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Hybrid membranes based on block co-polymer ionomers and silica gel. Synthesis and characterization

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Abstract

This work reports on the synthesis (via heterogeneous sulfonation) structural and electrical characterization of hybrid membranes based on block co-polymer ionomers (HSBR and EPDM) and silica gel prepared by sol–gel reaction.

The structural characterization consisted of the analysis of their thermal and mechanodynamical transitions by DSC and DMA, respectively. The ion-exchange capacity of each polymer was determined by both titration and elemental analysis (EA). The introduction of sulfonic groups was verified by means of infrared spectroscopy (ATR). The electrical characterization was made using ac impedance at different hydration times, the conductivity being calculated from the corresponding impedance spectra. Finally, methanol crossover through the membranes was carried out, comparing the results obtained with Nafion 117.

The results indicate the existence of a complex microstructure formed by different phases corresponding to both ionic and non-ionic blocks of the co-polymer as well as the aggregates or clusters owed to the electrostatic interaction among ion pairs. Conductivity values are similar to Nafion and they improve with hydration time for hybrid membranes due to the absorbent nature of the inorganic filler. Likewise, methanol crossover is lower than in Nafion, probably due to the barrier effect exerted by the non-sulfonated blocks of the co-polymer.

Keywords: Block co-polymer ionomers; Ionic conductivity; Methanol crossover

1. Introduction

Polymers with ionic groups attached to their structure, more known as ionomers, are indispensable electrolyte materials for numerous electrochemical applications such as batteries, sensors, low temperature fuel cells and in particular, direct methanol fuel cells (DMFC) that are already outlined as a future alternative energy source [1,2]. For this application, Nafion® (Dupont) is still the most frequently used membrane although it has mainly two disadvantages, high cost and high methanol permeability (methanol crossover) [3,4]. Current research is focused on the development of new polymer membranes to make the DMFC an economical and practical option [5–8].

In this sense, our group has been working on the synthesis and characterization of ionomers based on block co-polymers like an alternative to the commercial membrane Nafion [9–12]. Block co-polymers are constituted by two or more polymers blocks, placed throughout the same chain following an ordered sequence. When one of these blocks contains ionic groups attached to its structure, then we are talking about block co-polymer ionomers [13–19]. The interest for this type of materials is due, on the one hand, that non-ionic blocks can act as a barrier for methanol crossover and on the other hand, that the ordered microstructure can exert on ionic transport, definitively on the conductivity of the membrane.

Thus, in this work we have carried out the synthesis (via heterogeneous sulfonation), the microstructural and electrical characterization and also the methanol diffusion through of two ionomers based on block co-polymers. The two most desirable functional groups for reacting with sulfonating agents are double bonds and aromatic groups, particularly phenyl groups. Poly(butadiene–styrene) block co-polymer possesses a two phase microstructure consisting of polystyrene (PS) domains dispersed in a rubbery

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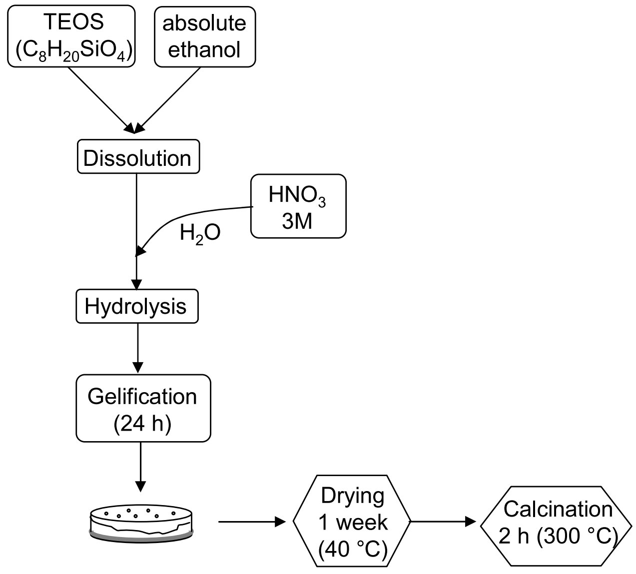

Fig. 1. Schematic of silica gel preparation.

continuous phase of polybutadiene. To overcome the instability problems due to the high reactivity of carbon double bonds, hydrogenated poly(butadiene–styrene) block co-polymer (HSBR) was used to limit the amount of unsaturations in the starting polymer to the extent of the sulfonation reaction. The other polymer used was ethylene–propylene–diene terpolymer (EPDM). In this case, sulfonation reaction occurs only through double bonding of norbornene block of the co-polymer.

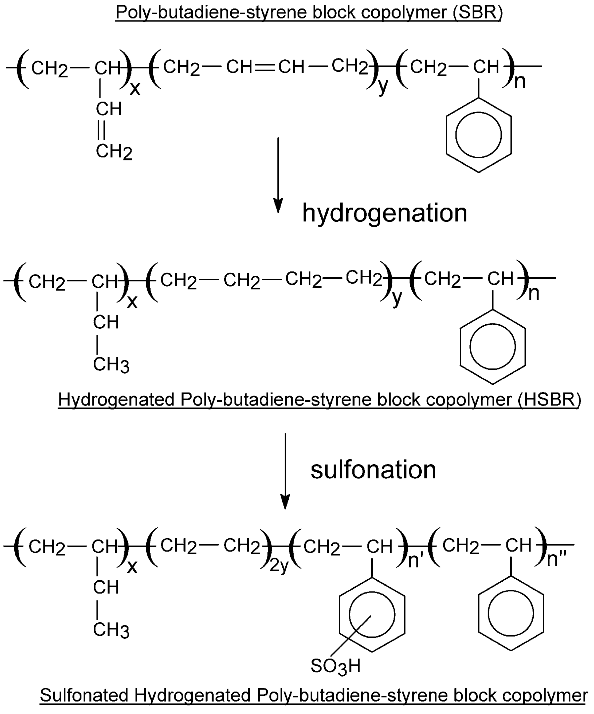

Fig. 2. Mechanism of sulfonation reaction of hydrogenated poly(butadiene–styrene) block co-polymer (HSBR).

