

Proton Conductive Reinforced Poly(ethylene-co-styrene) Membranes

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ABSTRACT: Polymers with ionic conductivity are useful materials for ion exchange membranes, separators, and electrolytes in electrochemical cells. New ionomers are currently being sought to replace the ionomers, which contain fluorine and are harmful to environment and expensive. A new and promising ionomer is a sulfonated ethylene/styrene copolymer. A nearby alternating copolymer with styrene content of 47 mol % was polymerized with metallocene/MAO catalyst. Membranes were prepared by hot-pressing copolymer films with a glassfiber tissue. Phenyl rings in the copolymers were sulfonated with chlorosulfonic acid as a sulfonating agent. As the alternating structure of the copolymer, sulfonic groups were evenly distributed along the membranes. The

membranes were characterized by determining water uptake, ion exchange capacity, proton conductivity, and mechanical properties. The studies revealed that the sulfonated copolymers have promising properties for proton-conducting applications. All membranes had good ion exchange capacity, ~ 3.5 meq/g, and proton conductivity, over 50 mS/cm. Due to the high water uptake of the sulfonated copolymer, mechanical properties of the membranes were improved by using the glassfiber tissue as reinforcement. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1511–1519, 2012

Key words: copolymers; ionomers; membranes; metallocene catalyst; reinforcement

INTRODUCTION

Polymers with ionic conductivity are gaining ground from traditional ionically conducting materials, as useful materials for ion exchange membranes, separators, sensors, and electrolytes in electrochemical cells.¹ Many polymeric electrolytes exhibit properties that other electrolytes are lacking, i.e., adequate ionic conductivity for practical purposes, low electronic conductivity, good mechanical properties, and chemical, electrochemical, and photochemical stability. They are also easy to process. These attributes are necessary for any materials to be considered as a replacement for their liquid counterparts and hydrogels. One ionomer of interest is a proton-conducting polymer, where ionic conductivity is caused by hydrogen ions. Proton-conducting polymer membranes have been used as actuators and sensors,^{2–5} electron-injecting and hole-blocking material in LEDs,⁶ and electrolytes in fuel cells.^{7–9}

Proton-conducting polymer membranes are mostly prepared by adding sulfonic acid groups to the

hydrophobic backbone, where hydrophilic sulfonic acid groups create paths for proton transportation and hydrophobic part of the polymer provides mechanical strength for the membrane. The sulfonated polystyrene¹⁰ is mostly used proton-conducting ionomer in ion exchange applications. Highly sulfonated polystyrene exhibits good proton conductivity, but it becomes water soluble as the sulfonation degree increases. A better chemical stability and high proton conductivity are achieved, when perfluorinated or partially perfluorinated polymer membranes are radiation grafted with styrene, and subsequently sulfonated.^{11,12} In addition, more environmentally friendly materials without fluorine are needed.

Weak mechanical properties of proton-conducting membranes are usually caused by high water uptake leading to swelling of membranes. When hydrophilicity of the membranes is high, crosslinking^{13,14} and reinforcement^{15–17} can be used to improve the mechanical properties. The mechanical properties can be improved by adding hydrophobic blocks to sulfonated polystyrene.^{18–22} In block copolymers, the hydrophobic blocks stabilize the ionomer, and the sulfonic acid groups form cluster networks for protons to diffuse.²³ The same idea is exploited in polymer blends, where one blend component acts as an ionomer.^{24,25} In block copolymers and polymer blends, mechanical and conducting properties can

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be improved by modifying morphology of the membrane and restricting the swelling of the hydrophilic part. The copolymer polystyrenesulfonate-block-polyethylbutylene (PSS-b-PMB) was more effective in retaining water with the improved proton conductivity at elevated temperatures, when the hydrophilic domains had been reduced under 6 nm width.²⁶

Solution casting is widely used processing method for polymeric electrolytes. However, it does not give any processing benefit over hydrogels or liquid electrolytes that cannot be melt processed. Though electrolytes have been used to process in solution, solid thermoplastic electrolytes can be melt processed. The benefits of melt processing are clear when time and materials are concerned. Solution casting can take days due to the evaporation of solvents,^{4,27} as melt processing takes minutes. In melt processing, there are no additional solvents, which can affect the morphology of the membranes, are needed to remove, and can be very harmful or toxic.

We have investigated the possibility to use functionalized polyolefins, polymerized with metallocene catalysts,^{28,29} in proton-conducting membranes. In comparison with polyolefins prepared by conventional Ziegler-Natta catalysts, polyolefins synthesized with metallocene catalysts have better mechanical properties due to better tailoring of molar mass and molar mass distribution. Moreover, metallocene catalysts allow a direct copolymerization of functional monomers with even comonomer distribution throughout the whole polymer chain and the molar mass region. With metallocene catalysts it is possible to prepare random ethylene/styrene copolymers, i.e., without polystyrene blocks. After sulfonation of the phenyl rings, the copolymer becomes a proton conductor. The use of glass fiber tissue forms the support structure for highly sulfonated copolymer.

