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Composite Proton-Conducting Hybrid Polymers: Water Sorption Isotherms and Mechanical Properties of Blends of Sulfonated PEEK and Substituted PPSU

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Mechanical properties (elastic modulus, ultimate strength, and elongation at rupture), water sorption isotherms, and chemical diffusion coefficients of water are reported for composite polymers made from a majority polymer (93 wt %), sulfonated (DS = 0.9) poly-ether-ether-ketone (S-PEEK), and a minority polymer (7 wt %), sulfonated (DS = 2) and/or silylated poly-phenyl-sulfone (PPSU). S-PEEK is responsible for proton conductivity of the membranes, whereas the minority component is added to maintain the mechanical and morphological stability. It is shown that the addition of sulfonated PPSU reduces the mechanical strength and leads to important membrane swelling. In contrast, addition of silylated PPSU highly improves the membrane strength and reduces considerably membrane swelling, indicating a suitable strategy to improve polymer electrolytes for PEM fuel cells. The calculated water uptake coefficients and diffusion coefficients are consistent with those of other members of the S-PEEK polymer family.

Introduction

Proton exchange membrane (PEM) fuel cells are today a credible alternative for powering mobile applications, such as automotive vehicles and portable electronics. The heart of the PEM fuel cell is the polymer electrolyte membrane. Relevant membrane properties include high proton conductivity to reduce ohmic drop during fuel cell operation, low permeability to reactants, and negligible electronic conductivity to avoid chemical or electrical short circuit, good thermal, and mechanical and chemical stability to guarantee long life span.[1,2] Furthermore, easy membrane processing and easy fabrication of membrane-electrode assembly are advantageous for reducing fuel cell cost.

The proton conductivity of acidic polymer electrolytes is generally low unless water is sorbed. Proton conductivity and water self-diffusion coefficients increase with increasing relative humidity (RH).[3–5] Under hydrated conditions, nanometer-size hydrophilic domains are formed, where dissociated protons are present together with solvating water molecules and which percolate at higher water partial pressures. The sulfonate groups remain at the interface between hydrophilic and hydrophobic domains in the polymer. The hydrophilic domains are responsible for the proton conductivity of the membranes, but the hydrophobic domains maintain the morphology and mechanical stability of the membrane. Whereas water sorption improves on one hand the proton conductivity, it leads on the other hand to morphological instability and, at elevated water content, to membrane swelling.[6,7] Membrane swelling is a serious drawback for use in a membrane electrode assembly, leading to risks of rupture and degradation of electrical contacts.

An optimization of the mechanical properties of membranes and a better understanding of the relation between mechanical properties and water uptake is thus an extremely important task. A relation was recently established between lower tensile strength and higher water uptake of ionomer membranes.[8,9] Nafion, a perfluorinated polymer with sulfonic acid-terminated side chains, is mostly used today as proton exchange membrane in PEM fuel cells. However, a major drawback of this material is the conductivity loss observed at higher temperature, which makes it useless above 100 °C. This loss of performance was recently related to a morphology change of the polymer.[10]

Fully aromatic polymers are currently much investigated because they exhibit promising features, such as excellent thermal and chemical stability, low cost, and easy availability,

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10.1021/cm800155r CCC: $40.75

and they can be easily functionalized.[11,12] For applications as fuel cell membranes, they are usually sulfonated by reaction with various sulfonating agents.[13,14] Most important examples are poly-ether-ether-ketone (PEEK) and poly-phenyl-sulfone (PPSU) polymer families. These polymers present appreciable proton conductivity when sufficiently sulfonated; unfortunately, mechanical properties deteriorate with increasing sulfonation and highly sulfonated materials show large membrane swelling at high RH, leading finally to dissolution in water.[15,16] Therefore, cross-linked, hybrid, and composite polymers are studied to improve these properties.[17,18]

We have in recent years synthesized various hybrid organic−inorganic membranes based on sulfonated and/or silylated PEEK [19–21] and PPSU.[22] The objective was to find an optimal compromise between enhancement of proton conductivity by sulfonation and improvement of thermal and morphological stability by silylation. In this work, we propose a new strategy by preparing composite materials with a majority partner (93 wt %), sulfonated PEEK with a high degree of sulfonation (DS = 0.9), and a minority partner (7 wt %), PPSU in unsubstituted, sulfonated, and/or silylated form. The majority partner should ensure good proton conductivity of the composite membrane and the minority partner should improve the mechanical properties and stabilize the morphology of the composite polymer. The mechanical properties of these composite materials were measured by traction experiments and confronted with water sorption isotherms. The objective is to reveal correlations of mechanical properties with chemical composition of the minority phase and with water uptake properties of the composite polymer. The final objective is to develop a polymer membrane not swelling under fuel cell operation conditions.