In addition and with the purpose of improving membrane hydration, 10% of an inorganic filler has been introduced, concretely silica gel prepared from TeOs by sol–gel reaction. The incorporation of this type of fillers has already been studied in Nafion with interesting results [20–25].

2. Experimental

2.1. Materials

Hydrogenated styrene butadiene block co-polymer (HSBR) with an insaturation level below 2.6% and containing 30% of aromatic units was supplied by Repsol-YPF Química under the trade name Calprene CH-6110. EPDM terpolymer containing 60% ethylene, 29% propylene and 11% norbornene was Vistalon 9500 Exxon Chemical. The cross linking agent used was dicumyl peroxide (Aldrich).

The precursors used in the preparation of silica gel (GS) were tetraetoxisilane ($C_8H_{20}SiO_4$, TEOS) from Aldrich, absolute ethanol and aliquot amounts of concentrated nitric acid (3 M) was necessary in the hydrolysis process.

2.2. Silica gel preparation

In Fig. 1 schematic of the preparation is shown. Dissolution of TEOS and ethanol was carried out in a reactor with vigorous stirring. Then hydrolysis process began incorporating stoichiometric amounts of water. The solution so obtained was allowed to gel for 24 h on a Petri dish covered with a perforated parafilm. Drying process was carried out at 40 °C during 1 week. Thus, a transparent gel was obtained which was calcinated at 300 °C for 2 h. The amorphous colloidal dust (X-rays diffraction did not display any crystallinity) has a specific surface of 225 m^2/g measured by BET, being the particle size 7 nm and the agglomerate size of 50 nm. Finally, the material was sieved to 33 μm.

2.3. Blend and membrane preparation

An open two-roll mill at 40 °C was used to blend the different samples with concentrations HSBR-GS (90–10) and EPDM-GS (90–10). The cross-linking agent (dicumyl peroxide) was added during mixing in a ratio of 2 g of peroxide by each 100 g of blend. Blending time was 20 min to maximize intermixing of the components. In all the cases homogenous and flexible bands were obtained.

Membranes with thicknesses between 150–200 μm were prepared by compression moulding using a hydraulic press Collin, weighing 2.5 g of material for each membrane. The temperature of plates was 160 °C, the applied pressure 200 bars and the curing times were determined using a rheometer MDR 2000-E Monsanto. The tests were carried out at 160 °C during 60 min.

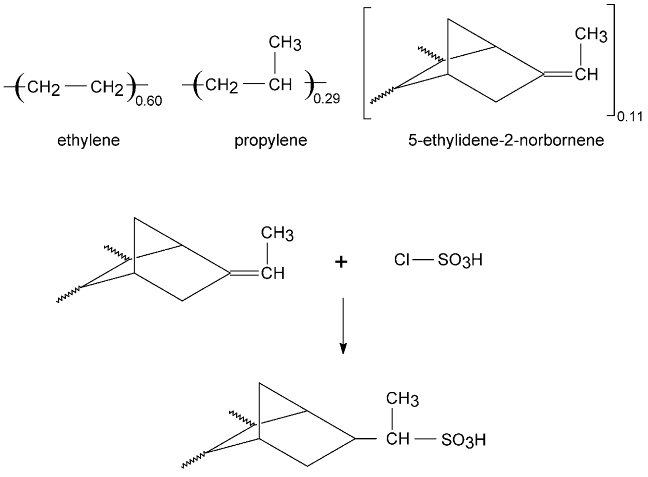

Fig. 3. Mechanisms of sulfonation reaction of ethylene–propylene–diene terpolymer (EPDM).

2.4. Heterogeneous sulfonation procedure and sulfonation analysis

Membranes were placed in a solution of chlorosulfonic acid in 1,2-dichloroetane 3 M during 6 h. Then they were washed several times in Milli-Q water until the bath remained neutral. Finally the samples were vacuum dried until a constant weight was reached. The mechanism of the sulfonation reaction for both polymers is shown in Figs. 2 and 3.

The ion-exchange capacity (IEC) (mmol of sulfonic acid/g of polymer) of each polymer was determined by both titration and elemental analysis (EA). Membrane samples of measured weight (ca. 0.5 ± 0.0001 g) were placed in 50 cm^3 of 0.1 M NaCl solution (Panreac analysis grade) for 12 days to convert the membrane from the H$^+$ to the Na$^+$ form. The NaCl solution was titrated against 0.01 M NaOH (Panreac analysis grade) using phenol red as indicator solution (Aldrich). NaOH solution was standardized against 0.01 M HCl (Panreac). Elemental analysis was conducted in a LECO CHNS-932.

Water content was calculated by drying the samples in a vacuum oven at 60 °C during 12 h. Then the membranes were immersed in deionized water and equilibrated during 5 days. The water uptake is a ratio of the weight of the swollen membrane and the dried one: wt% = [(wet polymer wt − dry polymer wt)/dry polymer wt] × 100. The weight of the swollen membrane was measured after removing the water from both surfaces. A balance with 0.0001 g accuracy was used and four experiments were conducted on each sample.

2.5. Analysis

IR analysis, attenuated total reflection technique (ATR) was carried out on a Perkin–Elmer spectrum one spectrometer. A resolution setting of 4 cm^{-1} and 32 scans were utilized. Samples were films of 150 μm thickness.

