

Proton Conducting Blends Based on Polysulfones and Elastomers

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ABSTRACT: With the aim of improving the performance of conventional proton conducting membranes, systems based on two poly(arylene ether sulfone)s and two elastomers were obtained by heterogeneous sulfonation with chlorosulfonic acid. Subsequently, they were characterized, morphologically and electrically, by techniques such as infrared spectroscopy (FTIR), differential scanning calorimetry, dynamic-mechanical analysis, and complex impedance spectroscopy. From the results, it was verified that the reaction of sulfonation had taken place, as well as that these materials formed incompatible and good proton conducting blends. In addition, the storage modulus and the conductiv-

ity were subjected to a statistical design to predict the optimum composition, presenting the best mechanical and conducting proton values and as a consequence the most suitable membrane from the point of view of its application in the field of the fuel cells. Very promising results have been found especially with membranes based on binary blends constituted by thermoplastic/elastomer polymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3474–3482, 2006

Key words: poly(arylene ether sulfone)s; elastomers; blends; ionomers; conducting polymers

INTRODUCTION

Polysulfones (PSU), important engineering thermoplastic polymers, are used in a wide variety of applications that take advantage of their hydrolytic¹ and acid/caustic stability, clarity, and high heat deflection temperature. Because of their excellent creep resistance, transparency, and mechanical and electrical properties, they are used as printed circuit boards, integrated circuit carriers, coil bobbins, etc.

Currently, PSUs have achieved special importance in the manufacture of asymmetric and composite membranes^{2,3} in the desalination of sea and brackish water. Hence, a certain hydrophilic nature of the base materials would be desirable, i.e., water affinity. Sulfonic groups have proved their suitability in this respect.

Furthermore, sulfonated polymers are the kind of ionomers known for many years as strong ion-exchange materials, and they have presently gained importance as materials for fuel cell membranes, since a strong demand has arisen for polymer electrolytes.^{4,5} Until recently, only perfluorinated ionomers, such as Nafion, could be used as membranes for fuel cells. They have, however, some disadvantages: high cost

together with a limited thickness range and ion-exchange capacity.

Consequently, there is an increasing interest in the development of alternative low cost ionomer membranes, which possess higher proton conductivity and are easier to process. In this respect, potential polymers for such applications include poly(arylene ether sulfone)s. To this purpose, some specific methods had to be developed for the effective incorporation of the sulfonic groups in the aromatic rings of PSUs.^{6–9}

Commercial PSUs consistently present a linear structure and behave, however regular their structure may be, as amorphous materials to any practical effects. The high T_g values (the high aromaticity throughout the chain triggers high glass transition temperature values) and the stiffness of the polymer backbone are the principal factors accountable for the high processing temperatures above 300°C. Even at these temperatures, the melts are extremely viscous, and the processing is very difficult. If materials are required that are easy to prepare as thin films, lower processing temperatures and better creep properties would certainly constitute a major asset.

The materials used in this study were obtained by blending PSU, polyphenylsulfone (PPS), and two thermoplastic elastomers, ethylene-propylene-diene terpolymer and hydrogenated poly(butadiene-styrene) block copolymer, at varying compositions. From these blends, membranes were obtained and subjected to a

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reaction of sulfonation in heterogeneous phase, with chlorosulfonic acid. After this, they were characterized from a morphological and electrical point of view.

In our researches, we have experience in dealing with the sulfonation of poly(arylene ether sulfone)s and elastomers,^{10–12} separately. For PSUs, the stability of the membranes was retained, but the conductivity reached was not high enough; on the other hand, in the case of the elastomers, the conductivity turned out to be very good, but significant deterioration in its physical properties was observed (mainly when they are in the fully hydrated state). Hence, with this work, we have the purpose of joining the excellent technological properties of both types of materials to get membranes that can really be considered as an alternative to the current commercial ones.

EXPERIMENTAL

Materials

The experimental polymers were commercial products and were used as received. The ethylene–propylene–diene terpolymer (EPDM) was supplied by Exxon Chemical (France) under the trade name VISTALON 9500 (contains 60 wt % ethylene, 29 wt % propylene, and 11 wt % 5-ethyliline-2-norbornene).

The hydrogenated poly(butadiene-styrene) block copolymer (HPBS) was CALPRENE H6120 (thermoplastic copolymer contains ethylene–butadiene/styrene (70/30)) delivered by Repsol (Spain).

The PSU, tradename UDEL P-1700 supplied by Amoco Chemical, has a weight-averaged molecular weight (M_w) of 2.5×10^4 and is an amorphous, hydrophobic polymer with excellent thermal stability and mechanical properties.

The PPS was RADEL R-5000, a Amoco Chemical product. It has high heat deflection temperature (207°C) and can withstand continuous exposure to heat and still absorb tremendous impact without deflecting or breaking plus its chemical resistance surpasses that of most amorphous polymers. The commercial membrane used as a reference was Nafion 117 from DuPont.