EXPERIMENTAL

Materials

The polymerization catalyst ($\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(N\text{-}t\text{-butyl})\text{TiCl}_2$) and cocatalyst methylaluminoxane, MAO (4.82 wt % in toluene), were purchased from Witco GmbH. Toluene (Merck, >99.5%) was refluxed over sodium/benzophenone and distilled under nitrogen. The styrene (Fluka, >99%) was dried over CaH_2 and distilled under pressure before use. Ethylene (grade 3.5, Air Liquide, Liege, Belgium) was further purified by passing it through columns with 3Å-molecular sieves, a copper catalyst (BASF R3-11) and activated Al_2O_3 . Tetrahydrofuran (THF, Fluka, >99.5%), chlorosulfonic acid (Aldrich/Fluka), 1,2-dichloroethane (DCE, Fluka), and deuterated chloroform (CDCl_3 , Aldrich, >99.8%) were used

as received. C-Glassfiber tissue was chemically resistant (CGFT-59K12-35, Ahlström Glassfiber Oy).

Polymerization

Polymerizations were carried out at 50°C in a 0.5 dm³ Büchi reactor equipped with a mechanical stirrer. The reactor was vacuumed three times before the addition of MAO, toluene (together 100 mL), and 100 mL of styrene. The ethylene was fed to the reactor and the pressure was kept constant at 2.5 bar. The catalyst (20 μmol) was added with a mechanical pump and the reaction was stopped after 120 min by pouring the reaction mixture into 300 mL of acidic ethanol. After filtration the product (~40 g) was washed once with ethanol and dried 24 h in vacuum. The minor residues of polyethylene and polystyrene homopolymers were removed by extracting the product in THF, the THF solution was filtrated and the copolymer regenerated by pouring the THF solution in excess of acetone.

Preparation of membranes

Membranes were prepared by hot-pressing copolymer into films using Fontijne Table Press TP400 and 0.2 mm thick mold at 150°C and 150 kN pressure in 3 min. The composite membranes were prepared by placing the glassfiber tissue between two copolymer films and melted in 0.2 mm thick mold at 150°C in 10 min at light pressure, 30 kN.

Sulfonation

An adequate amount of chlorosulfonic acid was added to 1,2-dichloroethane (DCE) to obtain 0.5 to 1 mol/dm³ solution. The solution was cooled in an ice bath before the membranes were added in the solution under magnetic stirring. The amount of solution was kept high enough that the concentration of the solution remained constant during the sulfonation reaction. The reaction was allowed to proceed for 1 to 4 h at 0°C. The reaction was terminated by addition of methanol. The membranes were washed at first with DCE and then with milli-Q water, until pH of water was neutral. The membranes were dried at ambient temperature over night. The pristine glassfiber tissue was subjected to sulfonation processes as well.

Characterization

The structure of the copolymers was examined with a ¹³C-NMR spectrometer (Varian Gemini 2000, 300 MHz) at 25°C. As an internal standard the CDCl_3 resonance peak was placed at δ 77.0 ppm in the ¹³C-NMR spectrum.

The molar mass and molar mass distribution of the copolymer was analyzed with a Waters Alliance GPCV 2000 gel permeation chromatograph equipped with four Waters Styragel columns (HT 3, HT 4, HT 5, HT 6, particle size 10 μm), a refractive index detector, and a viscometer. The solvent 1,2,4-trichlorobenzene was used at 140°C and was applied at a flow rate of 1.0 mL/min.

The thermal behavior of the ethylene/styrene copolymer was measured with a Mettler Toledo DSC 821^e differential scanning calorimeter (DSC) under nitrogen atmosphere. To achieve better contact between the sample and the aluminum sample pan, the sample (7.0 mg) was premelted in the pan (on a hot plate, 120°C) and the sample was pressed firmly on the bottom of the pan. Before nonisothermal runs, the thermal history of the copolymer was destroyed by heating the sample to 150°C at 20°C/min, and then the sample was cooled to -100°C at -10°C/min. The thermal behavior (glass transition temperature T_g , melting temperature T_m) of the copolymer was finally measured by reheating the sample at 10°C/min from -100°C to +150°C.

The water sorption was determined by boiling the sulfonated membranes for 1 h in the deionized water. The surface of the membrane was blotted dry with paper toweling and the membrane was weighed. The water uptake was determined according to eq. (1):

$$\text{water uptake} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \quad (1)$$

where w_{wet} is the mass of the wet sample and w_{dry} the mass of the dried sample.

The ion exchange capacity (IEC, meq/g) was measured by back titration. The sulfonated membrane was soaked in a known amount of 0.1M NaOH solution and equilibrated for 3 days. The excess of NaOH solution was titrated with 0.1M HCl using phenolphthalein as an indicator. IEC was calculated from eq. (2):

$$\text{IEC} = \frac{n_1 - n_0}{m_{\text{dry}}} \quad (2)$$

where n_1 is moles of hydroxide ions originally present, n_0 moles of hydrochloric acid consumed, and m_{dry} the mass of the dried sample.