Experimental Section

Membrane Synthesis. Sulfonated PEEK (S-PEEK) was prepared by reaction of PEEK (Victrex 450P, MW = 38300) with concentrated sulfuric acid at 50 °C for 5 days.[21] The solution was poured under continuous stirring into a large excess of ice-cold water. After standing overnight, the white precipitate was filtered and washed several times with cold water to neutral pH. The sulfonated polymer (S-PEEK) was then dried under vacuum for 4−6 h at room temperature. The degree of sulfonation (DS) was evaluated both by ^{1}H NMR[23] and by titration with the following results: DS = 0.9.

Silylated and sulfonated PPSU (SiS-PPSU, **1d**) was synthesized in two steps: (i) metalation reaction with butyl-lithium (BuLi), followed by electrophilic substitution by phenyl-trichlorosilane ($PhSiCl_3$), and (ii) hydrolysis and reaction with concentrated sulfuric acid.[20]

The original polymer PPSU (Solvay, MW = 46173) was added in a nitrogen atmosphere to anhydrous tetrahydrofurane. The solution was stirred at room temperature for 1 h and then cooled to −60 °C. After 1.5 h, an excess of BuLi and tetramethylenediamine (TMEDA) were added and the solution was stirred for 2 h at −60 °C. At this point, $PhSiCl_3$ (Aldrich, 97%) was added and the solution was slowly warmed to room temperature and then kept at reflux for 2 h. The precipitate formed is Si-PPSU (compound **1c**); it was filtered and washed with water until no chlorides were detected.

For sulfonation, the polymer (PPSU or Si-PPSU) was added to concentrated H_2SO_4 and the mixture was stirred at 50 °C for 5 h and then poured into ice-cold water. The precipitate was filtered, washed with water to neutral pH, and dried under vacuum for 5 h. Elemental analysis for S-PPSU and SiS-PPSU (compounds **1b** and **1d**, respectively) gave in both cases a DS = 2.

The procedure for membrane preparation was solution casting using dimethylacetamide (DMAc). In a typical experiment, around 250 mg sample (containing 93 wt % S-PEEK and 7 wt % secondary phase PPSU, unsubstituted, sulfonated, and/or silylated) was dissolved in 30 mL of solvent. The resulting mixture was stirred for 4 h, evaporated to 5 mL, cast onto a Petri dish, and heated to dryness. After cooling to room temperature, the resulting membranes were peeled off and dried at 120 °C for 12 h for solvent removal.

Membrane Structure. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded with a Bruker Avance 400 spectrometer operating at 400.13 and 100.56 MHz, respectively. The samples were dissolved in DMAc at 80 °C to ensure the complete dissolution of the polymers and the spectra were recorded using D_2O as external lock. Chemical shifts (ppm) are referenced to tetramethylsilane (TMS).

X-ray diffractograms of the composite membranes were recorded with a Siemens D5000 diffractometer using Cu Kα radiation (λ = 0.1540 nm), steps of 0.04° and 1 s step time.

The optimized conformation of substituted PPSU macromolecules was calculated using a semiempirical method (AM1[24]) by the Hyperchem program.[25] Geometric optimizations were erminated when the energy difference among successive iterations was lower than 4.2 J/mol.

Mechanical Properties. The mechanical properties of blends of sulfonated PEEK and substituted PPSU were investigated using an ADAMEL Lhomargy DY30 test machine at room temperature (RT) at a constant crosshead speed of 5 mm/min with aluminum sample holders. Particular attention was given to the macroscopic homogeneity of membranes made by casting and only apparently homogeneous membranes were used for the mechanical tests. The clamping pressure was determined according to a preliminary tensile stress−strain test: it was about 40% of the apparent elasticity limit, corresponding to the linear part of the tensile curve.

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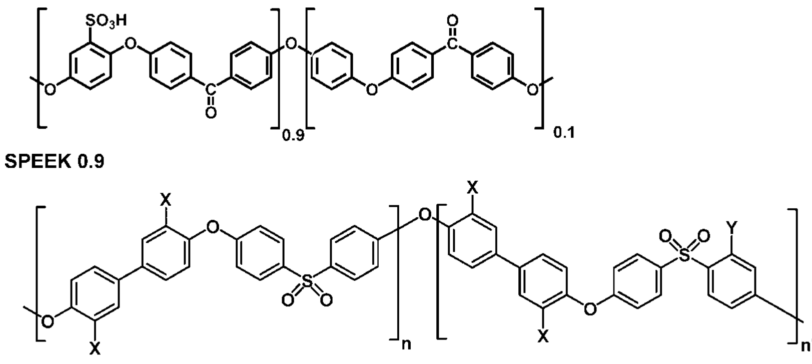

SPEEK 0.9

PPSU: X = Y = H (n = n') 1a

S-PPSU: X = SO$_3$H Y = H (n = n') 1b

Si-PPSU: X = H Y = Si(OH)$_2$Ph (n = 0.95 ; n' = 0.05) 1c

SiS-PPSU: X = SO$_3$H Y = Si(OH)$_2$Ph (n = 0.95 ; n' = 0.05) 1d

Figure 1. Structures of S-PEEK and SiS-PPSU.