Chlorosulfonic acid and 1,2-dichloroethane were obtained from Aldrich (Milwaukee, WI) and Scharlau (Spain), respectively.

Procedures

Blends were obtained by mixing the components in a Haake Rheocord 9000. The blending conditions were set at 280°C, 15 min, and 50 rpm for PPS/PSU blends, and 220°C, 10 min, and 50 rpm for the remaining ones.

Blend compositions were planned according to a statistical model proposed by Scheffé, which consists of studying blends whose compositions are distrib-

uted symmetrically in a “simplex” lattice over the experimental range. The purpose is to have the suitable experiences to apply the model to the study of two properties (storage modulus and conductivity), and to assess its suitability in the light of our finding. In case of proving to be adequate, a simple method would become available for the design of new materials from the polymers under study. A software NEMROD¹³ was used to calculate the coefficients of this model and further plot of the ternary diagrams corresponding to the isoresponse curve for the two properties studied.

The membranes were obtained by compression in a hydraulic Collin press, the samples being placed between stainless steel plates at the same blending temperature and a pressure of 220 bar, and held there for 10 min.

Subsequently, membranes were sulfonated with a 0.1M chlorosulfonic acid/1,2-dichloroethane solution at room temperature for 4 h. Then, they were washed several times with acetone and Milli-Q water until neutral pH was reached, and dried at vacuum and 50°C for four days. Although the sulfonation yield is not complete (for example the solvent used may contain water, which can decompose the sulfonation agent), the experimental conditions were chosen in such way that the maximum theoretical degree of sulfonation could be expected to be 10%. We tested that this value is suitable to obtain interesting conductivities and to preserve mechanical characteristics.

Techniques

FTIR analysis was carried out on Spectrum One with a Perkin–Elmer spectrophotometer, with scan number 32 and a resolution equal to 2.

A Mettler TA 4000 calorimeter was used for differential scanning calorimetry (DSC) analysis. Before recording the DSC-thermograms, the samples were heated to softening for 5 min to eliminate their previous thermal history and subsequently quenched to the respective DSC-initial temperatures. Thermograms were recorded at a heating rate of 10°C/min. The midpoint of the slope change of the heat capacity was taken as the glass transition temperature. For each sample, three thermograms were recorded; the mean value being established as the glass transition temperature.

Dynamic-mechanical analysis (DMA) was conducted with a 983 Dynamic Mechanical Analyzer TA Instrument in the tensile mode at the frequency of 0.1 Hz. T_g determination through was based on the loss modulus, as it has been shown¹⁰ that maximum E'' relates much better to DSC-determined T_g than $\tan \delta$.¹⁴

A computer-assisted Hewlett–Packard 4192A Impedance Spectroscopy Analyzer was used for impedance spectroscopy. The measurements were carried

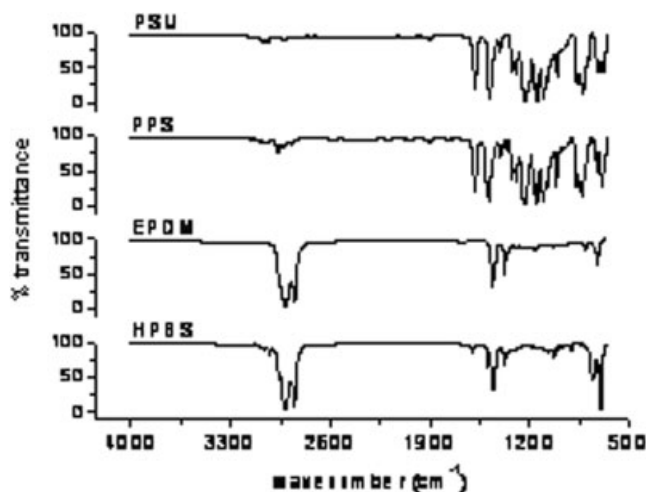


Figure 1 FTIR spectra corresponding to nonsulfonated polymers.

out in the two-electrode AC impedance mode at ambient temperature, frequency range 0.01–10,000 Hz, and 0.1 V amplitude of the signal applied. To measure the conductivity, we have designed a special cell composed of two silver electrode of 0.07 cm² of surface. The electrode surfaces were kept clean to avoid any contact resistance during measurements and the membrane sample was sandwiched in between these two flat circular electrodes. Prior to the measurement of the complex impedance, the samples were hydrated in deionized water at 50°C for different periods.

