

Evaluation of New Conducting Polymeric Membrane based on Sulfonation of Compatibilized NR/EPDM Blend

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ABSTRACT: In this study, research was undertaken to obtain new conducting polymer blend membrane based on compatibilized natural rubber/ethylene-propylene-diene monomer (NR/EPDM) by using different compatibilizers. To utilize them as membranes in polymer electrolyte membrane fuel cells, the blend membranes become conducting by sulfonation reaction, which inserts $-\text{SO}_3\text{H}$ groups into the macromolecular chain. The polymer blend membrane ratio (50/50), which was compatibilized by polyacrylonitrile compound was selected among the entire blend studied (A6), with the aim of determining its conductivity and water and methanol permeabilities. The degree of compatibility of NR/EPDM blend was improved by the use of polyacrylonitrile com-

pounds as compatibilizers. The effect of these compounds on the compatibility of blend was evaluated by ultrasonic spectroscopy and differential scanning calorimetry, DSC. It was found that a good compatibility has been achieved by using polyacrylonitrile because of the nitrile groups. When the polymer blend membrane (A6) was sulfonated with $-\text{SO}_3\text{H}$ groups good perspectives were shown regarding the methanol and water permeabilities and physical properties comparing to the commercial Nafion one. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3804–3812, 2007

Key words: polymer blend; ultrasonic; DSC measurements; sulfonation; methanol permeabilities; conductivity

INTRODUCTION

The direct methanol fuel cell (DMFC) has strongly emerged as a viable alternative source of power because of its high power density relative to other power sources.¹ In the DMFC, the polymer membranes used as electrolyte for proton transport are the perfluorosulfonic membranes, such as Nafion membrane. However, without large cost reduction, these expensive membranes are difficult to use in large scale commercial applications.² Therefore, it is necessary to develop an alternative membrane, which is less expensive and has high performance. To date, the new membranes being developed as alternatives to the Nafion membranes include hydrocarbon polymers,³ organic/inorganic hybrid membrane,^{4–5} acid-base polymer,⁵ and radiation-grafted membranes.^{6,7} The compatibilized polymer blend membrane was proposed as a new alternative conducting membrane in this study. Blending mixtures of polymers is a useful approach for the manufacture of new materials with specially tailored performance characteristics, which are often not exhibited by the corresponding

single component polymers.⁸ However, the concept of physically⁹ blending two or more noncompatible polymers to obtain a new product has not been developed as fully as the chemical approach to blending. The state-of-the-art to achieve compatibilization is to incorporate a third component into a polymer blend leading to a chemical interaction at the interface of the corresponding blend components. To make different useful polymer blends, they require specifically tailored chemicals with functional groups or block or graft copolymers. Therefore, the ability to make virtually any two or more polymers interacting chemically with each other is highly desirable for manufacturing a wide variety of stable polymer blends.¹⁰ NR/EPDM is two nonpolar and incompatible polymers.¹⁰ Each of them has certain desirable physical and chemical properties, which if combined in a blend would result in useful industrial products such as conducting membrane, especially after being sulfonated. Recently, El Sayed and Afifi¹¹ have epoxidized natural rubber (NR) and reported a compatible blend with EPDM. Methods determining the degree of compatibility have been reported, both theoretically and experimentally.^{12–14} Among these methods, DSC, IR, viscosity, dielectric relaxation, and electron microscopy¹² were used to prove on compatibility. Ultrasonic velocity measurements have been reported^{15–22} as a precise technique to investigate the degree of compatibility in highly viscous or solid forms of polymer blends. A new approach to study the polymer

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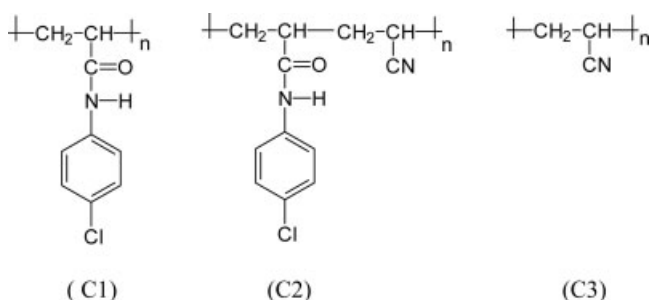