Ionic conductivities were recorded by impedance spectroscopy using data gathered in the frequency range 5 to 85 kHz. Measurements were done with an Autolab PGSTAT 20 instrument (Eco Chemie B.V.) supplied with FRA 2.4 software and connected to a two-electrode cell with 0.071 cm² platinum electrodes. Before the measurement the membranes were equilibrated with water vapor in a sealed vessel for a minimum of 3 days, after which the proton

conductivity was determined at 25°C at 100% relative humidity. During the measurements the membrane was flushed with humidified nitrogen flow and in addition extra water was retained in the bottom of the thermostated cell. Membrane resistance was determined by extrapolating the linear part and/or the semicircle of the Nyquist plot to the real axis of the complex impedance spectrum. The conductivity was calculated from the resistance using the electrode area and membrane thickness, the latter measured with a micrometer.

The mechanical properties of the membranes were analyzed by using dynamic mechanical analysis (DMA, TA Instruments Q800). DMA was operated in amplitude mode (30 μm) to get reliable data in temperatures over copolymer T_g in dry conditions using heating rate 2°C/min from 20 to 150°C, the sample size was 5 × 5 × 0.2 mm³.

Optical microscope (Olympus BH-2) was used to analyze the structure of glassfiber tissues and composite membranes before and after sulfonation.

RESULTS AND DISCUSSION

The ethylene/styrene copolymer was synthesized mainly according to a procedure reported by Sernetz et al.³⁰ The microstructure of the synthesized copolymer was determined according to the ¹³C-NMR spectra (Fig. 1), and nearly alternating structure with 47 mol % of styrene was verified. The shifts at 25.0 to 25.5 ppm ($\beta\beta$) and 36.5 to 37.5 ppm ($\alpha\gamma$) were assigned to the alternating styrene-ethylene-styrene structure with regioregular styrene insertions [Fig. 1(a)], whereas the shifts at 34.0 to 35.5 ppm ($\alpha\beta$) indicated an alternating structure with one regioirregular styrene insertion [Fig. 1(b)], or regioirregular tail-to-tail styrene block formation [Fig. 1(c)]. In addition, no signs of regioregular styrene block were observed (no shifts at \sim 41.5 ppm), and the amount of isolated methylene units formed after two or more consecutive ethylene insertions was low [Fig. 1(d), $\gamma\delta$ at 29.5–30.0 ppm, $\beta\delta$ at 27.5 ppm, $\alpha\delta$ at 37.0 ppm were overlapped by shifts from $\alpha\gamma$]. The styrene concentration in the copolymer was finally calculated from the areas of the methylene units in the ¹³C-NMR spectrum according to eq. (3).³¹

$$\text{Mol} - \% = \frac{A_{36.6-37.1} + A_{34.0-35.5}}{A_{29.8} + A_{25.5} + A_{27.5-28.0} + 1.5(A_{36.6-37.1} + A_{34.0-35.5})} \quad (3)$$

The thermal behavior of the copolymer was studied with DSC. A clear sign of glass transition temperature (T_g) was found at \sim 30°C (Fig. 2), which correlates well with the previous results where alternating ethylene/styrene copolymer were synthesized.³²⁻³⁴