RESULTS AND DISCUSSION

Nonsulfonated systems

Figure 1 shows the IR spectra of the four commercial polymers. The aromatic PSU and polyphenylsulfone show the aromatically bonded SO₂ group that pro-

duces strong bands at ~1290 and 1150 cm⁻¹. The long wavelength band is often somewhat stronger. There are other bands of the aromatically bonded SO₂ group at ~725 and 560 cm⁻¹. The aromatic ether bond in the poly(arylene sulfone) reveals itself as an intense broad absorption band at ~1245 cm⁻¹. EPDM and HPBS show characteristic bands corresponding to alkyl groups of long aliphatic chain hydrocarbons (—CH₂—CH₂) at 3030–2845 cm⁻¹ and 1485–1451 cm⁻¹; EPDM a band at 1680–1635 cm⁻¹ assigned to unsaturated hydrocarbon (trisubstituted alkene) and the band corresponding to phenyl group in HPBS appears at 700–760 cm⁻¹.

Table I compiles the glass transition temperature measured from DSC and Table II shows the data corresponding to T_g and E' (at room temperature) obtained through DMA analysis; moreover, as an example, in Figure 2, we plot the variation of E' with temperature. As it can be inferred, on the whole, all the samples of our series show noncompatible blend behavior, as both DSC and DMA reveal separate glass transition temperatures for each of the homopolymer constituents in the respective blends. However, the temperatures as such do vary as a function of blend composition.

While analyzing T_g variation as a function of PSU concentration in the samples, the glass transition temperature proves to be higher in all cases than that of the unblended homopolymer; the differential being higher, the greater is the PSU portion in the blend. At 50/50 concentration, the binary PSU/PPS samples present the highest values, followed by those containing EPDM, whereas the HPBS samples present the lowest values. Nevertheless, the data do not differ significantly among themselves. Although there does not exist accurate numerical agreement between the DSC and DMA techniques, material behavior can safely be termed as analogous when determined by

TABLE I
Glass Transition Temperature Obtained from DSC Measurements for Nonsulfonated Systems

Sample	Composition (wt %) (PSU/PPS/EPDM/HPBS)	Glass transition temperature (°C)			
		PSU	PPS	EPDM	HPBS
PSU	100/0/0/0	190.1	—	—	—
PPS	0/100/0/0	—	226.0	—	—
EPDM	0/0/100/0	—	—	-45.0	—
HPBS	0/0/0/100	—	—	—	-49.7
UE	50/0/50/0	192.1	—	-44.8	—
UH	50/0/0/50	189.9	—	—	— ^a
RE	0/50/50/0	—	228.0	-50.1	—
RH	0/50/0/50	—	226.2	—	— ^a
UR	50/50/0/0	195.0	225.0	—	—
URE	33.3/33.3/33.3/0	194.6	223.2	-48.1	—
URH	33.3/33.3/0/33.3	192.7	223.2	—	— ^a

^a It is not able to analyze T_g from DSC thermograms.

TABLE II
Storage Modulus at Room Temperature and Glass Transition Temperature Obtained from DMA Measurements for Nonsulfonated Systems

Sample	Composition (wt %) (PSU/PPS/EPDM/HPBS)	E' (GPa)	Glass transition temperature ($^{\circ}\text{C}$)			
			PSU	PPS	EPDM	HPBS
PSU	100/0/0/0	1.720	183.2	—	—	—
PPS	0/100/0/0	1.840	—	219.0	—	—
EPDM	0/0/100/0	0.003	—	—	-35.4	—
HPBS	0/0/0/100	0.060	—	—	—	-49.4
UE	50/0/50/0	0.180	188.0	—	-40.2	—
UH	50/0/0/50	0.162	186.4	—	—	-39.3
RE	0/50/50/0	0.033	—	260.2	-42.1	—
RH	0/50/0/50	0.175	—	238.4	—	-42.1
UR	50/50/0/0	1.420	191.1	241.2	—	—
URE	33.3/33.3/33.3/0	0.041	189.1	222.5	-43.0	—
URH	33.3/33.3/0/33.3	0.430	187.6	236.3	—	-41.7

one or the other analytic procedure. It is necessary to consider that DMA relies on the measurement rate, whereas with DSC this circumstance has no effect at all; in addition, the response elicited by either of them for T_g determination is different.

T_g variation as a function of PPS content in the blends shows, again and in general terms, a temperature rise with respect to the T_g of the unblended homopolymer, and the magnitude of the variation depends both on the nature and the composition of the blend. In addition, the analysis of T_g variation with PPS concentration reveals greater differences between the two analytic techniques. Dynamic-mechanical measurements generally provide more information about a material than other tests, and this is over a wide temperature and frequency range, as it is especially responsive to the chemical and physical structure of polymers.