Figure 1 Chemical structures of the prepared poly *N*-(4-chlorophenyl) acrylamide, C1, poly *N*-(4-chlorophenyl) acrylamide-*co*-acrylonitrile, C2, and polyacrylonitrile, C3.

blend compatibility with ultrasonic attenuation was also reported by Arman²³ and Belaribi et al.²⁴ They reported poor adhesion between two polymers leading to high values of the attenuation coefficient. Singh et al.^{16–19} studied the ultrasonic velocity for compatible, semicompatible, and incompatible polymeric blends, and they found that in compatible blends, the ultrasonic velocity varied linearly to its composition. The reason of choosing NR/EPDM blend as new membrane because most of work done on EPDM showed a low possibility for performing good proton-conducting membrane because of their bad dimension properties. So, we used polymeric membrane by blending thermoplastic polymer, EPDM with rubbery one, NR, which can facilitate good processing properties of blend membrane. Also, within this scope, it is the goal of this research to propose new low-cost membranes possessing conductivity and showing good mechanical properties. To achieve this aim, we have chosen commercial and cheap polymers, which have good physical, chemical, and mechanical properties because of the presence of rubber and thermoplastic phase combined in homogeneous state. In this article, poly *N*-(4-chlorophenyl) acrylamide, poly *N*-(4-chlorophenyl) acrylamide-*co*-acrylonitrile, and polyacrylonitrile were prepared and each of the three polymeric compounds was added separately to a 50/50 blend of NR and ethylene-propylene-diene monomer (EPDM) as compatibilizers. The degree of compatibility of both polymers was assessed by ultrasonic and thermal analysis techniques. Second goal within this scope is also the objective of the research to develop a new low cost conducting polymer blend membrane possessing a high conductivity and showing no leakage and tear formation. Therefore, in this work, several conducting polymer blend membranes are synthesized by incorporating varying numbers of sulfonic groups into homogeneous polymer blend film. Since the evaluation of conducting polymer membrane based on homogeneous polymer blend made from rubbery and thermoplastic materials one has not received enough attention and clear studies. So, we proposed here a new conducting blend mem-

brane with good and desirable physical, chemical, and mechanical properties comparing to the commercial Nafion membrane.

EXPERIMENTAL

Materials

Acryloyl chloride, acrylonitrile, and triethylamine were supplied by Merck. Parachloroaniline was supplied by Aldrich and azobisisobutyronitril (ABIN) was supplied by Fluka, Germany. All solvents were of laboratory grade and supplied by EDWIC, Egypt. Natural rubber, NR, was a product of Guthrie, Biang City, Malaysia. EPDM rubber (Vistalon 6505) was a product of Esso Chimie, Germany. Chlorosulfonic acid and 1,2-dichloroethane was obtained from Aldrich. The commercial membrane used as a reference was Nafion 117 from Dupont.

Preparation of homopolymers and copolymer (compatibilizers)

Polyacrylonitril and poly *N*-(4-chlorophenyl) acrylamide were prepared and characterized as described elsewhere.²⁵ Ten grams of *N*-(4-chlorophenyl) acrylamide dissolved in 150-mL acetone were mixed with 3.14 mL of acrylonitrile in a 1 : 1 ratio and 0.1 g of ABIN was added as an initiator. The mixture was copolymerized at 60°C for 7 h. The solution was left to cool, and then poured into methanol to precipitate the copolymer, poly *N*-(4-chloro phenyl) acrylamide-*co*-acrylonitrile, which was then filtered and dried. The chemical structures of the three prepared polymeric compounds are shown in Figure 1. Whereas Table I shows the compositions of NR and EPDM polymer blends incorporated with the prepared compatibilizers C1, C2, and C3.