A Mettler 4000 differential scanning calorimeter was used for thermal analysis. Thermograms were recorded from −100 to 300 °C at 10 °C/min.

Dynamic mechanical analysis (DMA) measurements were performed with a TA Instrument 983 operating in the fixed frequency and film tension mode. The frequency used was 0.1 Hz and the temperature was varied from −70 to 275 °C at a heating rate of 2 °C/min.

The conductivity measurements were made by means of impedance spectroscopy (IS) using a Hewlett Packard 4192À analyzer. Frequency range was 10^{-2} to 10^4 kHz

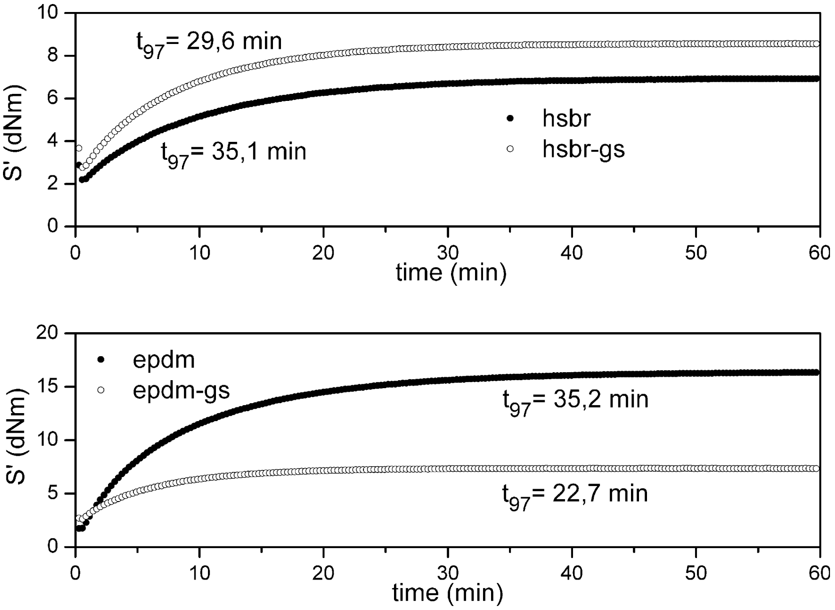

Fig. 4. Vulcanization rheograms and t_{97} values for the different samples.

Table 1
Ion-exchanges capacities and percent water absorption

Sample/composition	EA IEC (mmol/g)	Titration IEC (mmol/g)	wt%
Sulfonated Hsbr	2.47	2.56 ± 0.05	120.8
Sulfonated HSBR-gs 90/10	2.20	2.06 ± 0.05	131.0
Sulfonated EPDM	2.22	1.95 ± 0.05	54.97
Sulfonated EPDM-gs 90/10	2.30	1.90 ± 0.05	58.50

and the amplitude of the oscillation applied was 0.1 V. The tests were carried out on hydrated samples in nitrogen atmosphere at 80 °C during different hydration times (30 min, 1–6 h). Completely dry samples were initially placed on the cell ($t=0$).

Methanol crossover through the membranes was determined using a hand made device that consists of two glass containers (one contains water and the other methanol under mechanical stirring) with double shirt for water circulation and temperature control ($T=60$ °C). Both containers are interconnected through the membrane. The aliquot samples from methanol container are extracted at different times (30 min, 1, 2, 4, 6 and 24 h) to be analyzed by means of gas chromatography in a Hewlett Packard M5890 series II.

3. Results and discussion

3.1. Curing analysis

The suitable conditions of curing process were analyzed by means of rheometry tests. The vulcanization rheograms for the different samples are shown in Fig. 4 which represents the pair of forces applied as a function of time. These curves allow us to determine the optimal vulcanization time that will be used for preparing the membranes by compression moulding; this time corresponds to 97% of the material curing process (t_{97}). From the observation of the curves it can be stated that these materials are stable mixtures not being appraised degradation indications. On the other hand, the vulcanization process is rapid, being reached a prolonged plateau that it is indicating that the pair of forces remains stable, the vulcanization has taken place and the properties of the material do not vary.

3.2. Ion-exchange capacity and water content

The ion-exchange capacity (IEC) of each sample was determined by both elemental analysis (EA) and titration. Both proton conductivity and water content depend on the concentration of ion conducting units (sulfonic acid) in the polymer membrane. The ion content is characterized by the molar equivalents of ion conductor per mass of dry membrane and is expressed as the ion exchange capacity (EIC) with units of millimole per gram or as equivalent weight (EW) with units of grams of polymer per mol (EW = 1000/EIC). Percent water absorption (wt%) of the membranes is also a very important factor. Water is needed as the mobile phase to facilitate proton conductivity. The results are listed in Table 1.

In the case of HSBR-based membranes, the IEC's determined from EA are within the standard deviation of those calculated from titration and water content is higher than that observed for EPDM-based materials. Furthermore from visual observations, HSBR-based membranes