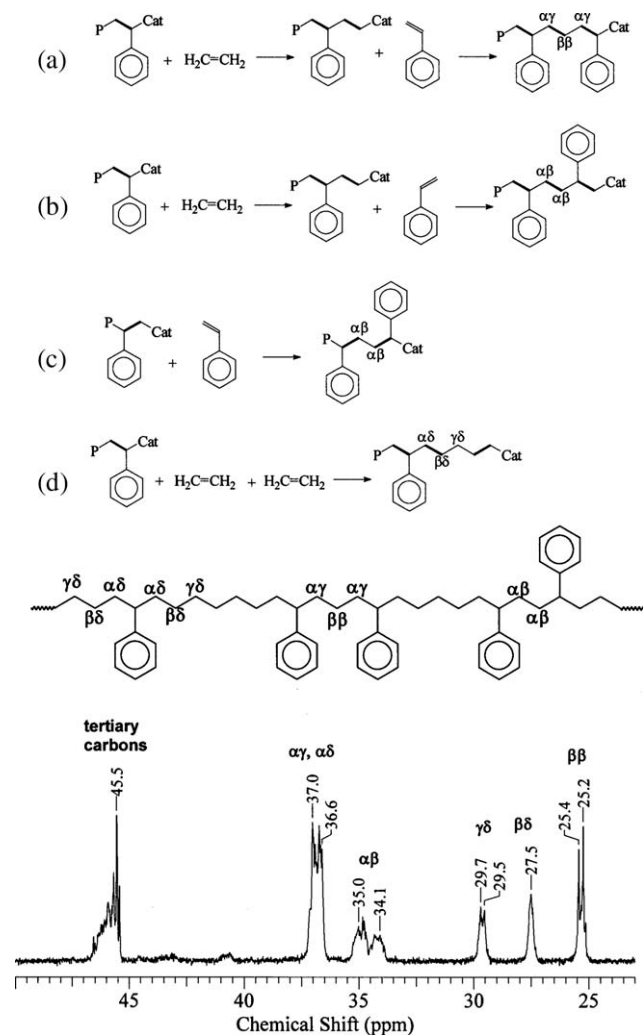


Figure 1 The formation of the different microstructures (a–d) defined according to the ^{13}C -NMR spectrum of the synthesized poly(ethylene-co-styrene). The Greek letters indicate the position of the nearest branching carbons.

In addition, the copolymer was found to be totally amorphous as no melting endotherm was observed. The reason was mostly the absence of stereospecific insertion of styrene units, which resulted in atactic alternating styrene-ethylene-styrene sequences. In ^{13}C -NMR spectrum, this atactic structure was seen in splitting of the peaks. Whenever the styrene insertion was found to be stereoselective, e.g., with *ansa*-zirconocenes, also the formed alternating copolymer was crystalline due to the isotactic sequences.^{31,33,35–37}

GPC was used to determine the molar mass of the synthesized copolymer. Both refractive index detector and viscometer data were used due to the absence of the Mark-Houwink K and α parameters for this kind of copolymer. The determined K and α values for ethylene/styrene copolymer ($K = 0.00023$, $\alpha = 0.686$) were relevant, when they were compared with the ones found for homopolyethylene and homopolystyrene (polyethylene $K = 0.000406$, $\alpha =$

0.725 ³⁸; polystyrene $K = 0.000121$, $\alpha = 0.707$ ³⁹). The “absolute” number average molar mass (M_n) of the copolymer was finally found to be 33 100 g/mol with polydispersity value of 2.3.

The sulfonic groups were evenly distributed along the membranes based on the ^{13}C -NMR and DSC results. Styrene comonomer was alternating in the copolymer and there were not large polystyrene and polyethylene blocks in the copolymer, as the styrene/ethylene molar ratio was nearly 1 : 1. The orientation of polymer chains during melt state is limited compared with solvate state. Therefore large styrene and ethylene domains cannot form during melt processing, even though the melt processing time was several minutes. During the sulfonation step, the membrane was swollen and polymer chains can rearrange toward lower thermodynamic state e.g., the phase separation occurred due to the large value of solubility parameter between sulfonated and nonsulfonated domains, but not in the same extent than in solvate state and without large blocks of polyethylene and polystyrene.

To strengthen the copolymer membrane, the glass-fiber tissue, instead of individual glassfibers, was used to form even distribution of glassfibers in the composite membrane. To keep the glassfiber tissue as intact as possible, very low pressure and long melting time were applied and the glassfiber tissue was covered in both sides with the copolymer film to wet the glassfibers properly. Optical microscope images show (Fig. 3) that the pristine glassfiber tissue after sulfonation reaction and the glassfiber tissue after hot-pressing with copolymer stayed almost intact. After sulfonation reaction of the reinforced membrane, the glassfiber tissue was covered by the copolymer without clear air pockets in the membranes.

High sulfonation degree was achieved due to high amount of styrene units in the copolymer and therefore water uptakes were high (Fig. 4). Concentration of the sulfonation solution was a significant parameter for preparing the membranes with sufficient

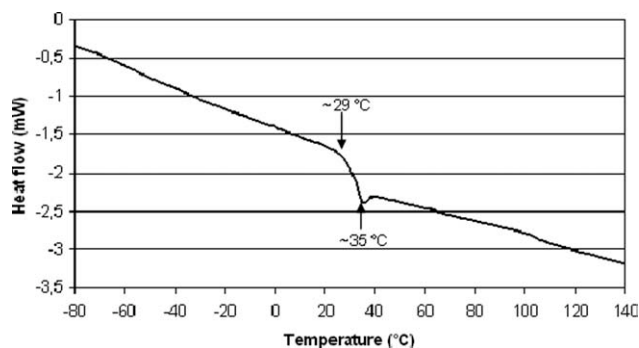


Figure 2 The DSC endothermic curve of the synthesized ethylene/styrene copolymer.