NR/EPDM blending and film preparation

The first step consisted of preparing a pre-mix of EPDM and NR on a two roll-mill at room temperature (50%–50 wt % ratio), and then the compatibilizer

TABLE I
Compositions of NR and EPDM Polymer Blends Incorporated with the Prepared Polymeric Compounds (Compatibilizers)

Ingredient	Sample No.					
	A1	A2	A3	A4	A5	A6
NR	100					
EPDM	100					
NR/EPDM			50/50	50/50	50/50	50/50
C1					10	
C2						10
C3						10

TABLE II
Density (ρ), Longitudinal Ultrasonic Velocity (V_l), Shear Ultrasonic Velocity (V_s) and the Glass Transition (T_g) Measured by DSC of the Studied Samples

Property	Sample No.					
	A1	A2	A3	A4	A5	A6
ρ (gm/cm ³)	0.7914	0.7730	0.7695	0.8237	0.7810	0.7951
V_l (m/s)	1510	1491	1482	1472	1435	1513
V_s (m/s)	888	880	874	868	830	896
T_g (K)	200	233				224

was added as 10 wt % as shown in Table I. The synthesized homopolymers and copolymer were incorporated as compatibilizers. Finally, thin films (0.9–1 mm) of these materials (50/50) blend ratio were obtained in a hydraulic press. In the second step, the sulfonation of these films was carried out by placing them in chlorosulfonic acid/dichloroethane solutions at different concentrations 0.1, 0.2, and 0.3M of sulfonating agent. These concentrations were chosen in such a way that the maximum theoretical degree of sulfonation reached were of 10, 20, and 30%, respectively. The reaction went on for at room temperature and preset times to improve the conductivity and preserve the physical integrity of the membranes. Then, the experimental samples were washed several times with acetone and distilled water until obtaining neutral pH. The sulfonation was verified by FTIR spectroscopy using total attenuated reflection (ATR), (JASCO-5300, Japan Spectroscopic). All spectra were collected from the membrane by transmission method using 128 scans with the resolution of 4 cm⁻¹ at room temperature.

Density measurements

The density of each sample was measured at 298 K by the hydrostatic weighing method using dimethylformamide, DMF, as an immersion liquid. The sensitive balance used in the measurements is Mettler AT 21, capacity 160 g, and readability 0.002 mg.

Glass measurements

The ultrasonic longitudinal and shear velocities (V_l and V_s) were measured on the basis of the pulse-echo technique,²⁶ using an oscilloscope (54615B Hewlett-Packard). A direct measurement of the time required for the pulses to travel twice the length of the specimen, allowed immediate calculation of the ultrasonic wave velocity as given in eq. (1)

$$V = 2X/\Delta t \quad (1)$$

where X is the sample thickness and Δt is the time interval. The velocity measurements using this method were carried out at room temperature and at a frequency of 2 MHz. The measurements were

repeated three times to ensure the reproducibility of the data.

Differential scanning calorimetry

The glass transition temperatures (T_g) of the compositions (Table II) were measured with a DSC (differential scanning calorimetry) (Shimadzu 50, Kyoto, Japan) under nitrogen atmosphere at a heating rate of 10 K min⁻¹. The inflection point of the slope of the heat capacity plot was taken as the glass transition temperature.

Ionic conductivity measurements

The ionic conductivity of membrane at 25°C was obtained by impedance spectroscopy. Impedance measurements were carried out at room temperature by using Shimadzu impedance spectroscopy. At ambient temperature, frequency 0.01–10,000 kHz and 0.1 V amplitude of the signal were applied. We designed a special conductivity cell composed of two silver electrode of 0.07 cm² of surface. The electrode surface was kept clean to avoid any contact resistance during the measurements, and the membrane samples were inserted between these two flat circular electrodes. Membrane electrode assembly consisted of gluing two electrodes on both sides of membrane, with the help of a hydraulic press. The samples were hydrated in water at different times, and clamped between two electrodes for recording of the impedance spectroscopy. The measurements were taken at room temperature after hydrating the samples by immersing them in deionized water at 50°C. The real impedance taken at zero imaginary impedance was used to calculate the proton conductivity of the membrane.

Water and methanol permeability (diffusion coefficient)

The methanol permeabilities of the polymer electrolyte membrane was tested in a two-compartment diffusion cell. Two glass cylinders were used, equipped with external jackets to ensure reagent circulation coming from a thermostat. Each cylinder was filled with an equal amount of water and methanol, respectively, and the polymeric membrane was held between the

two cylinders with the help of fixed clamp. About 100 mL of 10M methanol solution and 100 mL of distilled water were added, respectively, and stirred to avoid concentration gradient. Then methanol crossover was analyzed by gas chromatography (Hewlett Packard M-5890) and water crossover by Karl Fisher analysis. Karl Fisher analysis refers to the valuation of the following Red-Ox reaction between iodine and sulfur oxide in the presence of water.