Sulfonated systems

In Figure 3, the IR spectra are compiled corresponding to the sulfonated polymers. Regarding these samples

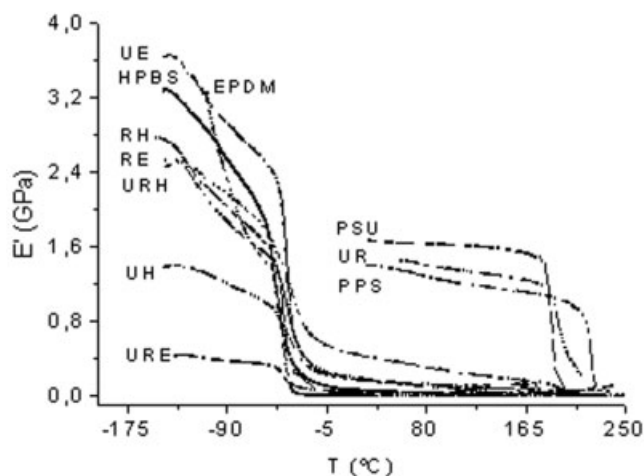


Figure 2 Storage modulus versus temperature for nonsulfonated systems.

and because of the complexity of the zone between 1000 and 1500 cm^{-1} (specially in the case of SPSU and SPES), it is indeed very difficult to assign bands to each group. Nonetheless, in all the cases, it is possible to observe a broad band at 3400 cm^{-1} , which is assigned to $-\text{OH}$ vibrations from sulfonic acid groups interacting with molecular water, and the most characteristic band, centered at 1200 cm^{-1} , are associated to asymmetric $\text{O}=\text{S}=\text{O}$ stretching of the sulfonated group vibrations. Moreover, in SHPBS spectrum, changes in the combinations vibrations (finger bands) between 1950 and 1650 cm^{-1} , particularly characteristics of the phenyl group, are observed.

Before analyzing the results of glass transition temperature for sulfonated systems, it is convenient to consider the theoretical model proposed by Eisenberg et al.¹⁵ to explain the relationship existing between the highly special properties presented by ionomers and their morphology. It postulates that ionomers containing ionic groups linked directly to the polymer back-

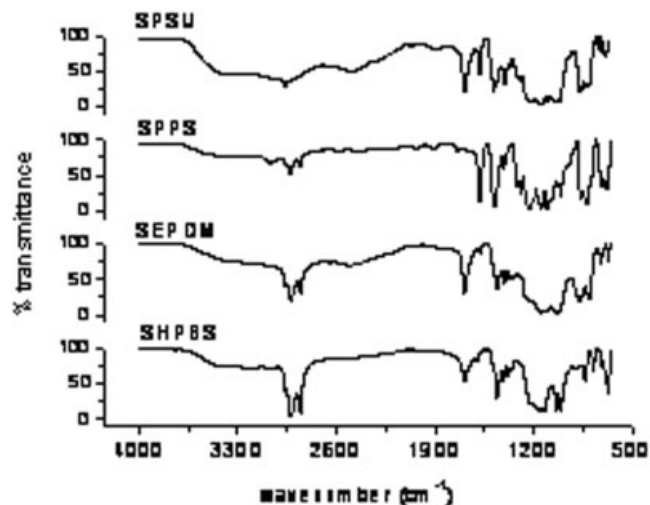


Figure 3 FTIR spectra corresponding to sulfonated polymers.

TABLE III
Glass Transition Temperature Obtained from DSC Measurements for Sulfonated Systems

Sample	Composition (wt %) (SPSU/SPPS/SEPDM/SHPBS)	Glass transition temperature (°C)			
		SPSU	SPPS	SEPDM	SHPBS
SPSU	100/0/0/0	186.4	—	—	—
SPPS	0/100/0/0	—	220.8	—	—
SEPDM	0/0/100/0	—	—	-37.0	—
SHPBS	0/0/0/100	—	—	—	-54.2
SUE	50/0/50/0	156.7	—	-41.8	—
SUH	50/0/0/50	183.4	—	—	— ^a
SRE	0/50/50/0	—	224.5	-43.2	—
SRH	0/50/0/50	—	235.7	—	— ^a
SUR	50/50/0/0	188.4	216.8	—	—
SURE	33.3/33.3/33.3	184.5	213.7	-35.1	—
SURH	33.3/33.3/0/33.3	186.3	220.5	—	— ^a

^a It is not able to analyze T_g from DSC thermograms.

bone exhibit notable differences from their initial constituents as a result of strong electrostatic attractive forces (opposite to the elastic ones), the ionic groups, incorporates at random, form ion pairs.¹⁶ These ion pairs aggregate to form quadruplets, sextuplets, and higher aggregates, collectively called multiplets. The multiplets cause a restriction of the mobility of the polymer segments adjacent to the multiplet. With increasing ion content, the partially immobilized regions begin to overlap. Eventually, when the ion content is high enough, the immobilized regions begin to form sufficiently large domains, the so-called "cluster," in which the material exhibits phase-separated behavior, including a second glass transition at higher temperatures than that of the matrix. Simultaneously, this restriction in the movement provokes new arrangements with changes in free volume.

While analyzing the results from DSC for our sulfonated polymers (Table III), no such phase separation behavior is observed, but important changes in the single glass transition temperature were observed. If we consider the unblended matrices, all the cases,

except SEPDM, show lower glass transition temperature than the corresponding to the pristine nonsulfonated polymers. Thus, it is possible to think that in these materials the changes in the macromolecular arrangements are more predominant than the terms corresponding to restriction in the movement of the chains, that is to say, the effect of increase in free volume is prevailed.