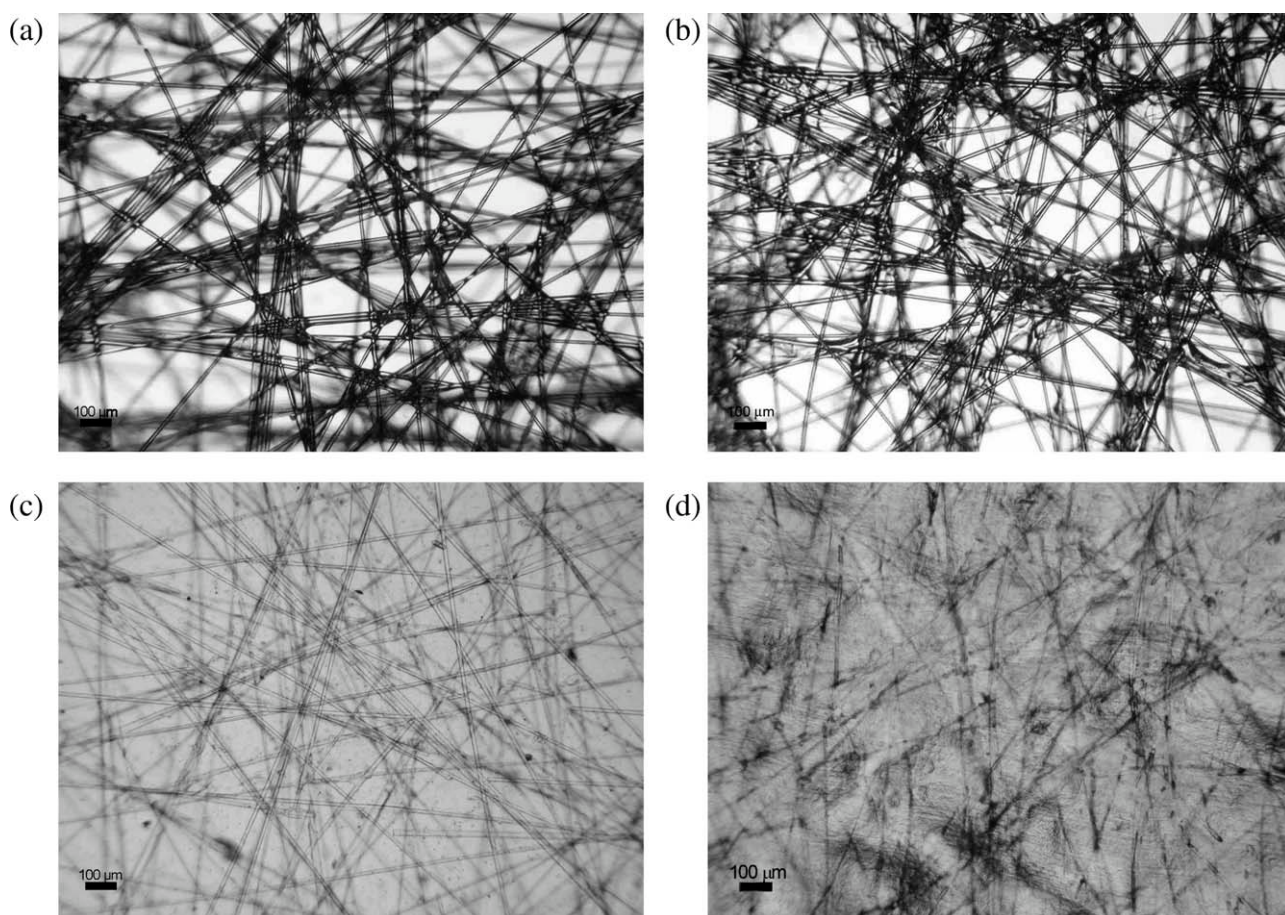


Figure 3 Optical microscopy images, (a) pure glassfiber tissue, (b) sulfonated glassfiber tissue, (c) composite membrane before sulfonation, and (d) composite membrane after sulfonation.

properties. DCE softened the membranes but did not totally dissolve them, when chlorosulfonic acid was present. Chlorosulfonic acid penetrated into the

swollen membrane and sulfonated the phenyl rings. At the same time crosslinks between sulfonic groups formed, which prevented the membrane to dissolve.