Dynamic mechanical measurements

The measurements were conducted by utilizing 983 Dynamic Mechanical Analyzer, TA at 0.1 Hz. The temperature ranged from 173 to 373 K, and heating rate was 5 K min^{-1} .

RESULTS AND DISCUSSION

Evaluation of degree of compatibilization of NR/EPDM polymer blend

Ultrasonic absorption coefficient

The dependence of the temperature on the ultrasonic absorption coefficient of longitudinal waves at a 2 MHz frequency along with the range of temperature 160–260 K for all samples are shown in Figures 2–5. Figure 2 shows a main peak at 235 K for 100% EPDM and another main peak at 200 K for 100% NR. It also shows two separate peaks for the blend ratio 50NR/50EPDM, one peak is at 210 K and the other is at 233 K. Those two peaks indicate that the two polymers

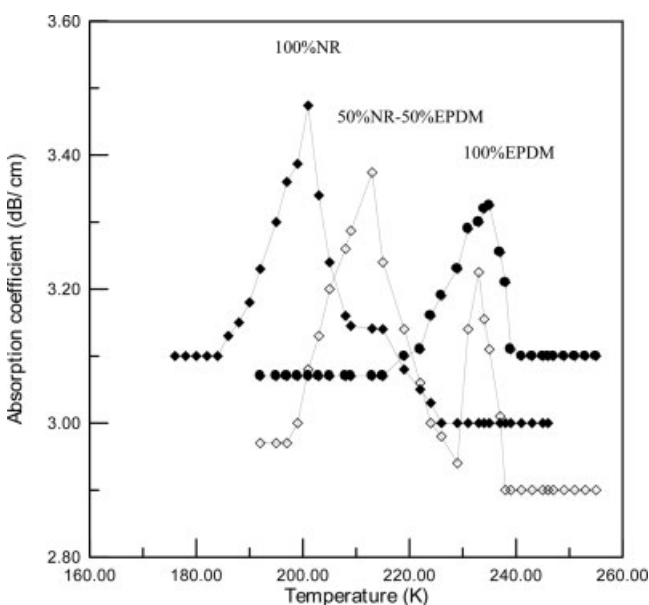


Figure 2 Variation of ultrasonic absorption coefficient with temperature for 100% NR, 100% EPDM, and 50% NR-50% EPDM samples.

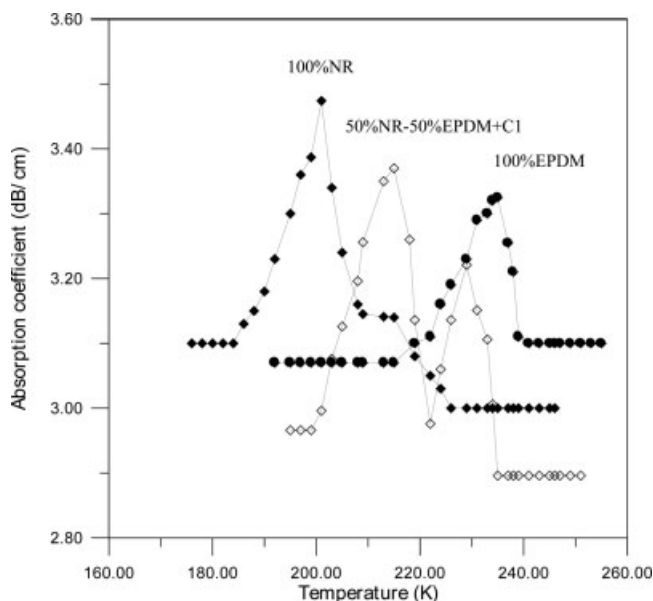


Figure 3 Variation of ultrasonic absorption coefficient with temperature for 100% NR, 100% EPDM, and 50% NR-50% EPDM + C1 samples.

are phase separated and are incompatible. The addition of the polymeric compatibilizer, C1, did not improve the compatibility of the two polymers significantly, as it can be seen in Figure 3, where the two separate peaks of NR and EPDM are still quite distant to each other. On the one hand, this means that chlorine atoms contained in the polymer structure are not charged enough to bring about a considerable extent of phase interaction, i.e., compatibility of NR and EPDM. On the other hand, the introduction of CN

