the heterogeneous membrane. In the later experiments, we used the SPPS resin with IEC = 2.6 mEq/g (sulfonation degree 0.35) for preparation of heterogeneous membranes.

The final product is water swollen and insoluble in any solvents, indicating the resin is crosslinked to some extent. The existence of sulfonation groups was approved by the peaks at 1171cm^{-1} in FTIR spectrum as shown in Figure 2.

Microscopic observations of the physical appearance of membranes

Physical appearance of the prepared membranes permits a preliminary evaluation of the membrane-apparent properties such as the homogeneity of the membrane, the compatibility of resin SPPS, and binder PES, as well as the mechanical strength. In this article, the particle size of resins having three different mesh numbers (MN) of 100–200, 200–300, and >300 are used. The average particle sizes are equivalent to 150–76, 76–52, and <54 μm, respectively. The physical appearance of cation-exchange membranes prepared from PES and of SPPO resin of different loading is presented in Table I.

It can be seen that, for all sizes of resin particles, with an increase in resin loading, the membrane changes from the flexibility to brittleness, suggesting that the compatibility of resin-binder decreases with increasing in SPPS loading. This may be due to the fact that for such membrane preparation, the binder PES is
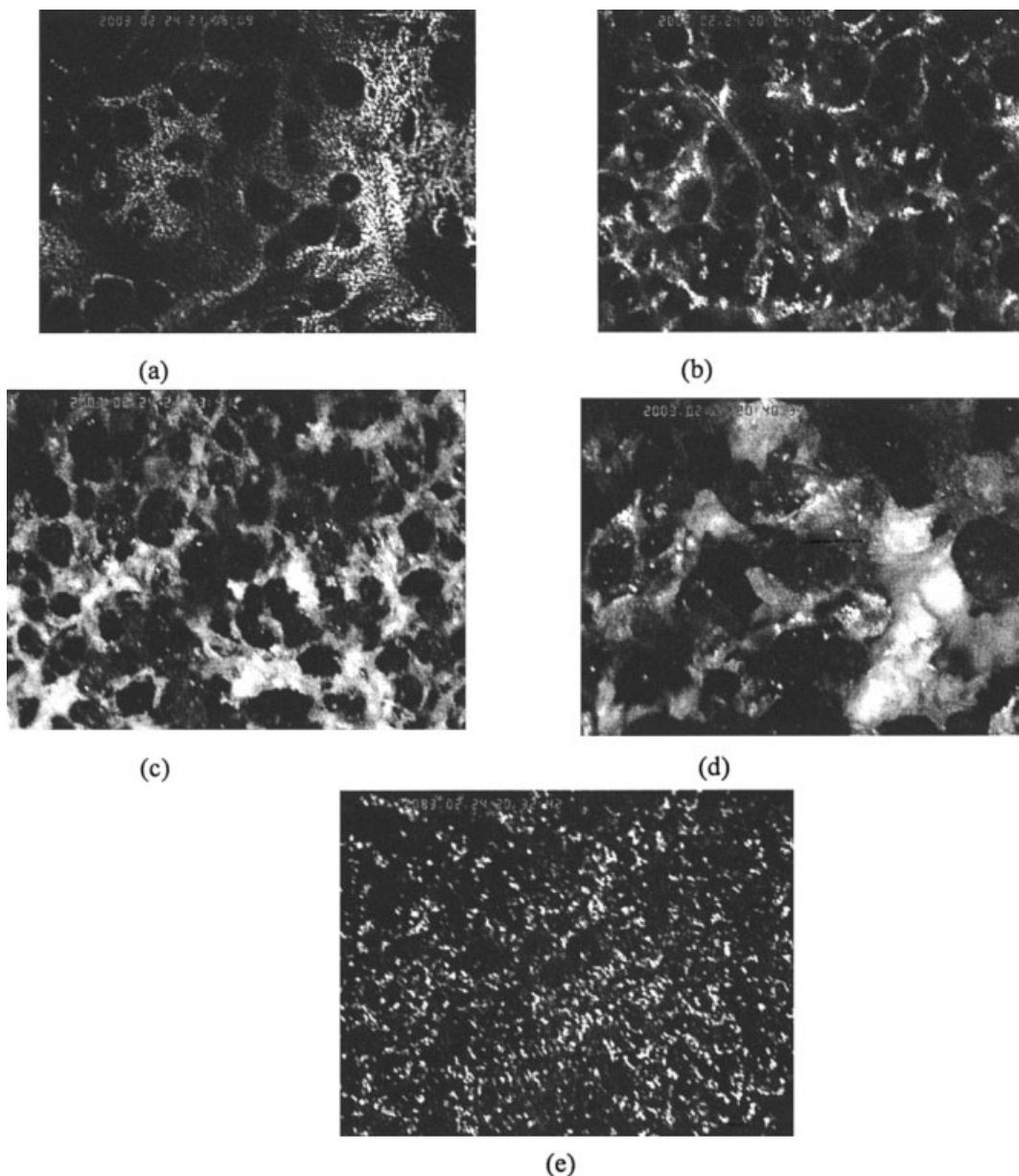
Figure 3 Optical micrographs of heterogeneous cation-exchange membranes (magnification 5×). (a)–(C) for PES : SPPS = 2 : 1, 1 : 2, and 1 : 4 at one mesh number of 200–300 and (d), (b), and (e) for a mesh number (MN) of 100–200, 200–300, and >300 at PES : SPPS = 1 : 2.