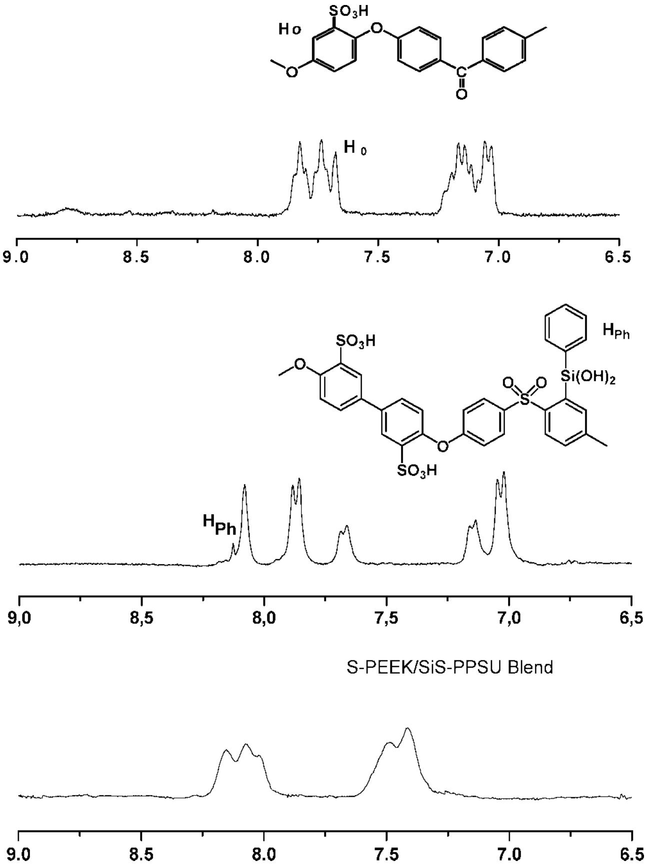

Figure 2. ^{1}H NMR spectra in DMAc. From top to bottom: S-PEEK, SiS-PPSU, and S-PEEK/7 wt % SiS-PPSU composite.

The aluminum sample holders were selected to give rigidity to the clamping system and to optimize the mechanical testing. Figure 6a shows the shape and geometry of the clamps and specimens used in the uniaxial tensile tests. The aluminum sample holders and the membranes have the same width. The uniaxial tensile properties were measured on membrane samples of 200 μm thickness, 5 mm width and 25 mm length. The border of the membranes, where inhomogeneities of composition may exist, was eliminated by cutting carefully the specimens.

The selected tensile curves corresponded only to tests with a final rupture in the useful part of the specimens. The other cases of rupture (<20%), e.g., near or under grips, were systematically eliminated. Prior to the measurements, the polymer samples were stabilized at ambient temperature and humidity, which was around 50% RH. The measurement time was below 5 min.

Water Uptake Measurements. Water uptake was measured by two complementary experiments: (i) By full immersion in deionized water at 25 °C: Polymer samples were weighed before and after immersion for times between 1 h and 6 days. (ii) By equilibration with water vapor at 25 °C under 0−95% RH: The water sorption isotherms were recorded using a TA5000 thermogravimetric analyzer. RH was modified in 5 or 10% steps and the water uptake recorded at each step for 2 h. Furthermore, sorption isotherms were recorded as a function of temperature under a fixed RH = 75%. Prior to all experiments, the membranes were first dried in situ for 3 h at 80 °C under 0% RH.

Results and Discussion

Chemical Structures and Optimal Conformations. The chemical structures of S-PEEK and substituted PPSU are represented in Figure 1. Figure 2 shows ^{1}H NMR spectra of S-PEEK,[26] SiS-PPSU, and S-PEEK/SiS-PPSU blend. All resonances in this latter spectrum appear downfield shifted with respect to the resonances present in the spectra of both components.

The ^{13}C spectrum of S-PEEK/SiS-PPSU blend, reported in Figure 3, shows instead a shift of the resonances toward higher field. The different chemical shifts of the peaks of the blend, both in ^{1}H and ^{13}C NMR, are indicative of interaction between the two blend components and can be explained by dipole−dipole forces between the two polymers, resulting in a deshielding of the hydrogen atoms and, consequently, a shielding of the carbon atoms. In the case of ^{13}C NMR, one can analyze which peaks are perturbed by the presence of the second phase, SiS-PPSU: the carbons near the ether functionality and near the ketone group are most influenced. The ketone carbon signal of the composite is split into two peaks. This effect is not attributable to interaction with sulfonic acid groups, present in high concentration also in the pure S-PEEK macromolecule. It might instead be related to interactions with phenyl-silanol