Regarding the blends, first of all, it is possible to point out that although it is described in the literature that the incorporation of ionic groups so as to favor specific and favorable interactions,¹⁷ such as ion-ion bonds,¹⁸ have proved to be a useful route to achieve polymer compatibilization,¹⁹ in our case, same as in nonsulfonated blends, we observe the T_g corresponding to each of the constituents of the blends. This fact indicates that as result of sulfonation reaction, no changes are observed and these blends, from a thermal point of view, behave as incompatible. There is not a clear relationship between blend composition and the T_g 's variation of unblended sulfonated matrices, and some especial cases, as SPSU and SEPDM,

TABLE IV
Storage Modulus at Room Temperature and Glass Transition Temperature Obtained from DMA Measurements for Sulfonated Systems

Sample	Composition (wt %) (SPSU/SPPS/SEPDM/SHPBS)	E' (GPa)	Glass transition temperature (°C)			
			SPSU	SPPS	SEPDM	SHPBS
SPSU	100/0/0/0	1.50	187.3	—	—	—
SPPS	0/100/0/0	1.81	—	223.1	—	—
SPDM	0/0/100/0	0.04	—	—	-33.4	—
SHPBS	0/0/0/100	0.05	—	—	—	-51.2
SUE	50/0/50/0	0.36	185.1	—	-41.6	—
SUH	50/0/0/50	0.18	182.3	—	—	-50.3
SRE	0/50/50/0	0.27	—	214.8	-39.2	—
SRH	0/50/0/50	0.30	—	209.0	—	-48.7
SUR	50/50/0/0	1.20	186.3	221.8	—	—
SURE	33.3/33.3/33.3/0	0.43	189.1	212.1	-36.3	—
SURH	33.3/33.3/0/33.3	0.35	187.6	217.6	—	-48.7

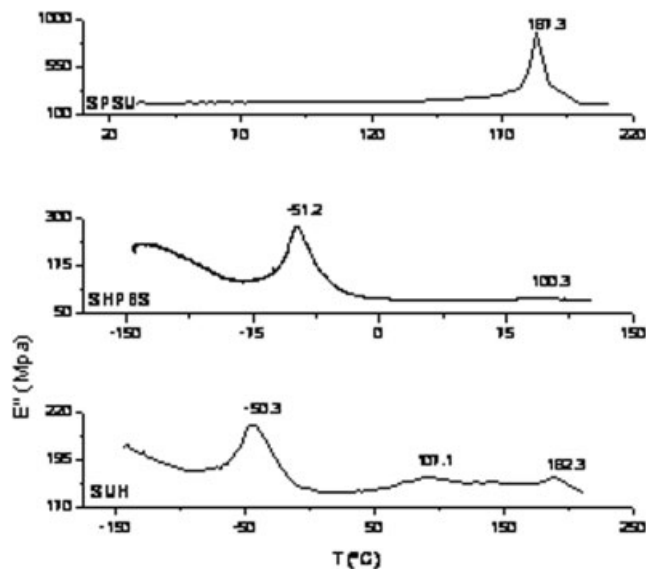


Figure 4 Representation of E'' versus temperature for the indicated samples.

show significant displacements on the glass transition temperature value. On another hand, in general lines, if we compare the T_g data of these blends with the corresponding nonsulfonated ones, in all cases, except SEPDM, a decrease in the value of glass transition temperature is observed.

In Table IV, the T_g 's and storage modulus (at room temperature) obtained from DMA for sulfonated polymers and their blends are listed; as an example, Figure 4 shows the variation of loss modulus with temperature for SPSU, SHPBS, and SUH. In same sense, the information obtained by thermal analysis was commented, with the exception of sulfonated EPDM, and the rest of the polymers present values lower than the counterparts nonsulfonated, although the differences are less remarkable. It is not possible to establish a simple relation between the variation of glass transi-

tion temperature and composition. However, in general terms, the T_g corresponding to SPSU and SHPB increases lightly when blends are formed, whereas for those containing SPPS and SEPDM it diminishes. In any case, the most important consequence that can be outlined is the presence of the relaxations, in the zone of glass transition, of all the constituents of the different blends. Thus, it is also confirmed that from the morphological point of view, these systems have to be considered incompatible. On the other hand, if we consider the values of the storage modulus at room temperature, it is possible to emphasize that for unblended polymers slight decreases are observed, with the exception of SEPDM whose value is significantly improved. In general, for the blends significant increases are obtained.

Table V compiles the data of conductivity obtained from complex impedance spectroscopy at the hydration conditions detailed in the experimental part. As an example, in Figure 5 the arcs are plotted corresponding to the unblended sulfonated polymers.