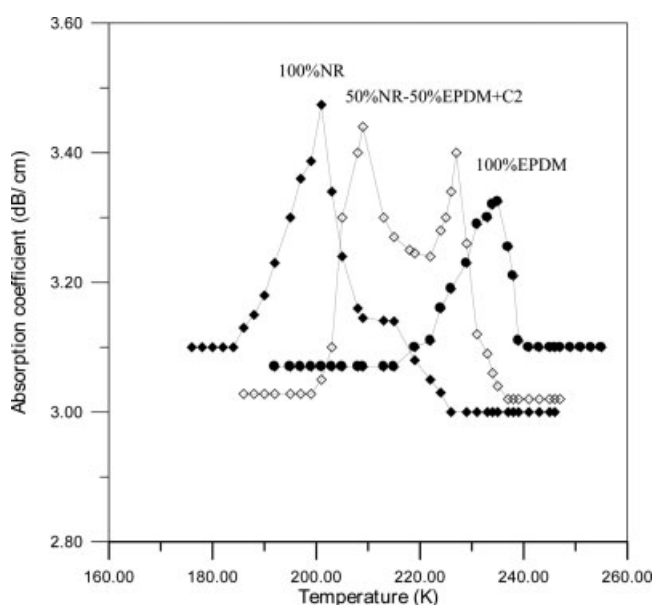


Figure 4 Variation of ultrasonic absorption coefficient with temperature for 100% NR, 100% EPDM, and 50% NR-50% EPDM + C2 samples.

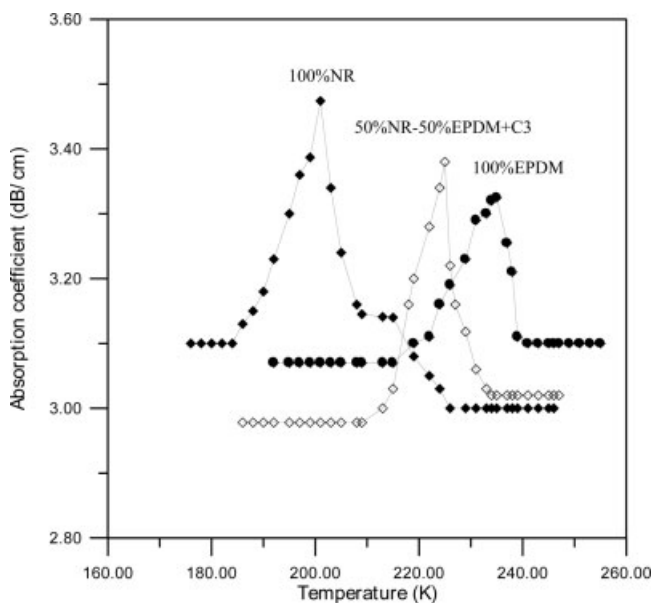


Figure 5 Variation of ultrasonic absorption coefficient with temperature for 100% NR, 100% EPDM, and 50% NR-50% EPDM + C3 samples.

groups into the copolymer structure C2 resulted in a significant enhancement of the compatibility of NR and EPDM as it can be noticed from Figure 4 where the two separate peaks shifted closely towards each other and tend to form one peak. This enhancement in the compatibility can be owed to the polar nature of the CN groups, which can create some sort of dipole–dipole interaction that would contribute to the compatibility. Furthermore, a highly compatible NR and EPDM blend system can be obtained by the addition of polyacrylonitrile, C3, as compatibilizer as shown in Figure 5. One reason for this is believed to be the high polarity CN groups of the polymer, which can create a strong dipole–dipole interaction that would help the two polymers phases to achieve a strong degree of miscibility. Another reason for such a good compatibility is that the highly crystalline polyacrylonitrile spread in the blend sample can act as a binding intermediate, which can help bringing the two polymers into one phase.