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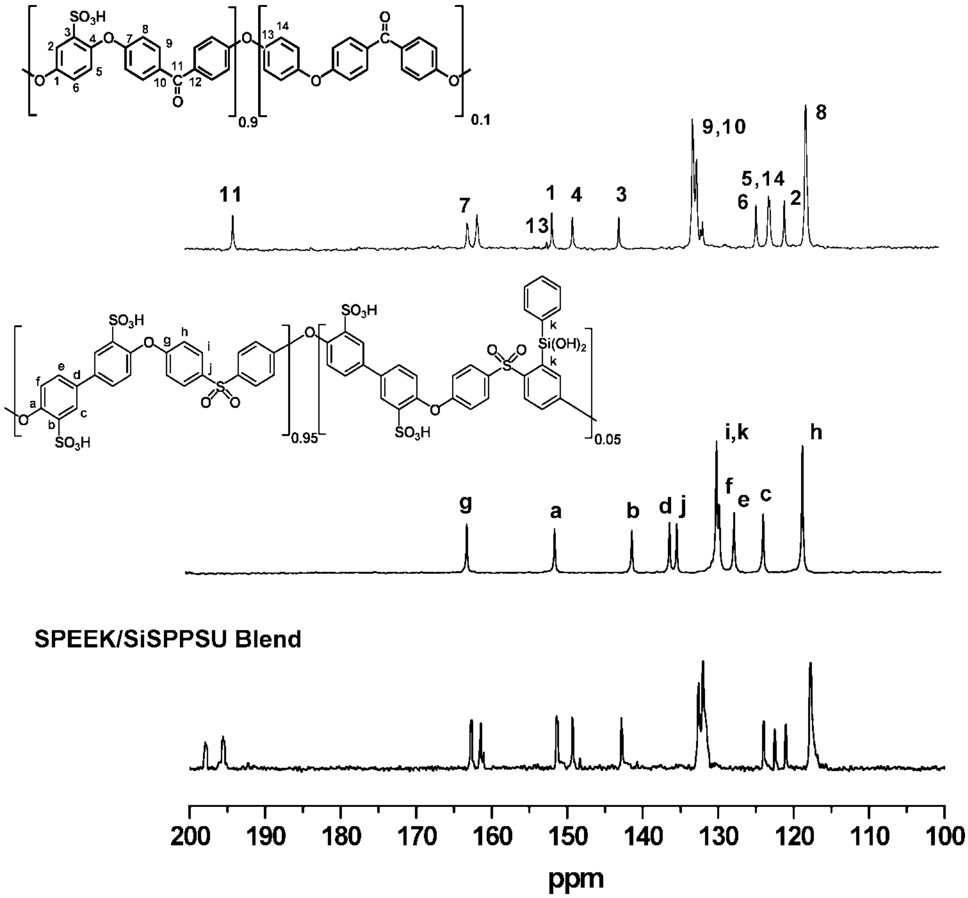


Figure 3. ^{13}C NMR spectra in DMAc. From top to bottom: S-PEEK, SiS-PPSU, and S-PEEK/7 wt % SiS-PPSU composite. Labels refer to the assignments reported in the structures.

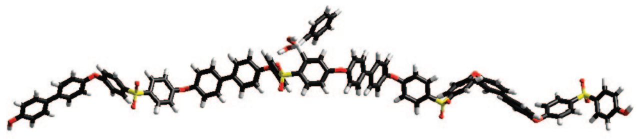
groups in SiS-PPSU, which play also a major role in mechanical properties.

To ascertain if the different properties of the 7 wt % composite are also due to steric factors, given that polyaromatic polymers can exist in a variety of interconvertible conformational forms, a conformational study of compounds SiS-PPSU and Si-PPSU was carried out at a semiempirical level (AM1). Semiempirical methods are less reliable and more restrictive than ab initio, but do not require considerable computer capacity and computational time. Given the high number of degrees of freedom, we did not carry out a systematic study of the potential energy surfaces, but only varied (in 90° steps) the torsion angles φ_1 and φ_2 of the model compounds with four repeat units. (See Figure 1).

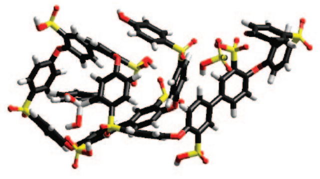
Figure 4 presents the optimal conformation of only silylated PPSU (**1c**) compared with the conformation of SiS-PPSU (**1d**). The most stable conformers resulted in (170°, −100°) for **1c** and (−86°, 66°) for **1d**. The difference between the energy values of such minima and those relative to the other conformations is around 42 kJ/mol. (It is not the absolute values of enthalpy of the various species that should be considered, but only their variation[27]).

All composite samples are fully amorphous, as can be seen in the typical XRD pattern of S-PEEK/SiS-PPSU (Figure 5). The broad signal indicative of an amorphous phase is observed around the reflections of crystalline S-PEEK.

Mechanical Properties. Figure 6b shows tensile stress−strain curves obtained for composites with differently substituted PPSU. The corresponding mechanical properties—elastic modulus, ultimate strength, and elongation at rupture—(Table 1) correspond to mean values of at least three uniaxial tensile tests at RT. The "apparent" Young's moduli were determined for all specimens under the same test conditions. One notices an important decrease of elastic modulus and tensile strength in blends with S-PPSU, whereas blends with Si-PPSU show enhanced elastic modulus and tensile strength.