The most relevant aspects are the high values of conductivity reached, especially with blends composed by SEPDM or SHPBS, even in very short periods of hydration. Moreover, this very important improvement in conductivity is maintained throughout. These values seem to be very attractive taking into account that the measurements were accomplished at room temperature and the conductivity increases with temperature. With the purpose of comparing, we also analyzed a Nafion 117 sample at the same experimental conditions as that of our membranes.

These promising results are unsuccessful, as some of these systems suffer loss of the physical and mechanical properties. In fact, we verified that blends rich in EPDM component have good proton conductivity characteristics, but, in spite of the improvements observed in the modulus when the membranes are sulfonated, their dimensional stability (specially the

TABLE V
Conductivity Values Obtained from Complex Impedance Spectroscopy

Sample	Composition (wt %) (SPSU/SPPS/SEPDM/SHPBS)	Conductivity ($S\ cm^{-1}$)				
		0 (min)	60 (min)	120 (min)	180 (min)	240 (min)
Nafion	—	7.2×10^{-5}	2.1×10^{-3}	6.0×10^{-3}	6.4×10^{-3}	6.9×10^{-3}
SPSU	100/0/0/0	1.6×10^{-9}	6.9×10^{-6}	5.8×10^{-6}	4.9×10^{-6}	3.7×10^{-6}
SPPS	0/100/0/0	2.5×10^{-9}	—	2.2×10^{-6}	1.9×10^{-6}	1.7×10^{-6}
SEPDM	0/0/100/0	3.6×10^{-9}	1.6×10^{-4}	1.9×10^{-4}	2.3×10^{-4}	3.4×10^{-4}
SHPBS	0/0/0/100	2.1×10^{-9}	1.8×10^{-2}	1.3×10^{-2}	3.6×10^{-3}	3.5×10^{-3}
SUE	50/0/50/0	1.8×10^{-4}	1.1×10^{-3}	1.2×10^{-3}	1.1×10^{-3}	6.0×10^{-3}
SUH	50/0/0/50	1.3×10^{-4}	2.2×10^{-4}	1.2×10^{-2}	2.9×10^{-3}	1.2×10^{-3}
SRE	0/50/50/0	3.3×10^{-3}	3.2×10^{-3}	2.9×10^{-3}	1.0×10^{-3}	7.8×10^{-3}
SRH	0/50/0/50	2.9×10^{-6}	1.8×10^{-2}	1.8×10^{-2}	6.9×10^{-2}	5.6×10^{-2}
SUR	50/50/0/0	1.3×10^{-9}	1.2×10^{-8}	0.6×10^{-7}	1.0×10^{-7}	1.2×10^{-7}
SURE	33.3/33.3/33.3/0	8.7×10^{-7}	2.4×10^{-3}	1.5×10^{-3}	4.6×10^{-3}	1.6×10^{-3}
SURH	33.3/33.3/0/33.3	1.6×10^{-4}	1.3×10^{-2}	5.9×10^{-2}	1.2×10^{-2}	1.9×10^{-2}

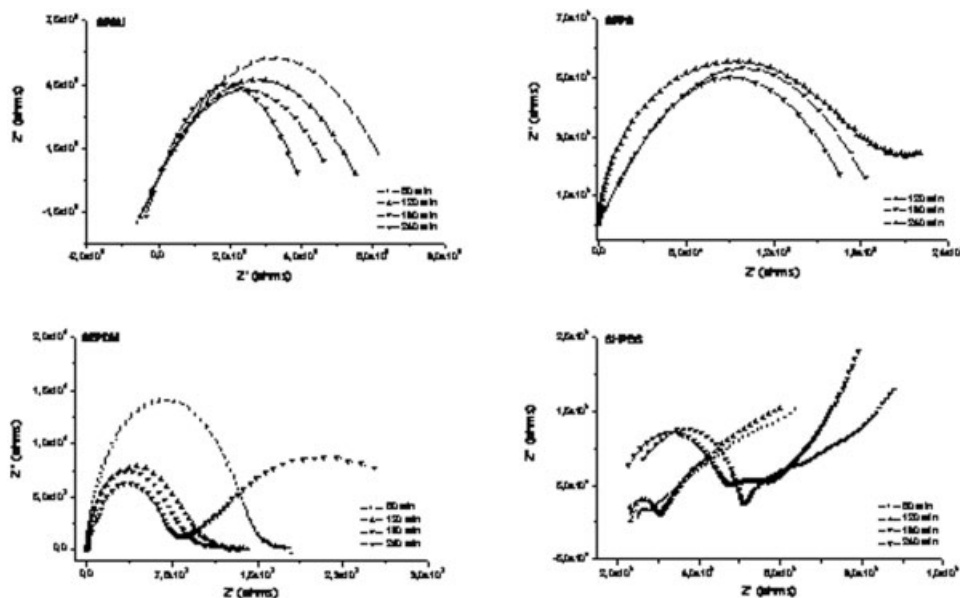


Figure 5 Complex plane diagram for unblended sulfonated polymers.

thickness) is altered after hydration, and in some cases, even small fissures were observed.