Ultrasonic transition temperature

The glass transition temperatures of the various blend compositions were measured using DSC are given in Table II. Samples A1, A2, A3, A4, A5, and A6 represent 100% NR, 100% EPDM, 50 wt %/50 wt % NR/EPDM without compatibilizer, 50%/50% NR/EPDM with C1 compatibilizer, 50%/50% NR/EPDM with C2 compatibilizer, and 50%/50% NR/EPDM with C3 compatibilizer, respectively. It can be seen that there is a noticeable deviation between the measured glass transitions in case of 100% NR, 100% EPDM, and

50NR/50EPDM blend. The two measured T_g values tend to approach each other upon using the prepared compatibilizers. This approach is found to be fairly good in sample A6 containing polyacrylonitrile, which is a source of CN groups. This confirms the argument that CN groups assist the interaction between the two polymers component blend and therefore the blend goes through only one transition temperature peak at 224 K, as shown in Figure 5. This single peak indicates that the cyanide groups increase the degree of the compatibility of the polymer blend system and therefore only one phase is formed.

Ultrasonic velocity

The experimental data of the longitudinal ultrasonic wave velocity V_l and the shear wave velocity V_s as well as the density of the prepared samples ρ are also given in Table II.

From the table, it can be seen that the ultrasonic velocity and the shear velocity are reduced upon blending NR and EPDM, sample A3. Such a reduction can be justified as a result of the absence of a strong intermolecular interaction between the components of the blend system, which indicates their immiscibility and formation of two phases, i.e., incompatible blend. This behavior is in good agreement with the results reported earlier and proves the incompatibility of NR/EPDM with a different composition.¹⁰ It is also to be recorded that V_l and V_s of sample A4 were not improved upon the addition of the prepared polymeric compatibilizer, C1, which contains chlorine atoms. This proves that the two polymer phases are still incompatible. However, the use of compatibilizer C3 containing CN groups, sample A6 has markedly enhanced the ultrasonic and shear velocities to the extent that they surpassed those of the reference blend 50NR/50EPDM, sample A3. These results confirm the good miscibility and the formation of one single phase of the two polymers. It is also interesting to detain that V_l and V_s of sample A5, containing the copolymer C2 showed significantly lower values in spite of the presence of polar CN groups, which enhanced the compatibility. This may be understood on the basis of a synergistic effect of unknown nature of Cl atoms and CN groups, which may be responsible for wave retardation.

Elastic moduli

The longitudinal modulus, L , shear modulus, G , Young's modulus, E , bulk modulus, K , together with Poisson's ratio, σ , and microhardness, H , were calculated^{20,27} using eqs. (2)–(7) and the results are given in Table III.

$$L = \rho v_l^2 \quad (2)$$

TABLE III
The Longitudinal Modulus, L , Shear Modulus, G , Young's Modulus, E , Bulk Modulus, K , Together with Poisson's Ratio, σ , and Microhardness, H

Property (Gpa)	Sample					
	A1	A2	A3	A4	A5	A6
L	1.80	1.72	1.69	1.78	1.61	1.82
G	0.62	0.60	0.59	0.62	0.56	0.64
K	0.97	0.92	0.90	0.95	0.86	0.97
E	1.53	1.48	1.45	1.53	1.35	1.57
H	0.110	0.107	0.105	0.110	0.097	0.115

$$G = \rho v_s^2 \quad (3)$$

$$K = L - (4/3) G \quad (4)$$

$$E = 2G(1 + \sigma) \quad (5)$$

$$\sigma = (L - 2G)/2(L - G) \quad (6)$$

$$H = (1 - 2\sigma)E/[6(1 + \sigma)] \quad (7)$$

An observation of Table III reveals that the elastic moduli of the 50NR–50EPDM reference blend showed the same trend in behavior as the ultrasonic wave velocities as a result of the decrease in rigidity of the blend system, which is due to the weak phase interaction of the blend components. One can also note that the addition of the compatibilizer C1, containing chlorine atoms, to the investigated blend system NR-EPDM has improved the elastic constant and microhardness although it is not a good compatibilizer of this polymer system. It is also noticed that all the studied mechanical properties except Poisson's ratio were reduced upon the addition of compatibilizer C2 although the absorption coefficient studies in Figure 4 indicated that it has a good compatibilizing effect on both polymers. This can be attributed to the synergistic effect of chlorine atoms and cyanide groups, which may hinder the improvement of these properties. Meanwhile, the use of C3 has greatly improved the studied mechanical properties. The higher degree of crystallinity of polyacrylonitrile may

be responsible for the higher strength properties and hence higher elastic constant and microhardness. As for Poisson's ratio, it is formally defined, for any structure, as the ratio of lateral to longitudinal strain, is produced when tensile forces are applied. It is clear from the results that its values are almost constant for all samples except sample A6, which showed a lower value. It might be that the enhancement of the compatibility produced by the use of C3 has resulted in increasing the association between NR and EPDM, which is responsible for the reduction in the value of Poisson's ratio.²⁸