physically blended with the resin, so the higher the resin loading means the less PES to provide materials for the frame. It is interesting to find that the physical appearance may also change with the mesh number of the resins, for example, the resin loading for mesh number higher than 200 can attain as high as 75% without any brittleness, while for the same loading of mesh number 100–200, the membrane goes into brittleness. This may be due to the fact that as resin particles become finer and finer, it distributes almost uniformly through the membrane, making it nearly homogeneous. For larger particles (low mesh number), the inhomogeneity tend to give rise to the dis-

continuity of binder at high loading, and hence, become brittle more easily.

To further investigate the nature of the membranes, the morphological behavior of the membranes of different loading and mesh numbers were characterized by optical microscope (Olympus BX51) at a magnification of 5×.

Figure 3(a)–(c) illustrated the effect of variation of PES : SPPS ratio (resin loading) at a particular mesh number (200–300) . Obviously, for the investigated loadings, the resin particles are homogenously dispersed in the PES polymeric phase. With an increase in resin loading, a gradual increasing in the resin

content in the matrix is clearly visible, as shown in micrographs (a) to (c). Taking the distribution of resin particles into account, the phase distribution in micrograph (c) is found to be more naked resin particles so the membrane of this loading tends to be brittle, as shown in Table I. The effect of variation of mesh number of the resin particles, at a particular loading (PES : SPPS = 1 : 2) is indicated in Figure 3(b), (d), and (e). The micrographs clearly reveal that with increasing the mesh number (decreasing in the SPPS particle size), the number of SPPS particles per unit area of the matrix gradually increases. Thus, the phase distribution becomes more and more uniform and homogeneous.

Ion-exchange capacity, water content

For a practical purpose, such a membrane should have sufficient ion-exchange capacity (IEC) and proper water moisture. As shown in Figure 4, the IEC of the membrane prepared from the resin having different particle size linearly increases with an increase in resin loading and conforms approximately to the curve calculated from SPPS IEC values. This is because in the membrane, the resin particles, having exchangeable ions in it, are responsible for the IEC of membrane, while the binder PES, acting as a neutral polymer, contribute nothing to the active point. Thus, more resin loading means more exchangeable ions and higher ion-exchange capacity in the membrane. On the other hand, the ion exchange capacity of SPPS resin do not change with the particle size, and only depend on the total mass of the resin, so the IEC of the membrane remains unchanged with the particle size.