As several aspects are implied when a material is considered to be used as membrane (among them good electrical and mechanical characteristics), it is necessary to establish the “ideal” conditions for their balance.

To obtain new materials with desirable properties, the usual procedure is to prepare, at random, more or less complicated mixtures of the different components and select empirically the most suitable. However, in the present article, we propose to apply a statistical method, the classical Scheffé Simplex Design,²⁰ which is well suited for this kind of blends,²¹ to the conductivity and the storage modulus, as representative properties, with the aim of establish the more favorable compositions. In this sense, there are two complementary objectives regarding the general problem of mixtures: to find the proportions of the compounds required to optimize one or more properties, and to obtain an empirical equation, which satisfactorily describes the properties of the mixtures over the whole area that might be used.

In the general case, the empirical mathematical models, also named equation of response surfaces, are polynomials,^{21,22} and correspond to the development of Taylor serial functions. To determine the coefficient of a particular model, Scheffé proposed the study of mixtures whose compositions are distributed symmetrically in a “simplex” lattice over the experimental range. This kind of design contains a number of points equal to the coefficients in the corresponding polynomial that allows the equations to be solved directly.

In our case, the experimental blends obey the following plan:

Exp. no	Composition wt % SPSU/SPPS/ SEPDM (or SHPBS)	Variables of the model		
		X_1	X_2	X_3
1	100/0/0	1	0	0
2	0/100/0	0	1	0
3	0/0/100	0	0	1
4	50/50/0	0.5	0.5	0
5	50/0/50	0.5	0	0.5
6	0/50/50	0	0.5	0.5
7	33.3/33.3/33.3	0.33	0.33	0.33

when it is fulfilled: $\sum_i X_i = 1$, where X_i are the weight percentages of the different sulfonated polymers. With the results of experiments 1–6 and using the software NEMROD, coefficients for a quadratic model were calculated.

$$Y = b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3$$

While experiment 7 was used as test of the model. Y represents the property to be studied.

In our case, applying this statistical design to the conductivity (after 120 min of hydration say for example) and to the storage modulus (values taken at room temperature from DMA) led to the following equations.

For SPSU/SPPS/SEPDM systems:

$$E' = 1.50 X_1 + 1.81 X_2 + 0.04 X_3 - 1.80 X_1 X_2 - 1.63 X_1 X_3 - 2.59 X_2 X_3 \quad (1)$$

$$\log \sigma = -5.24 X_1 - 5.66 X_2 - 3.72 X_3 - 7.08 X_1 X_2 + 5.96 X_1 X_3 + 8.60 X_2 X_3 \quad (2)$$

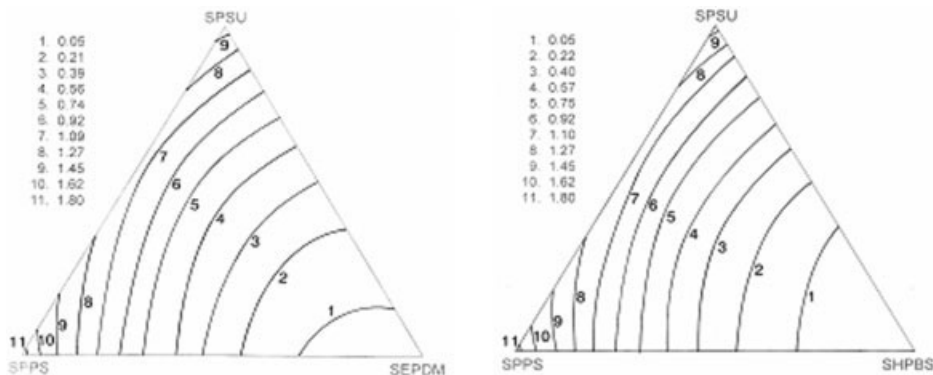


Figure 6 Response-surface contours for E' .

and for SPSU/SPPS/SHPBS systems:

$$E' = 1.50 X_1 + 1.81 X_2 + 0.05 X_3 - 1.80 X_1X_2 - 2.37 X_1X_3 - 2.49 X_2X_3 \quad (3)$$

$$\log \sigma = -5.24 X_1 - 5.66 X_2 - 1.88 X_3 - 7.08 X_1X_2 + 6.56 X_1X_3 + 8.08 X_2X_3 \quad (4)$$

Once the coefficients are known, it is possible to calculate E' and σ for any composition, and to obtain the response-surface plots shown in Figures 6 and 7.

As it was mentioned, experiment 7 was used as test of the validation of the statistical model to the behavior of our systems.