1c (170°, -100°)



1d (-86°, 66°)

Figure 4. Calculated optimal conformation of Si-PPSU (1c) and SiS-PPSU (1d) macromolecules, derived from the restricted rotation around φ_1 and φ_2 (see Figure 1).

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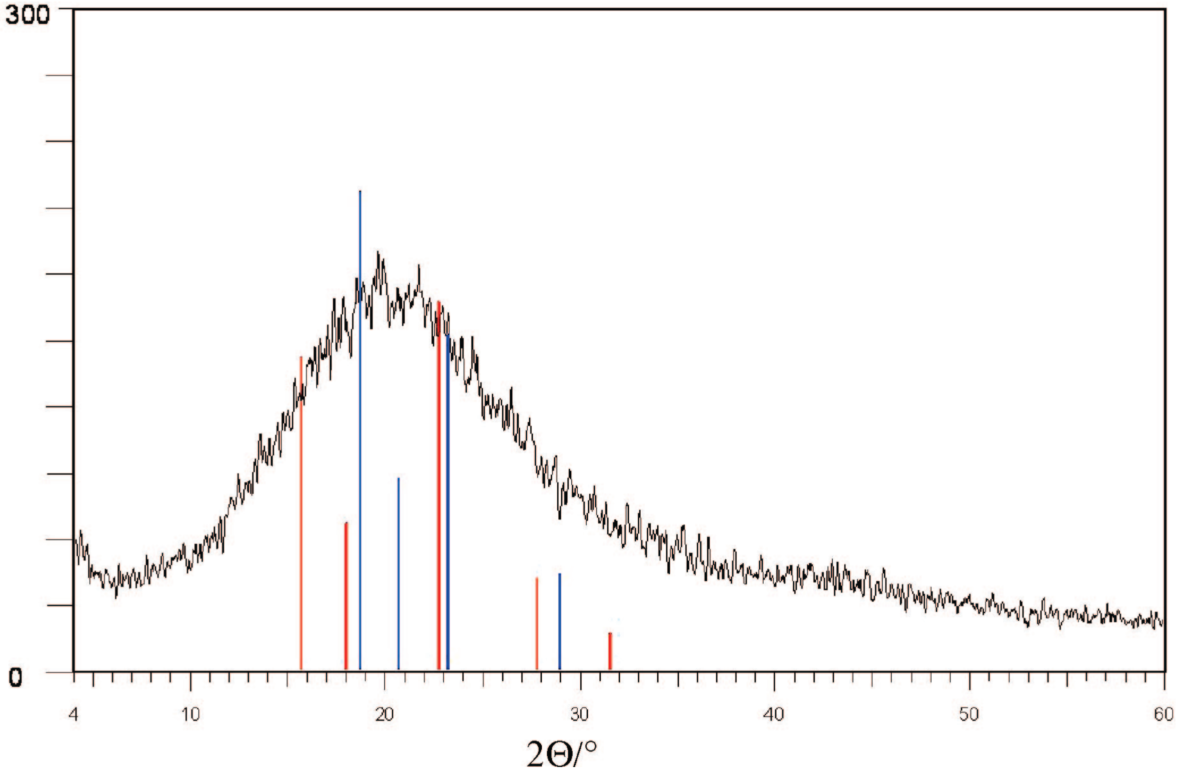

Figure 5. X-ray diffractogram of S-PEEK/7 wt % SiS-PPSU composite. The indicated reflections correspond to crystalline PEEK polymer (JCPDS data files 00-052-2277 and 00-052-2278).

In the optimal conformation of Si-PPSU and SiS-PPSU macromolecules (Figure 4), one notices immediately the extreme difference between the favorite elongated conformation of the Si-PPSU and the spherical one of SiS-PPSU. This can explain the strong dipolar interaction with neighboring macromolecules, corresponding to strong shifts of the NMR resonances. One can easily imagine the profound role these conformations play also in the mechanical properties of a composite polymer. Furthermore, the position of the phenylsilanol side group, which stands out of the main chain and can impede the movement of adjacent polymer chains, is remarkable in Si-PPSU. Both factors can explain the important increase of elastic modulus and tensile strength of composites with silylated PPSU as second phase.

Water Sorption Isotherms. The mechanical strength of polymer electrolyte membranes has been related to their water uptake and swelling. We have shown recently that the water uptake coefficient after 1 h of full immersion is inversely proportional to the elastic modulus for various polymers of the S-PEEK family.[9] Water uptake of various composite polymers is reported in figure 7 as a function of immersion time in deionized water at 25 °C. The water uptake coefficients λ are calculated according to the following equation:[28]

$$\lambda = \frac{1000 \times (W_{\text{wet}} - W_{\text{dry}})}{18 \times W_{\text{dry}} \times \text{IEC}} \tag{1}$$

IEC is the ion exchange coefficient (in mequiv/g, Table 1), which can be calculated from the degree of sulfonation of the membranes. One notices a very large increase of λ with time for S-PPSU containing membranes, whereas the water uptake coefficient of Si-PPSU reaches rapidly a stable value of about 8.