As far as water content is concerned, it increases with an increase in resin loading (Fig. 5). The result is not difficult to understand, because, like most charged membranes, the water content increases in the order of
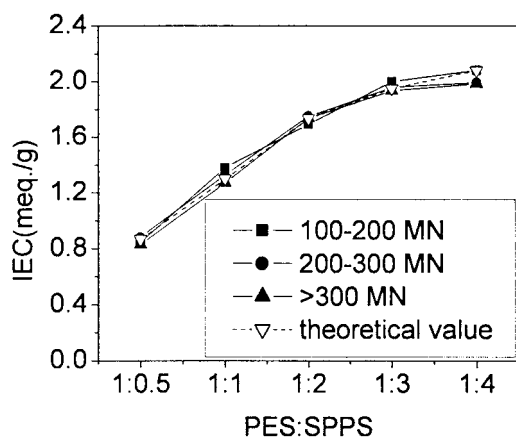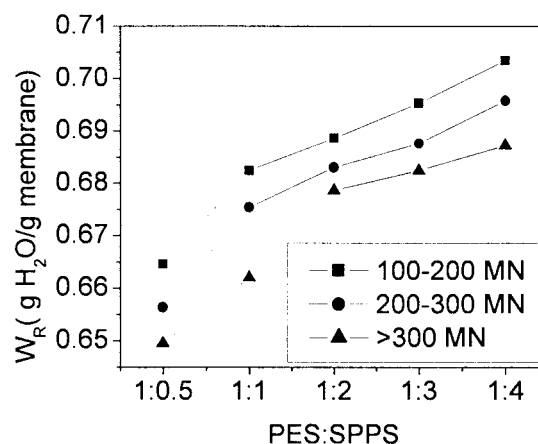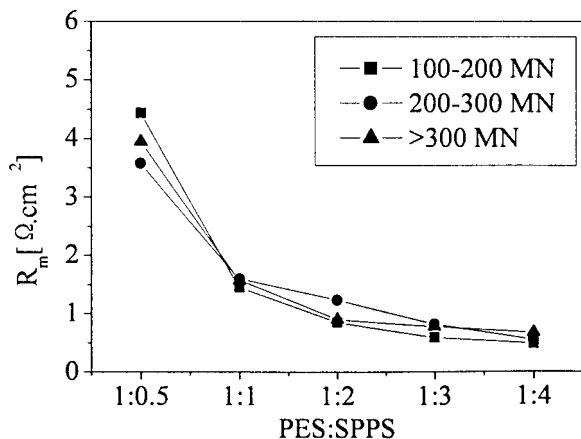

Figure 5 Effect of SPPS resin loading and particle size on the water content.

IEC due to the strong hydration effect of the functional groups. It has been noticed that for a given mesh number resin, the membrane water content increases with the particle size (i.e., decrease with mesh number). A possible explanation for this is that, for membrane of fine particles, more resin particles are wrapped with PES polymer, which is hydrophobic. Thus, the contact region of water with resin particle increases with an increase in particle size if the loading keeps fixed. This finding is very useful, because one can adjust the membrane water content by changing the particle mesh number without affecting its IEC. In other words, by adjusting the ratio of PES : SPPS and resin particle size, a series of membranes with both desired IEC and water content can be reasonably acquired to satisfy with different industrial demands.

Area resistance

Besides sufficient IEC and proper water content, the membrane should have good electrical resistance. As expected, the area membrane resistance decreases with an increase in SPPS loading in the matrix. This trend is related with an ionic conductivity mechanism in a charged membrane. Ionic conduction in a charged membrane depends mainly on two factors: water content, and active point (IEC). An exchange membrane has been considered from the viewpoint of a three-phase membrane model where the membrane consists of hydrophobic polymer, an active exchange zone, and an interstitial zone.[15,19–20] A counterion transport occurs mainly through the active region where it moves by a hopping mechanism, and a coion transport occurs mainly through the interstitial region due to the minimal repulsive force caused by ion exchange sites. Thus, both the interstitial region and active exchange zone make a contribution to the conductance. The necessity for an insulator transition to a conductor


Figure 4 Effect of SPPS resin loading and particle size on the ion exchange capacity.

Figure 6 Effect of SPPS resin loading and particle size on the membrane area resistance.