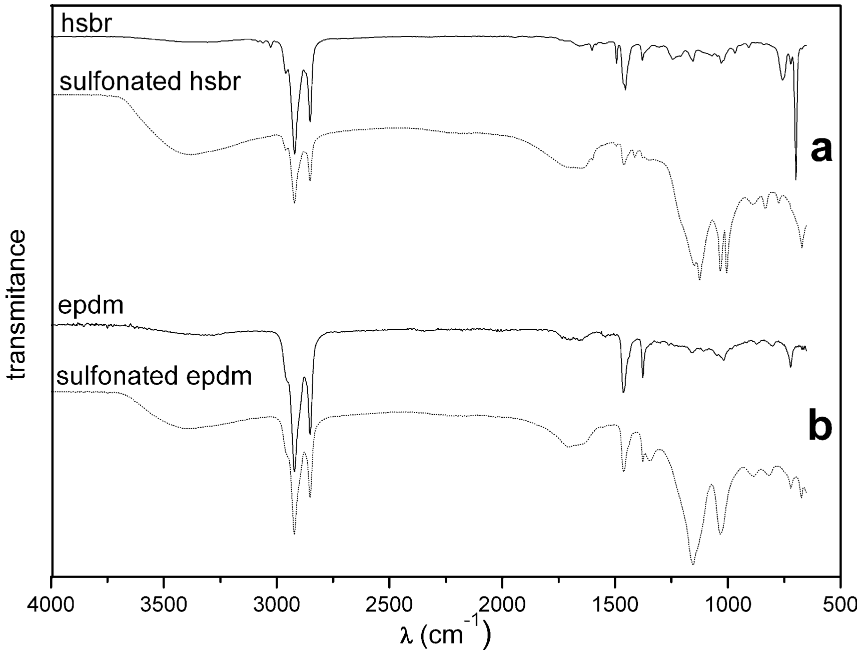

Fig. 5. Infrared spectra for HSBR (a) and EPDM (b) before and after sulfonation.

Table 2
DSC and DMA results for the different samples

Sample/composition	DSC		DMA			Log E' at 23 °C
	T_g^{PB} (°C)	$T_{cluster}$ (°C)	T_g^{PB} (°C)	T_g^{PS} (°C)	$T_{cluster}$ (°C)	
HSBR	−52.7	–	−42.6	91.4	–	6.749
Sulfonated HSBR	−47.7	180.9, 214.0	−42.4	119.6	163.9, 228.8	7.618
HSBR-gs 90/10	−56.8	–	−48.6	115.3	–	7.158
Sulfonated HSBR-gs 90/10	−50.1	165.6	−46.4	130.0	163.9, 224.0	8.096

Sample/composition	DSC		DMA		Log E' at 23 °C
	T_g (°C)	$T_{cluster}$ (°C)	T_g (°C)	$T_{cluster}$ (°C)	
EPDM	−47.4	–	−43.8	–	7.465
Sulfonated EPDM	−41.4	137.8, 168.2	−40.6	153.0	8.135
EPDM-gs 90/10	−47.3	–	−43.3	–	6.630
Sulfonated EPDM-gs 90/10	−42.3	152.0, 185.6	−40.6	152.0, 199.7	8.582

increased approximately three times their areas. This behaviour is not observed for EPDM-based membranes being their percent water absorption values significantly lower.

The EIC's for EPDM membranes obtained from titration are slightly smaller than those determined from EA. Previous to the sulfonation reaction, the materials were subjected to curing process and they could not be solubilized for titration analysis. Thus, titration measurements were carried out placing the membrane in 0.1 M NaCl to convert it from the H^+ to the Na^+ form and assuming complete conversion to the salt form. The minor capacity for water absorption of EPDM-based membranes is probably the reason of the smaller EIC's found by titration experiments.

3.3. Infrared spectroscopy analysis

The infrared spectroscopy was used to verify the sulfonation of membranes. Fig. 5(a) compares the HSBR spectra before and after sulfonation. The most characteristic bands associated to the vibrations of sulfonic groups (SO_3H) are the O=S=O symmetric and asymmetric stretching vibrations; these bands appear at 1149 cm^{-1} (1250–1140 cm^{-1}) and 1032 cm^{-1} (1070–1030 cm^{-1}). On the other hand, the bands observed at 1005 and 1125 cm^{-1} are associated, respectively, with the vibrations of a phenyl ring substituted with a sulfonated group and a sulfonated anion attached to a phenyl ring [26,27]. Finally, the broad band that appears to 1651 cm^{-1} could be associated with the O–H stretching vibration of the hydrated sulfonic group.

The spectra of EPDM before and after sulfonation reaction are shown in Fig. 5(b). As it can be observed, pure EPDM shows the characteristic bands of C–H stretching vibration for long aliphatic chains 2922 and 2852 cm^{-1} (3000–2840 cm^{-1}). The band corresponding to the asymmetric deformation of the methyl groups is observed at 1463 cm^{-1} (1470–1430 cm^{-1}) that coincides with deformation of methylene groups (1475–1450 cm^{-1}). The shoulder at 1436 cm^{-1} could be assigned to the methyl group of the diene group (CH_3–C=C) that usually appears out of the interval 1440–1400 cm^{-1}. Finally, the symmetric deformation band of the methyl groups is observed at 1377 cm^{-1} (1395–1365 cm^{-1}).

With regards to sulfonated EPDM, the spectrum changes remarkably. The bands associated with the vibrations of the sulfonic groups $-SO_3H$ are the O=S=O asymmetric and symmetric stretching vibrations. They appear, respectively, at 1153 cm^{-1} (1250–1140 cm^{-1}) and 1033 cm^{-1} (1070–1030 cm^{-1}). On the other hand, and like sulfonated HSBR, a broad band at 1700 cm^{-1} could be assigned to the O–H stretching vibration of the hydrated sulfonic group.

3.4. DSC and DMA analysis

The structural characterization has consisted of the analysis of the main thermal transitions and mechanodynamic relaxations by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively. The results obtained in both techniques are listed in Table 2. The values of glass transition temperatures (T_g) obtained by DSC have been defined as the inflection point in the corresponding thermograms. In the particular case of the samples based on HSBR, DSC technique only the T_g associated to the polybutadiene units is detected (T_g^{PB}), not being observed that corresponding to the polystyrene domains (T_g^{PS}). As it can be observed, as much for the samples based on HSBR like in EPDM, the values of T_g increase slightly with sulfonation (between 5 and 7 °C). Furthermore, in all sulfonated samples endothermic transitions are observed (between 125 and 250 °C) (Fig. 6) that disappears when the sample is subject to a second heating scan. They are directly related to the existence of strong ionic associations (multiplets and clusters) formed after the introduction of the sulfonic groups in the polymer chain. These ionic associations cause a certain reduction of the mobility that is translated in a slight increase of T_g.