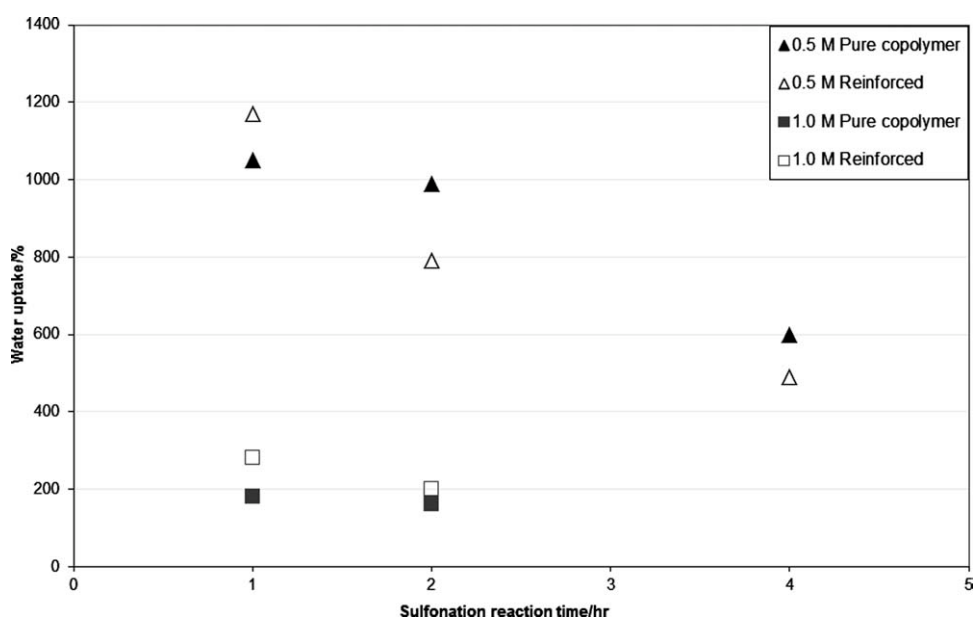


Figure 4 Water uptake of the membranes; 0.5M indicates weaker chlorosulfonic acid concentration and 1.0M stronger chlorosulfonic acid concentration.

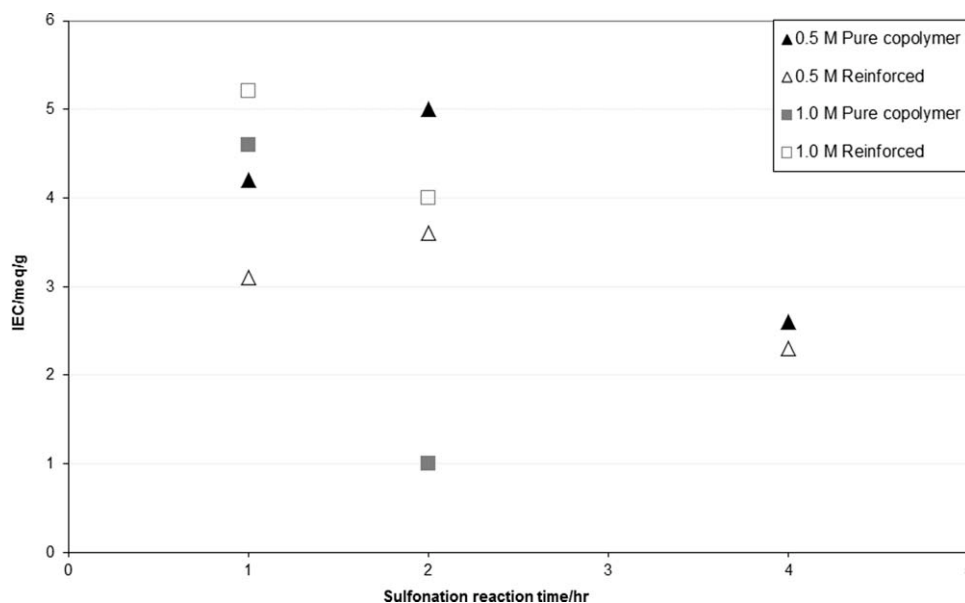


Figure 5 Ion exchange capacity (IEC) of the membranes; 0.5M indicates weaker chlorosulfonic acid concentration and 1.0M stronger chlorosulfonic acid concentration.

By using longer sulfonation reaction time, crosslinking increased and water uptake decreased. When stronger acid concentration was used, the amount of crosslinks increased and water uptake decreased even more.

Ion exchange capacity (IEC) depicted the actual amount of free sulfonic groups in the membrane and the effect of crosslinking (Fig. 5). IEC decreased as the water uptake decreased, but not in the same extent. When weaker chlorosulfonic acid concentra-

tion, 0.5 mol/dm³, was used, after 1 h reaction time water uptake was very high but IEC sufficiently low (Figs. 4 and 5). With weaker acid concentration, DCE could swell the membrane more efficiently, but sulfonation and crosslinking reactions were slower. When reaction time was extended, sulfonation reaction continued and IEC first increased and then decreased as the crosslinking increased. When stronger chlorosulfonic acid concentration, 1.0 mol/dm³, was used, high IEC was obtained with much lower