A typical water vapor sorption kinetic is shown for a S-PEEK/Si-PPSU composite blend in Figure 8: water uptake is plotted versus time at RH between 0 and 95%. Stationary plateaus of water uptake are obtained at RH values up to 90% RH. At 95% RH, an equilibrium water sorption value is not reached during the equilibration time of 2 h. The corresponding water sorption isotherm is represented in Figure 9. A hysteresis between sorption and desorption branches can be observed, corresponding to water condensation into membrane pores (hysteresis loop type H3 in IUPAC classification [29]). The water uptake coefficients at high RH are consistent with the value obtained after full immersion in water for S-PEEK/Si-PPSU (Figure 7). It was previously pointed out that the so-called "Schröder paradox", a divergence between water uptake coefficients obtained by sorption of water vapor and liquid water, is characteristic of an out-of-equilibrium material; one can conclude that it is also related to membrane swelling.[7,30]

Water Diffusion Coefficients. Chemical diffusion coefficients D of water in the polymer membranes can be evaluated from the water sorption kinetics using an approximate solution of Fick's second law. For a thin sample with thickness L, the water uptake M at time t can be written at short times ($[M(t)/M\infty] < 0.5$ or $(\sqrt{(Dt)}/L) < 0.2$[31]):

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$$\frac{M(t)}{M\infty} = \frac{4}{L}\sqrt{\frac{Dt}{\pi}} \qquad (2)$$

Equation 2 shows that the chemical diffusion coefficient D is proportional to the square of the membrane thickness L; consequently, membrane swelling has an important impact on the apparent chemical diffusion coefficient. The chemical diffusion coefficients D of water were calculated from the initial slope of the curves. They are reported in Figure 10 as a function of RH for different polymer composites. The variation of D observed at RH above 50% for membranes containing SiS-PPSU and especially S-PPSU as second phase is an artifact, related to membrane swelling and the proportionality of D with L^2. This is a sensitive indicator of the humidity range where membrane swelling occurs. For S-PEEK/Si-PPSU membranes, the chemical diffusion coefficients show a similar tendency to Nafion membranes:[32] at low RH, the chemical diffusion coefficients increase with RH up to a maximum value around 50% RH and decrease at higher RH, due to the variation of the water activity coefficients. The self-diffusion coefficients $\tilde{D}$ can be calculated from the chemical diffusion coefficients D according to the equation

$$D = \tilde{D}\left(\frac{\mathrm{d}\ln a_{\mathrm{H_2O}}}{\mathrm{d}\ln x_{\mathrm{H_2O}}}\right) \qquad (3)$$

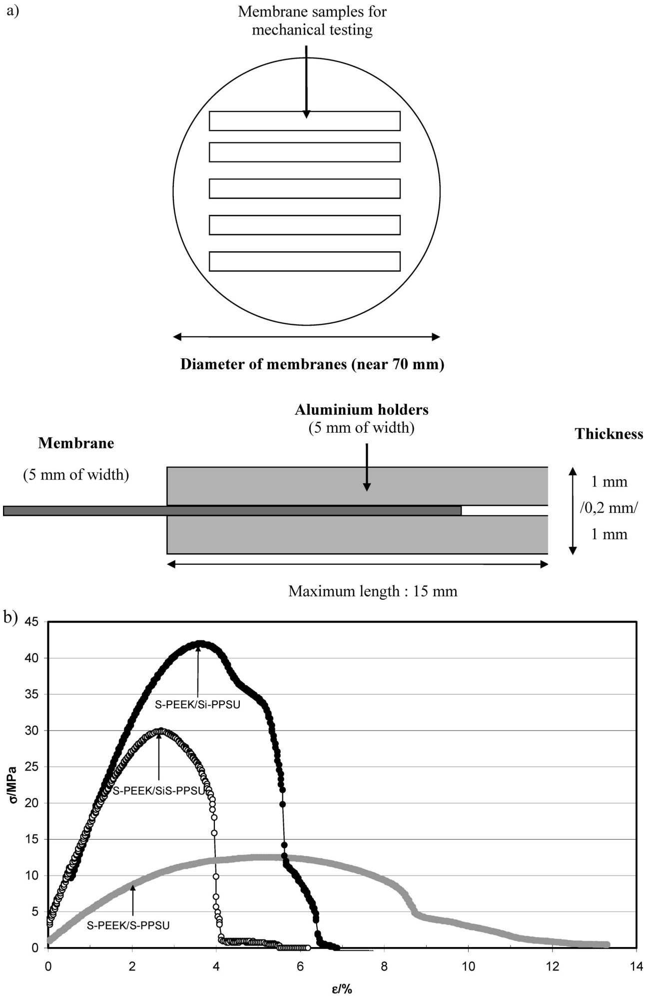

Figure 6. (a) Specimens, shape, and geometry of the clamps for tensile tests. (b) Stress−strain curves for composite polymer membranes with 7 wt % Si-PPSU, SiS-PPSU, and S-PPSU.