With regards to (DMA) analysis, in the case of the systems based on HSBR, T_g associated to butadiene units

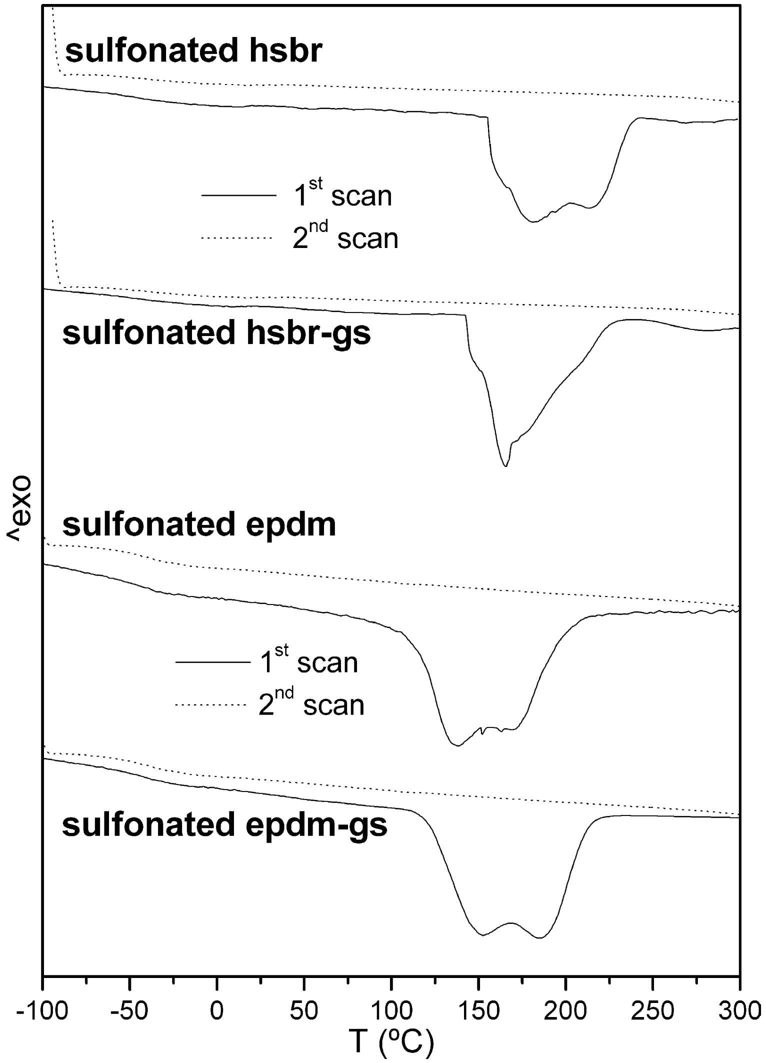

Fig. 6. DSC thermograms for the different samples.

practically does not vary (slight increase of 3 °C for sulfonated systems) whereas the T_g corresponding to the polystyrene domains increases considerably in all the samples with respect to the pure HSBR ($T_g^{PS} = 91.4$ °C), being this increase of almost 40 °C for the sulfonated hybrid system ($T_g^{PS} = 130.0$ °C). This increase is directly related to the appearance of restrictions in the segmental movements of the styrene blocks and is due to the introduction of the sulfonic group in the phenyl ring. In addition, in the case of the hybrid systems it is necessary to consider that the impediment of mobility caused by the presence of the inorganic filler. In the case of the systems based on EPDM the introduction of silica does not affect the value of T_g, a small increase of approximately 3 °C is observed in sulfonated samples.

Like in DSC, several relaxations due to the presence of clusters or strong ionic associations (graphical extended of Figs. 7 and 8) are observed in all sulfonated systems. They appear, depending on the sample, between 150 and 250 °C. These relaxations that appear to minor or greater temperature could be assigned to structures or ionic aggregates of minor or greater size, respectively (quadruplets, sextuplets, multiplets or, finally, to denominated clusters [28]). In addition, another relaxation at lower temperature is observed which can be attributed to the mobility of those polymer segments that do not take part directly in the sulfonation but they are adjacent to the ionic domains and for that reason, they have a more restrictive mobility [29]. Finally, the values of logarithm of storage modulus at 23 °C are given in Table 2. Comparing with the value for pure polymer, the modulus is higher for the ionomers due to the physical cross linking between ionic aggregates.

3.5. Conductivity analysis

Ionic conductivity of the membranes was determined by means of impedance spectroscopy (IS). The samples were hydrated in humidified nitrogen at 80 °C and tested at