Figure 7 Transport numbers vs resin loading in membranes having different mesh numbers (MN) of resin particles.

requires at least one infinite cluster composed of these two regions. The more active the point exists, the more clusters are formed and the more conductive the membrane. As far as the heterogeneous membrane is concerned here, SPPS, having an exchange point, corresponds to the active point while PES corresponds to the hydrophobic polymer. Therefore, as the resin loading in the membrane increases, the active exchange zone also increases, and the membrane area resistance correspondingly decreases.

As also shown in Figure 6, there is no appreciable evidence that the area resistance is dependent on the mesh number of resins. A similar explanation as that mentioned above may be also given here because the active point is largely dependent on the resin loading but not the resin mesh number.

Static transport number

To characterize the permselectivity of the membranes prepared at different loading and different resin mesh number, the concentration membrane potential between 0.2/0.1 M KCl solutions were measured. The transport numbers of cations (potassium ions) were calculated based on these potentials and demonstrated in Figure 7. Obviously, the transport number increases with resin loading before 66% (PES : SPPS = 1 : 2), keeps a flat value within the loading range of 66–75% (PES : SPPS = 1 : 2 to 1 : 3), and then decreases after the loading 75% (PES : SPPS = 1 : 3). Theoretical explanation to this change trend brings us back to the change of both water content and ion-exchange capacity with the resin loading. As discussed above, both the ion exchange capacity (IEC) and water content (W_R) increase with the resin loading. Nevertheless, fixed group concentration (C_R), which is expressed as the ratio of IEC to water content, does not definitely follow the same order. As shown in Figure 8, a fixed
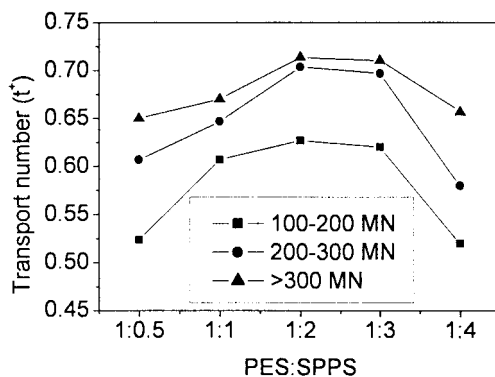
group concentration increase with the resin loading and then keep at flat values. Theoretically, a transport number or selectivity tends to increase with the same trend as a fixed group concentration, that is, an increase with resin loading and keep at flat values. However, It is followed from the three-phase model that hydrated ions will require a certain volume of water within the membrane to permit migration through the membrane.[19,20] In other words, if the water content in the membrane increases, it will provide more channels for coionic transport (adsorb more electrolyte ions due to Donnan equilibrium), and thus the selectivity of a counterion is decreased. This is the reason why the transport number decrease with resin loading after loading is attained 75%.

As shown in Figure 7, the mesh number has a little effect on transport number. In the investigated mesh number range, the transport number increase with the mesh number (decrease with the particle size). This may be due to the fact that for finer particles, the membrane looks more homogeneous and dense.
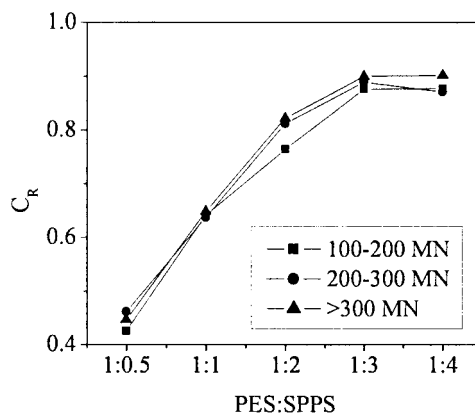
Figure 8 Fixed group concentration vs resin loading in membranes having different mesh numbers (MN) of resin particles.
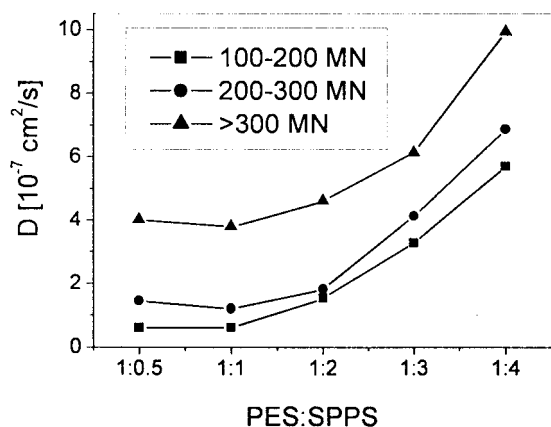
Figure 9 Diffusion coefficient vs resin loading in membranes having different mesh numbers (MN) of resin particles.