Table 1. Ion Exchange Capacity IEC, Elastic Modulus E, Ultimate Strength σ, and Elongation at Rupture ε, for S-Peek and Composite Membranes

Membrane	IEC/(mequiv/g)	E/MPa	σ/MPa	ε/%
S-PEEK	2.50	600 ± 200	25 ± 1	4.9 ± 0.9
S-PEEK/S-PPSU	2.67	400 ± 100	10 ± 3	8.5 ± 1.0
S-PEEK/PPSU	2.48	1100 ± 200	35 ± 2	4.4 ± 0.3
S-PEEK/SiS-PPSU	2.67	1200 ± 300	26 ± 4	2.9 ± 0.5
S-PEEK/Si-PPSU	2.48	1500 ± 100	41 ± 2	3.6 ± 0.4

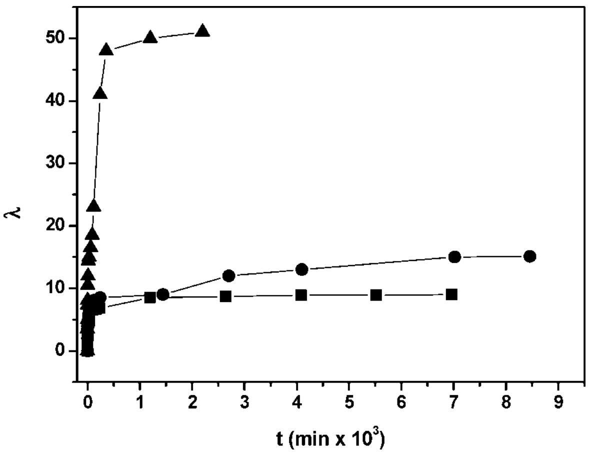

Figure 7. Water uptake coefficients as a function of immersion time in deionized water at 25 °C for (▲) S-PEEK/S-PPSU, (●) S-PEEK/SiS-PPSU, and (■) S-PEEK/Si-PPSU composite polymer membranes.

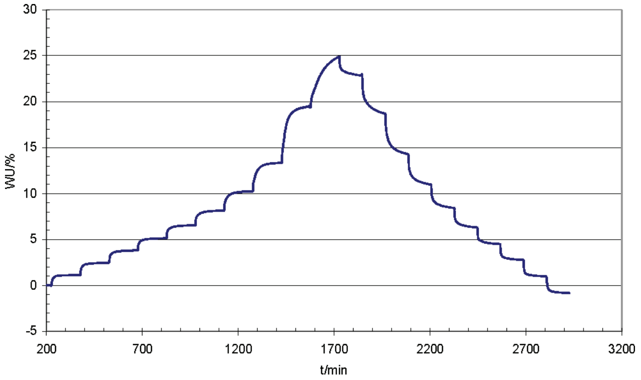

Figure 8. Water sorption/desorption kinetics at 25 °C of S-PEEK/Si-PPSU composite polymer membranes for RH between 0 and 95%.

The thermodynamic water activity $a_{\mathrm{H_2}}$O is equal, for an ideal system, to the relative humidity, whereas the water molar fraction $x_{\mathrm{H_2O}}$ is directly related to the water uptake coefficients λ at different RH values. The small enhancement of self-diffusion coefficients with increasing molar fraction of water is related to the increasing number of percolating pathways containing water molecules. The self-diffusion coefficients are in the order of those for pure S-PEEK,[32] which is reasonable given the large percentage of S-PEEK in the composites.

For the most stable membrane, containing Si-PPSU as second phase, chemical diffusion coefficients were also determined as a function of temperature at fixed RH = 75%.

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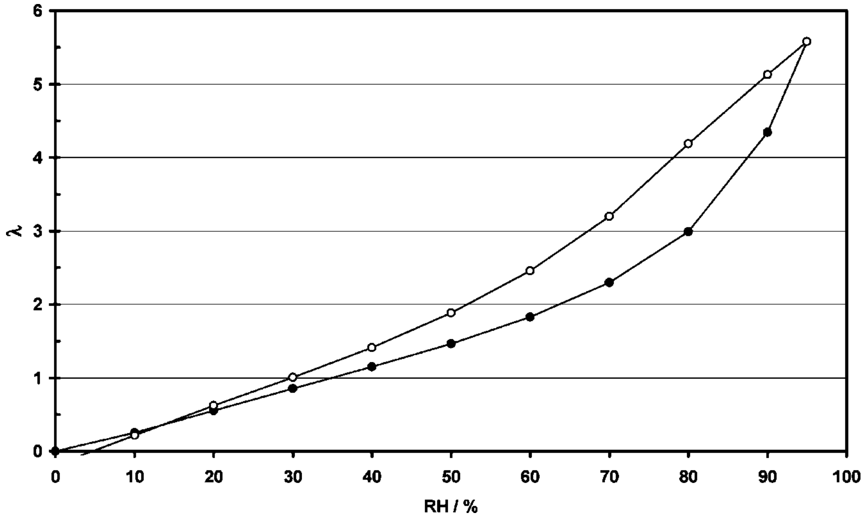

Figure 9. Water sorption/desorption isotherm at 25 °C for S-PEEK/Si-PPSU composite polymer membranes. Sorption, ●; desorption, ○.