Evaluation of compatibilized NR/EPDM (50:50%) polymer blend as a new conducting polymer blend membrane

In this step, the sulfonation of the compatibilized polymer blend (A6) is likely to occur in the double bond of the EPDM norbornene units (ethylene and propylene units known as norbornene), where the hydrogen of the CH bond is replaced by SO₃H group. The IR spectra of the nonsulfonated and sulfonated EPDM/NR blend with chlorosulfonic acid/dichloroethane solution at different concentrations: 0.1M (S1), 0.2M (S2), and 0.3M (S3) were measured by using FTTR technique, since it is very useful tool for opaque samples, as is the case with our sulfonated blend membrane. The spectrum of nonsulfonated compatibilized EPDM/NR blend membrane shows the presence of alkyl groups of aliphatic hydrocarbons (–CH₂–CH₂–) at 3030–2845 cm^{–1} and 1485–1451 cm^{–1}. When the polymer blend is sulfonated, the most important aspects are broad band at 3400 cm^{–1}, which is assigned to –OH and attributed to sulfonic group (it is significant that this band becomes wider as a function of increasing reagent concentration). Also, changes in the band centered around 1200 cm^{–1}, which is characteristic of the asymmetric stretching vibration corresponding to the O=S=O group.

All the samples were subjected to a structural study determining the glass transition temperature (T_g) through dynamic mechanical analysis (DMA) and DSC. The results obtained are shown in Table IV.

TABLE IV
Glass Transition Temperatures Obtained from DSC and DMA as a Function of Sulfonating Agent Concentration, for Binary Blend Based on EPDM/NR (C3)

Sample	EPDM/NR (wt %)	ClSO ₃ /DEC (mol/L)	Sulfonation time (h)	T_g (K)	DMA (K)
S	50/50	–	–	224	225
S1	50/50	0.1	24	229	229
			48	231	219
S2	50/50	0.2	24	233	233
			48	233	228
S3	50/50	0.3	24	235	234
			48	235	232

TABLE V
Conductivity Values at Different Hydration Times, Obtained from Impedance
Technique for Nafion and Sulfonated Compatibilized Blend Membrane (A6) at 24 h
Sulfonation

Sample	EPDM/NR (A6) (wt %)	ClSO ₃ /DCE (mol/L)	Sulfonation time (h)	Hydration time at 50°C (h)	Conductivity at 25°C (S/cm)
Nafion	–	–	–	0	7×10^{-5}
				3	2×10^{-3}
				6	6×10^{-3}
				24	8×10^{-3}
S1	50/50	0.1	24	0	3×10^{-6}
				3	4×10^{-4}
				6	5×10^{-4}
				24	1×10^{-3}
S2	50/50	0.2	24	0	3×10^{-4}
				3	6×10^{-3}
				6	2×10^{-2}
				24	3×10^{-2}
S3	50/50	0.3	24	0	1×10^{-5}
				3	3×10^{-3}
				6	3×10^{-3}
				24	1×10^{-3}

Although both techniques show single glass transition temperature, the values are different as the dynamic mechanical measurements are sensitive to the chemical and physical structure of polymers and provide more information about material over a wide temperature and frequency than thermal analysis. The glass transition temperature obtained by DSC and DMA techniques show the upward trend as a function of increasing sulfonation agent concentration. This fact suggests an increase of sulfonic groups with strong polar in nature and, as a consequence, triggers the rise in T_g .²⁹

Conductivity of sulfonated polymer blend membrane compatibilized by acrylonitrile

The conductivity results of polymer membrane prepared from sulfonated EPDM/NR (A6) are shown in