Diffusion coefficient

The Diffusion coefficient (D) of the membranes prepared from resins of different loading and different particle sizes were shown in Figure 9. It is demonstrated that the diffusional coefficient increases with resin loading and decreases with particle size. Theoretical speaking, electrolytes transport in an ion-exchange membrane is related two important reasons: one is the active point that can attractive counterions of an electrolyte and thus speed the diffusion; another is the homogeneity of active points distribution that provides a channel for ionic transport. Therefore, an increase of D with loading is due to the increase in an active point, as discussed earlier, while a decrease with a particle size resulted from the inhomogeneity of the membrane at this condition.

The properties of a supported membrane

To increase the mechanical strength, some supported membranes were also prepared from inert porous polyvinyl chloride fiber. Because the fiber has a burst strength about 0.8 MPa, the supported membranes have the corresponding strength. Table II show the fundamental properties of these membrane prepared at same particle size (>300 MN) but different resin loadings. These properties change with resin loading can be explained in the same way as the above. As can be observed, due to the introduction of the inert substrate, the IEC, water content decreases a little, while the transport number remains approximately unchanged and area resistance increases to some extent. The diffusion coefficient also might decrease a little due to the introduction of support, but it does not. This may be explained by the phase inversion process. For an unsupported membrane, the solution is directly cast onto a glass plate and then immersed into gelation medium. It will take more time for solvent exchange with the gelation medium because gelation medium can only permeate through the top surface, while for unsupported ones, the solution is cast on a fiber and then put into the medium. The solvent–gelation medium can be exchanged through two sides, and thus the membrane looks a little looser. However, overall speaking, the change of membrane properties is not so appreciable due to a support, except for a significant increase in mechanical strength due to some extent to an increase in area resistance.

CONCLUSIONS

In this study, a new route for heterogeneous cation-exchange membranes using poly(ether sulfone) (PES) as binder and sulfonated poly(phenylene sulfide) (SPPS) powder as polyelectrolyte by the phase inversion was proposed. This new method does not require multiple stages such as milling the ion exchange resin into fine particles, pressing at high temperature, etc., and hence, proves to be simple, economical, and convenient.

As expected, the membrane fundamental properties such as ion-exchange capacity, water content, electrical resistance, transport number, diffusion coefficient of electrolytes, etc., are largely dependent on SPPS loading and resin particle size. By using suitable reinforced material the mechanical strength of the membranes can be greatly improved. In that case, resin loading and particle size are to be adjusted to have both acceptable electrical resistance, selectivity, and water content to comply with different industrial requirements such as replacing homogenous membranes for electrodialysis and diffusional dialysis.

TABLE II
Main Characteristics of Various Blend Ratio Supported Membranes with Particle Size of >300 MN

PES : SPPS	IEC mEq $\cdot$ /g	W_R g H_2O/g	Static transport number t^+	Diffusion coefficient D (cm^2/s)	Area resistance R_m ($\Omega \cdot$ cm^2)
1 : 0.5	0.71	0.60	0.64	4.9E-7	6.74
1 : 1	1.14	0.62	0.67	4.19E-7	4.12
1 : 2	1.57	0.63	0.72	5.56E-7	2.62
1 : 3	1.74	0.64	0.71	6.60E-7	1.74
1 : 4	1.78	0.64	0.63	1.01E-6	1.67

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