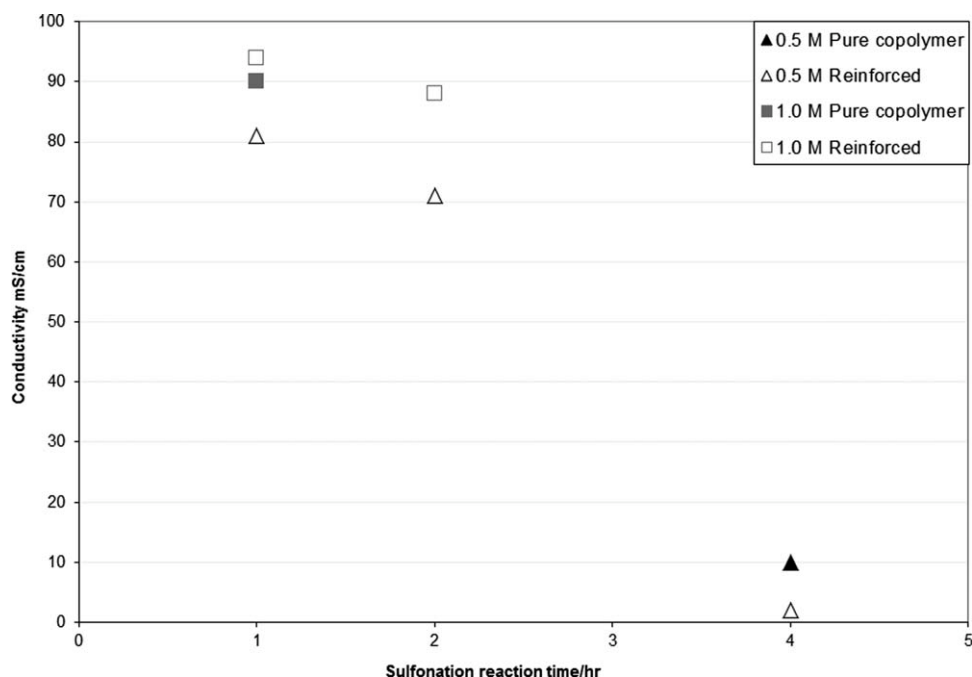


Figure 6 Proton conductivity of the membranes; 0.5M indicates weaker chlorosulfonic acid concentration and 1.0M stronger chlorosulfonic acid concentration.

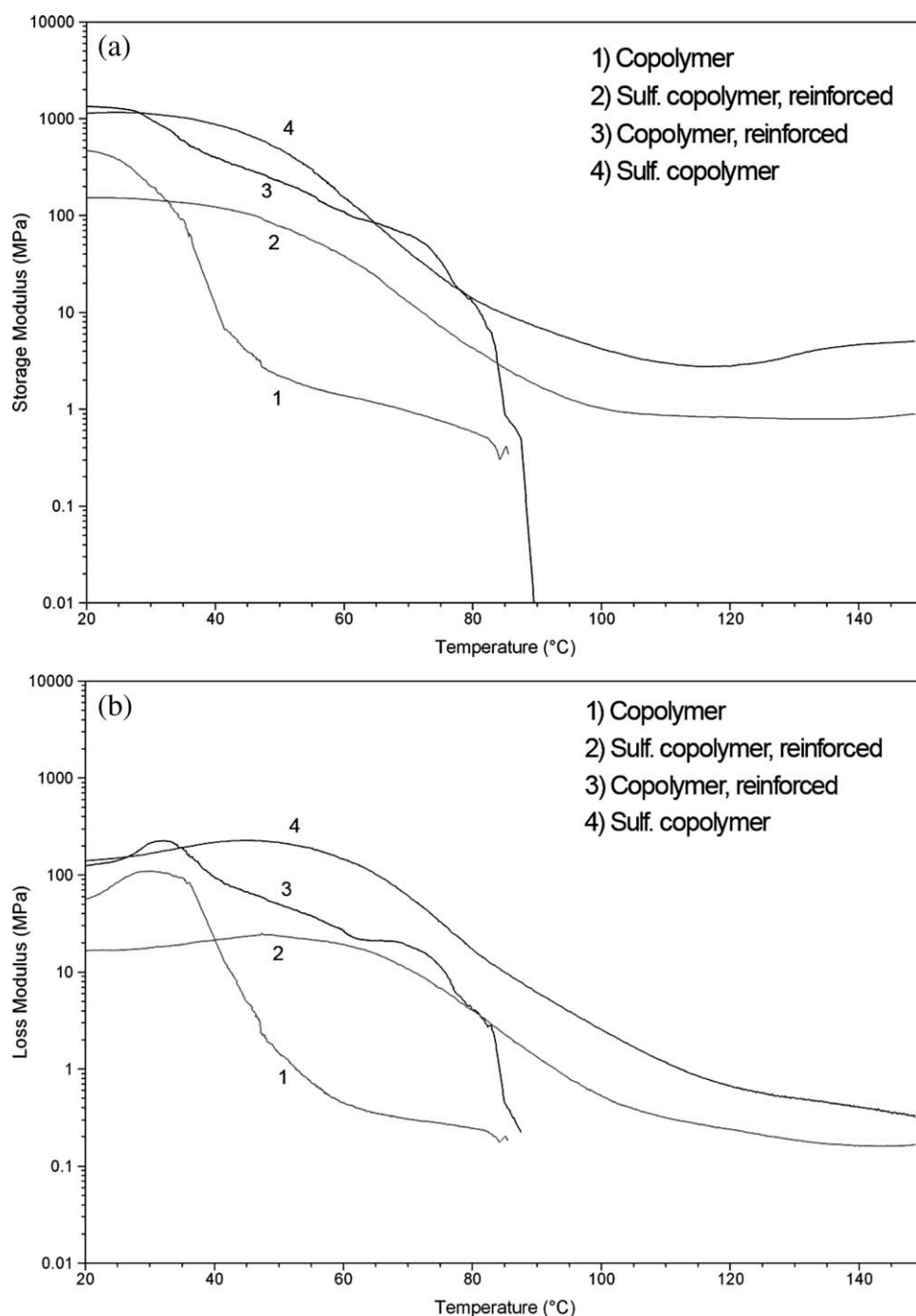


Figure 7 Dynamic mechanical scans of the membranes as a function of temperature, (a) storage modulus, (b) loss modulus.

water uptake value. By extending reaction time with stronger acid concentration, IEC decreased rapidly, as the reactions were faster.