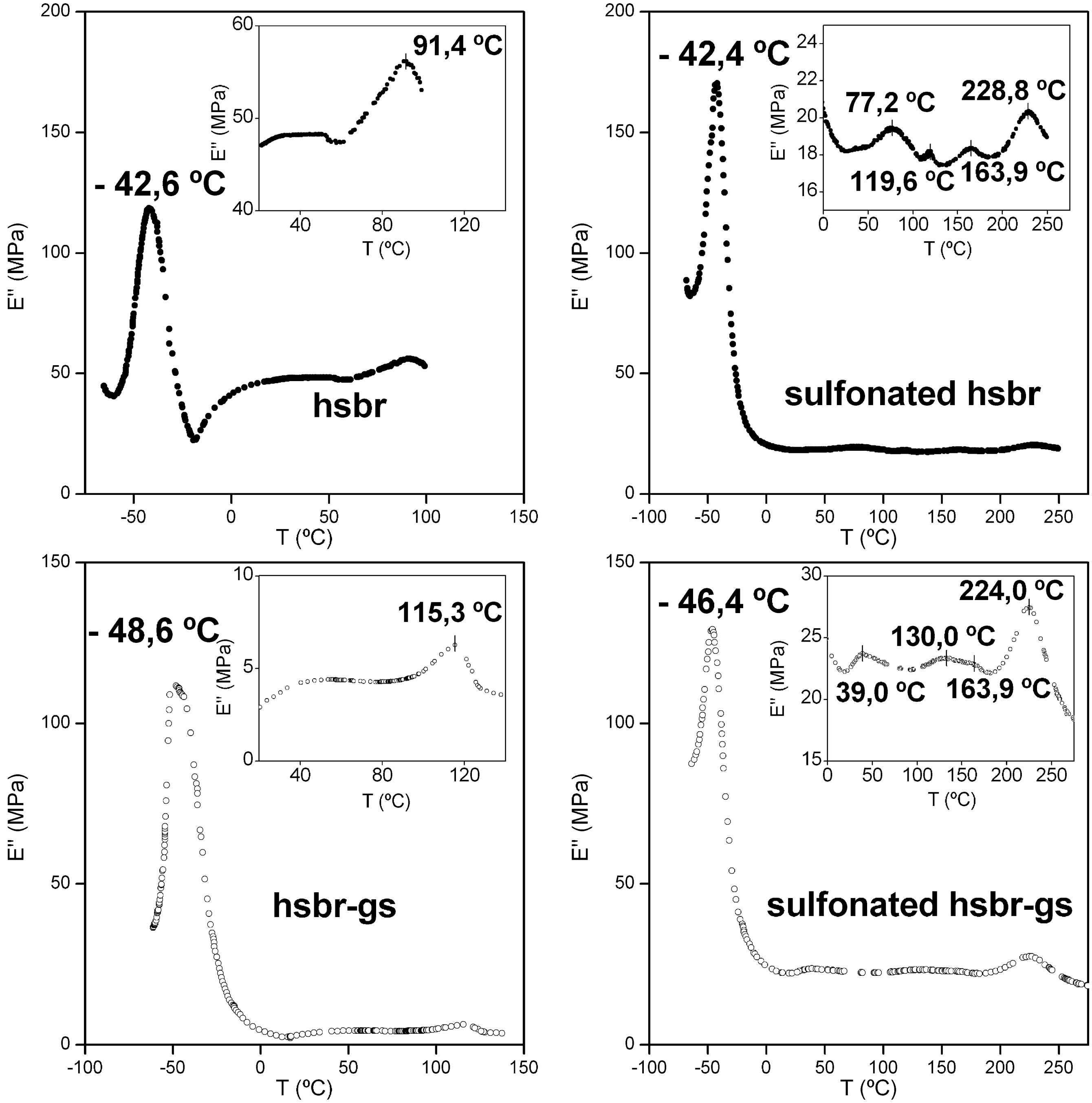

Fig. 7. Loss modulus as a function of temperature for HSBR based samples.

different hydration times. Fig. 9 shows impedance spectra of the different membranes and also of the commercial membrane Nafion 117, measured in the same conditions with the purpose of comparing results. In all cases two well-differentiated regions are observed that allow separating the different contributions to the ionic conduction process. First, the high frequencies region that is related both to the conduction process in the bulk of the material under study and to the induction process relative to the electrical connections. Secondly, the low frequencies region that gives information about the interphase of the material with the electrodes. The resistivity of the membrane ρ (Ω cm) is obtained from the intercept of high frequency curves with the real axis (ρ'), being the conductivity σ (S cm^{-1}) the inverse of this value. Fig. 10 represents the logarithm of conductivity as a function of hydration time for experimental membranes and Nafion 117. Several aspects can be emphasized: in the first place, all the membranes show values of conductivity similar than Nafion (except EPDM due to a loss of water). Secondly, these values of