Tables V and VI at different hydration times, respectively. Measurements were taken at room temperature after hydrating the samples by immersing them in deionized water at 50°C for different periods of times. For the purpose of comparison, we used Nafion polymer membrane sample at the same experimental conditions as our membranes. The thickness of the membrane was 0.7 mm. The conductivity values increase as a function of chlorosulfonic acid concentration, some of which prove to be fairly good. Also, conductivity increases proportionate to hydration time, for the longest time, the property begins to deteriorate. This is indicative of the fact that, because of the strongly hydrophilic character of the sulfonic groups, the adsorbed water causes swelling and may deteriorate the film. It is relevant to state that the sulfonation reaction may be extended up to 48 h without occurring neither physical nor mechanical deteriora-

TABLE VI
Conductivity Values at Different Hydration Times, Obtained from Impedance
Technique for Nafion and Sulfonated Compatibilized Blend Membrane
(A6) at 48 h Sulfonation

Sample	EPDM/NR (A6) wt %	ClSO ₃ H/DCE (mol/L)	Sulfonation time (h)	Hydration time at 50°C (h)	Conductivity at 25°C (S/cm)
S1	50/50	0.1	48	0	5×10^{-6}
				3	1×10^{-3}
				6	3×10^{-3}
				24	6×10^{-3}
S2	50/50	0.2	48	0	6×10^{-6}
				3	2×10^{-3}
				6	2×10^{-3}
				24	4×10^{-3}
S3	50/50	0.3	48	0	5×10^{-6}
				3	7×10^{-4}
				6	1×10^{-3}
				24	5×10^{-3}

TABLE VII
Diffusion Coefficients of Water and Methanol in the Commercial and Sulfonated Compatibilized Blend Membranes (A6)

Sample	EPDM/NR (A6) (wt %)	ClSO ₃ /DCE (mol/L)	ADC water (mol cm ⁻² min ⁻¹)		ADC methanol (mol cm ⁻² min ⁻¹)	
			40°C	60°C	40°C	60°C
			Nafion	–	–	5 × 10 ⁻²
S2	50/50	0.2	3 × 10 ⁻³	7 × 10 ⁻³	1 × 10 ⁻³	1 × 10 ⁻³

ADC, Apparent diffusion coefficient.

tion of the film. For 24-h sulfonation time, the best conductivity values are obtained for chlorosulfonation concentration (0.2M, S2). However, at 48-h sulfonation time, variation is not straightforward, neither as a function of acid concentration nor of hydration time. For one and the same concentration and the same hydration time, the best results are obtained for 48-h sulfonation time.

Water and methanol permeability (apparent diffusion coefficients)

To study water and methanol permeability, the membrane S2 was selected. The apparent diffusion coefficient of water and methanol obtained from the membrane S2 and compared to those of Nafion membrane at two different temperatures, the result obtained are listed in Table VII. The most significant difference is observed in the diffusion coefficient of water at 40°C. With increasing temperature, the difference becomes smaller, especially in the diffusion coefficient of methanol. As can be observed, the commercial Nafion membrane showed higher values of the apparent diffusion coefficient. So, we can assume that these type of blended membranes to tolerate methanol as a fuel much better than Nafion one. We also observed that after the measurements were finished, the blended membrane in our study preserved its physical and dimensional stability, while small holes and loss of the initial dimensions could be observed in the Nafion film.

CONCLUSIONS

Polyacrylonitrile is a very good compatibilizer for NR/EPDM blend. The membrane was obtained by blending two polymers: EPDM and NR and compatibilized by polyacrylonitriles, as compatibilizer, are showed perspective valuable mechanical qualities. The reaction with chlorosulfonic acid was used to incorporate —SO₃H groups into macromolecular chain that would bring a conducting nature onto the membrane. The advantage of this method is to have membranes prepared in homogeneous, uniform structure, and dimensional stability. From water and

methanol measurements, we conclude that our membranes have good dimensional stability, because after the experiment, we observed that the geometric dimensions, especially thickness of the membrane remains unalterable. Moreover, we think that these membranes possess good mechanical properties because the Nafion membrane had fissures and small holes unlike our membrane. In view of the obtained results, it is legitimate to conclude that it is necessary to undertake further studies to optimize the composition and conditions of obtaining of the membrane, to improve some properties mainly in conductivity, power density, and other like effect of sulfonation on *T_g* should be concerned. The barrier properties of our new membrane against methanol and water crossover, apart from their good mechanical and processing properties, as well as their great dimensional stability and low cost, qualify them to be considered as an alternative to the commercial membrane.

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