Water uptake and IEC showed the effect of the glassfiber tissue in sulfonation reaction (Figs. 4 and 5). The pristine glassfiber tissue was subjected to sulfonation process to see, if the glassfiber tissue participated in the sulfonation reaction. IEC measurements confirmed that the properties of the glassfiber tissue did not change after different sulfonation

processes, and therefore the glassfiber tissue affected to the properties of the sulfonated membranes only indirectly, as hindering crosslinking of the copolymer and providing mechanical support and strength for the membrane.

In the case of weaker chlorosulfonic acid concentration, DCE could swell the membrane more efficiently and acid penetrated through the membrane more easily without the glassfiber tissue, therefore sulfonation reaction was more effective and the pure

copolymer membranes without reinforcement had higher IEC at all sulfonation reaction times (Fig. 5). However, after 1 h reaction time in weaker sulfonation solution, the pure copolymer membrane had lower water uptake than the reinforced membrane. With short sulfonation reaction time and weaker acid concentration, there was less crosslinking due to the slower reaction rate. The swollen membrane structure could be broken down by water, and the membrane could retain less water. When the membrane was reinforced, the glassfiber tissue supported the membrane structure and maintained the high water uptake, though IEC was lower compared with IEC of the pure copolymer membrane. When sulfonation reaction time was extended, crosslinking increased in the pure copolymer membrane and the membrane was more stable.

In the case of stronger chlorosulfonic acid concentration, 1.0 mol/dm^3 , both reactions, sulfonation and crosslinking, happened more effectively than in weaker solution. The glassfiber tissue acted as a barrier for crosslinking. Therefore there were more free sulfonic groups in the reinforced membranes, and water uptake and IEC were higher in reinforced membranes at all sulfonation reaction times. On the other hand, the glassfiber tissue maintained mechanical properties and restricted the swelling of the membranes, and water uptake did not increase considerably.

The proton conductivity of the membranes depended on the water uptake i.e., mechanical properties of the membranes and the amount of sulfonic groups in the membranes. All the measured conductivities were good (Fig. 6), mostly over 50 mS/cm . These conductivities were at the same level than conductivities of the commercial Nafion and radiation grafted PVDE membranes under the same conditions.⁴⁰ Long sulfonation time increased the crosslinking and reduced the amount of free sulfonic groups in the membranes, and conductivities decreased. All the reinforced membranes were mechanically good enough that the conductivity measurements could be performed. But the membranes without the glassfiber tissue were mostly too weak to hold the contact pressure build by the measuring electrodes. Probably these membranes would have good conductivities based on high water uptake and IEC values.

Mechanical properties of the membranes depended on the measuring conditions. The glass transition temperature (T_g) of pure copolymer was in the same region, at $\sim 30^\circ\text{C}$, measured with DSC and DMA. When the copolymer was reinforced, T_g was at the same temperature as the pure copolymer, but the collapse of the mechanical strength of the membrane shifted to higher temperature (Fig. 7). The crosslinks in the sulfonated membrane shifted T_g to higher temperature and inhibited the collapse of the mechanical

strength. In dry DMA measurement conditions, crosslinking affected more to mechanical properties than glassfiber tissue. The storage modulus and the loss modulus were higher in the sulfonated membranes without glassfiber tissue. However, the effect of moisture on the mechanical properties emphasizes the importance of reinforcement at high sulfonation level, which is required for good proton conductivity.

CONCLUSIONS

The studies showed that sulfonated ethylene-*co*-styrene copolymer membranes possess promising properties for proton-conducting application, where Nafion type materials are usually used. The membranes are based on inexpensive thermoplastic materials with the possibility to tailor styrene content and sulfonation degree. In general, when sulfonation reaction time was extended, water uptake, ion exchange capacity, and proton conductivity decreased due to increased crosslinking. The membranes are not containing fluorine, which makes them environmentally friendly. They are easy to melt process, with processing time of minutes and with competitive results compared with solution processing. Proton conductivities were over 50 mS/cm and ion exchange capacities over 3 meq/g . Mechanical properties of the sulfonated copolymer membranes were improved by using the glassfiber tissue as reinforcement. Due to high sulfonation level, the membranes were very sensitive to moisture, which opens novel possibilities to use these membranes in different sensor applications.

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