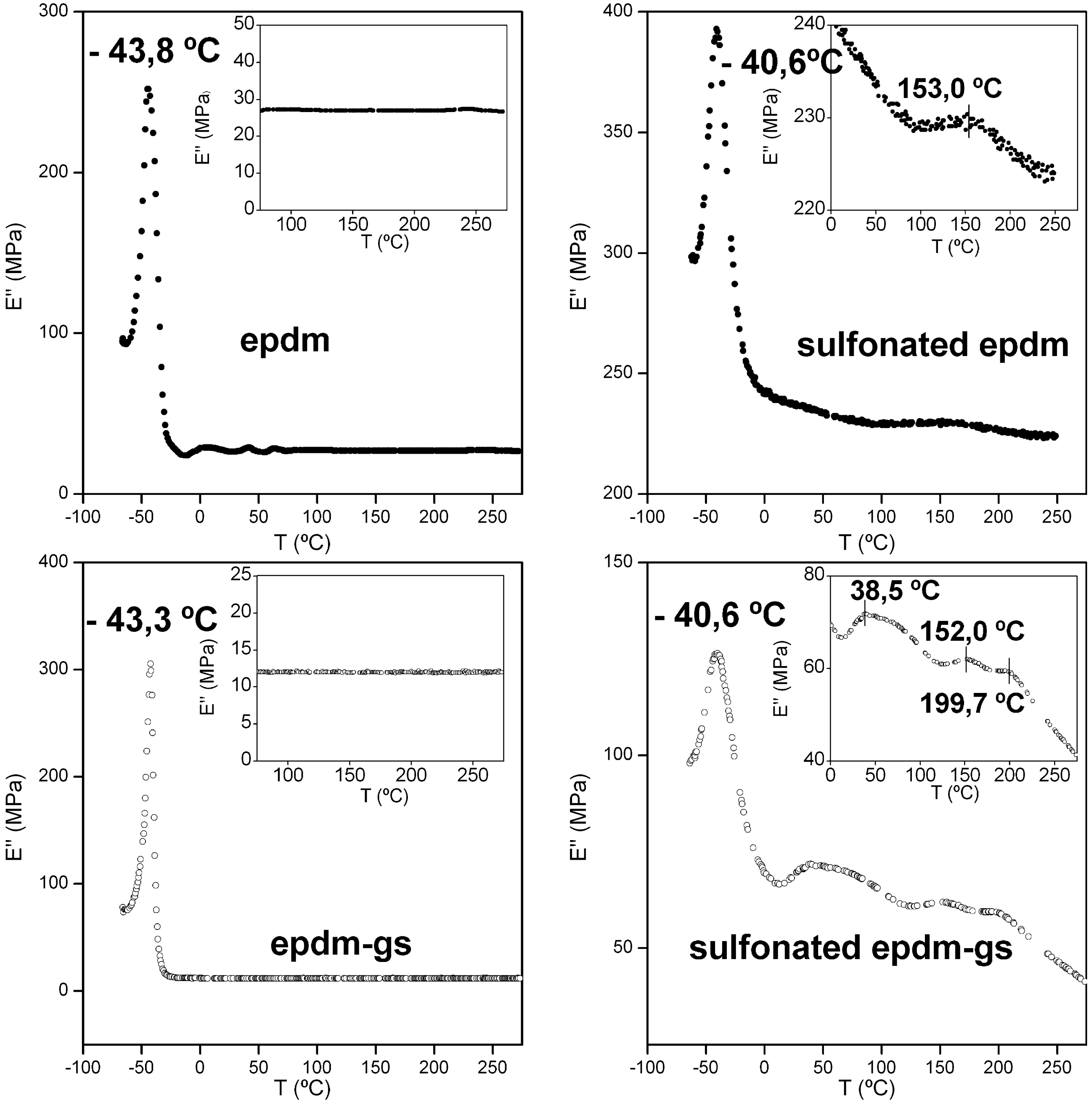

Fig. 8. Loss modulus as a function of temperature for EPDM based samples.

conductivity are already interesting at short times of the experiment (30 min). Thirdly, the incorporation of silica gel improves the results throughout the experiment with regard to the pure ionomers. This fact is indicating a greater capacity of hydration and water retention in the case of hybrid membranes. The highest values obtained are in the order of 6.9×10^{-2} S cm^{-1}.

3.6. Methanol crossover analysis

The apparent diffusion co-efficients (ADC) of methanol at 60 °C for pure and hybrid membranes as well as for Nafion 117, calculated in the same experimental conditions with the purpose of comparing results, are shown in Fig. 11. These co-efficients are obtained from the slopes of the straight lines represented. As it can be seen the methanol crossover in the experimental membranes is minor than in Nafion, probably due to the barrier effect exerted by the non-sulfonated blocks of the co-polymer. It is important to consider that the cured polymers are insoluble materials. This can be an advantage to reduce methanol crossover as it can be seen from the results [30].