The application to ternary blends of the eqs. (1)–(4) yield the calculated values of E' and σ :

$$E'_{\text{cal,SURE}} = 0.45 \text{ GPa}$$

$$E'_{\text{cal,SURH}} = 0.38 \text{ GPa}$$

$$\sigma_{\text{cal,SURE}} = 1.0 \cdot 10^{-4} \text{ S cm}^{-1}$$

$$\sigma_{\text{cal,SURH}} = 3.8 \cdot 10^{-4} \text{ S cm}^{-1}$$

The conformity between experimental (Tables IV and V) and calculated values would be a good validation of the statistical model. As it can be observed, in the case of E' the agreement is very good and is quite good for σ . It is necessary to bear in mind that the conductivity is measured after hydration and probably other factors, such as physical deterioration, can take place.

If we consider the response-surface obtained for E' (Fig. 6), both systems behave similarly, that is to say E' diminishes inversely proportional to SEPDM or SHPBS fraction. Moreover, when the content of elastomers approaches to 50%, the variation of E' with composition is less pronounced.

Regarding the response-surface corresponding to σ (Fig. 7), it is possible to point out that those binary blends constituted by SPSU and SPPS, at 50/50 composition, have the minor values of conductivity, even lower than that of unblended matrices, improving the conductivity when any of two components predominates.

For binary blends SPPS/SEPDM and SPSU/SEPDM, σ increases directly proportional to the elastomer content until a central zone is reached, where the value of conductivity practically does not vary,

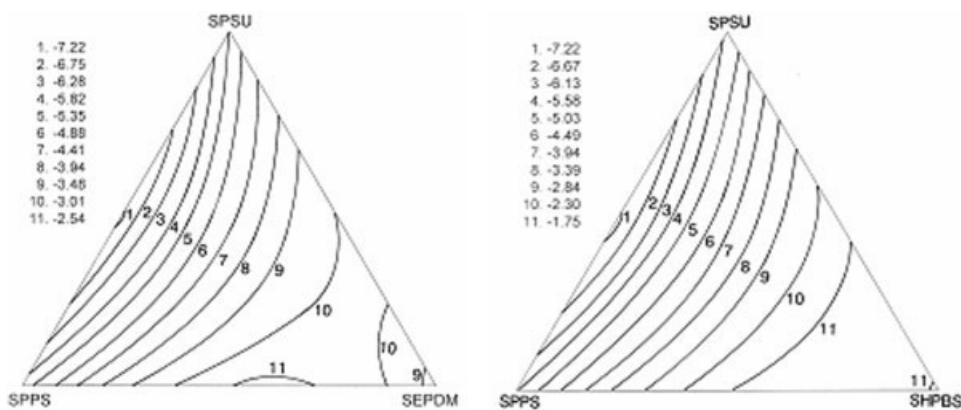


Figure 7 Response-surface contours for σ .

and then it begins to decrease when SEPDM is the majority component. The conductivity reached in that central zone is higher than that of unblended SEPDM.

With regard to binary blends SPSU/SHPBS and SPPS/SHPBS, conductivity increases directly proportional to elastomer content until a central zone is reached, and from which it continues improving, but more lightly. Same behaviors can be observed for to the ternary blends.

Analyzing the response-surface corresponding to E' and σ , it is possible to infer that the "ideal" systems, from the mechanical and electrical point of view, are binary blends constituted by SPSU or SPPS and any of the two elastomers, SEPDM or SHPBS, when the elastomer content is about 40%.

CONCLUSIONS

Blends have been prepared, at different compositions, based on two poly(arylene ether sulfone)s and two elastomers. Once they have been characterized, we have proceeded to the preparation of membranes and the subsequent reaction of sulfonation, in heterogeneous phase, with chlorosulfonic acid. These membranes have been also characterized from a morphological, mechanical, and electrical point of view. From the results, it is possible to conclude that these systems form incompatible and good proton conducting blends. The values of conductivity obtained are very promising when compared with those of the commercial membrane Nafion (at the experimental conditions set). The mechanical disadvantages observed in unblended SEPDM and SHPBS, such as loss of dimensional stability, fissures, or even little holes in the membranes after hydration, can be improved by preparing blends with SPSU or SPPS. By using a statistical method to design experiences, as applied in this work, it is possible to choose the blend with optimum composition to yield good electrical properties and the best mechanical behavior. Exactly, in our study, binary blends constituted by one of the thermoplastic polymers (SPSU or SPPS) and one of the elastomers (SEPDM or SHPBS) at the composition about 60/40 have demonstrated to be the most interesting.

The Scheffé model proposed to examine the loss modulus and conductivity has proved to be quite

satisfactory, as it is capable of reliably reproducing this behavior. This is of enormous relevance, because apart from the fact that its application to the study of ternary blends is not very common, it allows us, once the coefficients of the equation have been determined, to obtain, for each response that we desire to study, its exact value for any composition without the need of experimental determination. In addition, it becomes possible to select the range of concentrations where the behavior of a certain property is the most adequate, i.e. in a certain way the best suited material as a function of the properties required can now be designed.

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