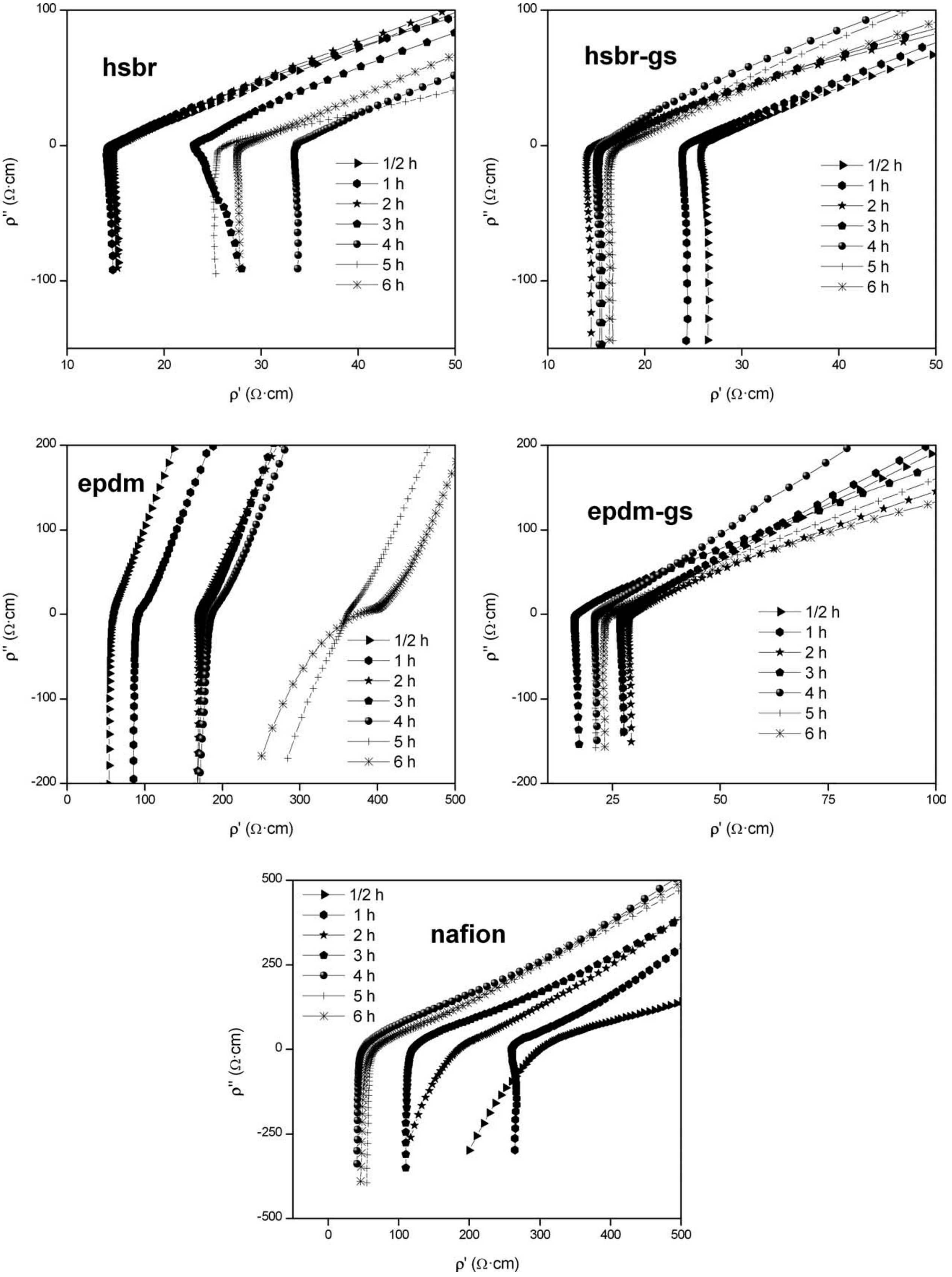

Fig. 9. Impedance spectra at 80 °C and different hydration times.

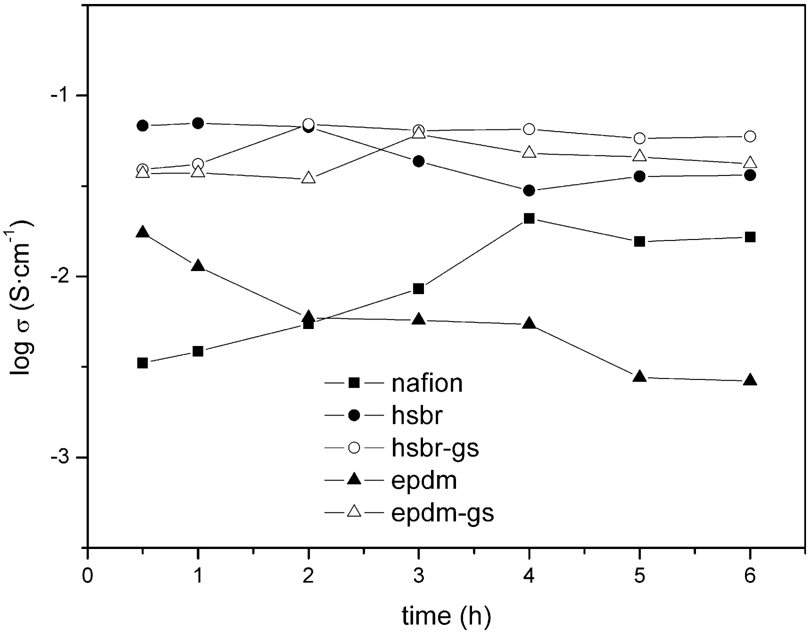

Fig. 10. Logarithm of conductivity as a function of hydration time for the different membranes and Nafion 117.

4. Conclusions

The results indicate the existence of a complex microstructure formed by different phases: ionic and non-ionic blocks of the co-polymer as well as aggregates or clusters formed as a result of the electrostatic interactions among ionic pairs. The ionic conductivity is similar to Nafion and improves with time for hybrid membranes due to the absorbent nature of the inorganic filler. The diffusion of methanol is much lower than Nafion, probably due to the barrier effect exerted by the non-sulfonated blocks of the co-polymer.

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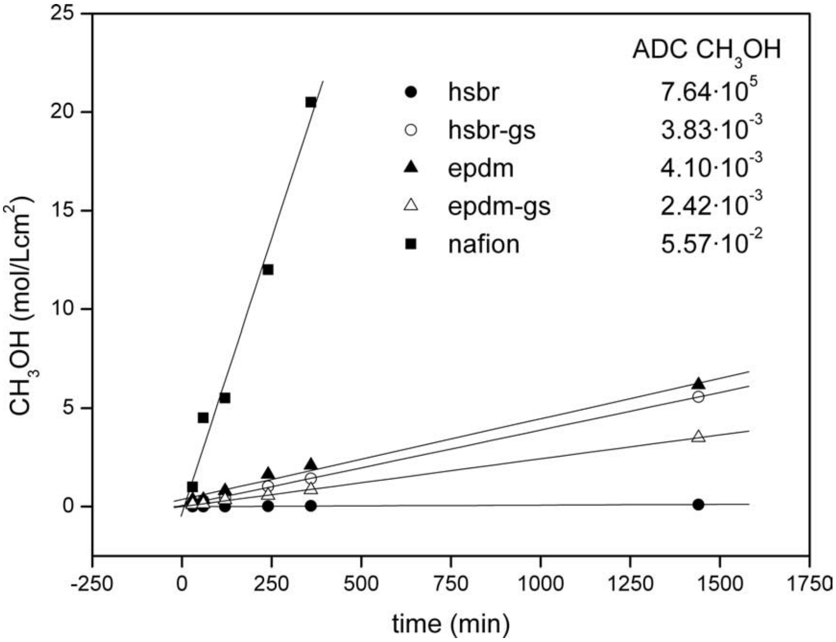

Fig. 11. Methanol diffusion through the different membranes ad Nafion 117 at 60 °C as a function of time.

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