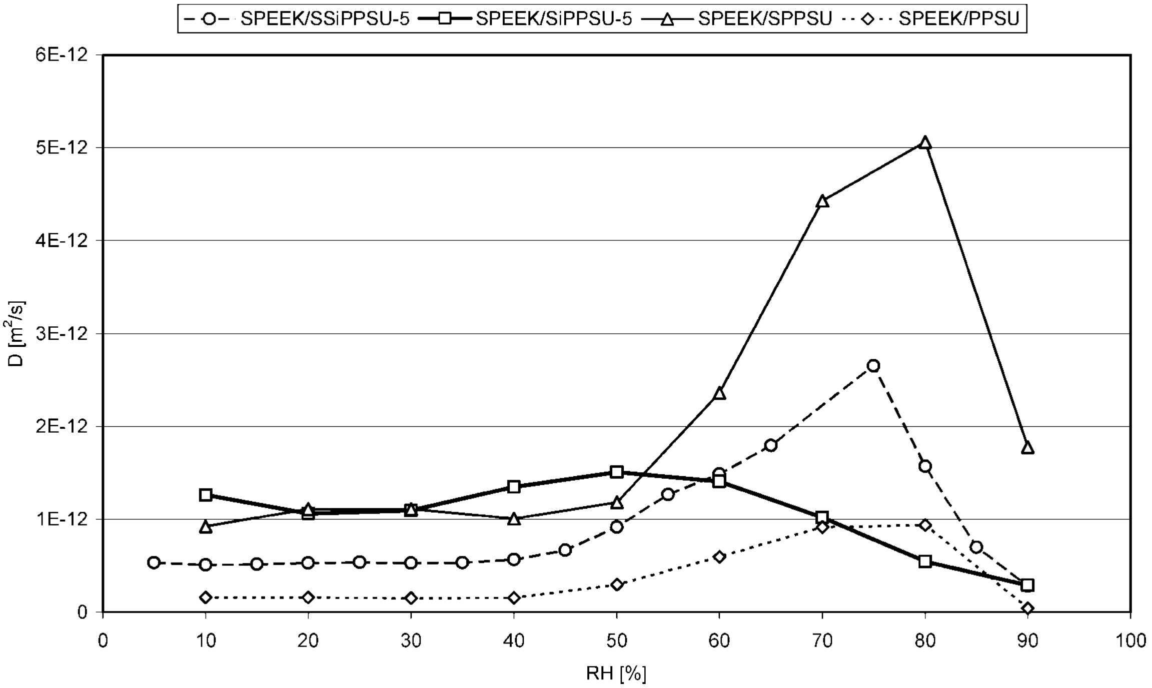

Figure 10. Apparent chemical diffusion coefficients of water in different composite membranes. The maxima observed above 50% RH are artifacts reflecting membrane swelling.

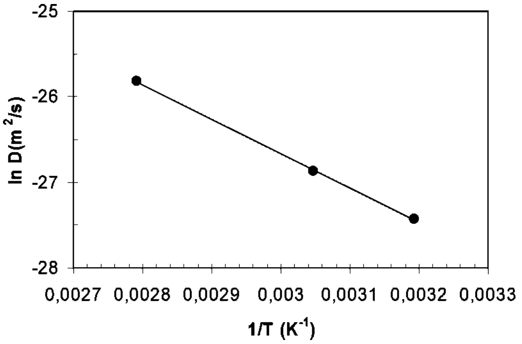

Figure 11. Temperature dependence of water chemical diffusion coefficient in S-PEEK/Si-PPSU polymer membranes.

The Arrhenius plot is represented in Figure 11. An activation energy of 34 kJ/mol for chemical diffusion can be calculated, which is consistent with previous data obtained from conductivity measurements in related membranes[32] and indicates that a Grotthuss-type diffusion mechanism is operating in this range of relative humidity.

Conclusions

This study confirms the correlation between mechanical strength, water uptake coefficient, and swelling of proton-conducting polymer membranes. We have investigated composites made from a majority phase, S-PEEK with high degree of sulfonation, and a minority phase, substituted (sulfonated and/or silylated) PPSU. The secondary phase is supposed to maintain the mechanical stability of the membrane, whereas the main component is responsible for proton conduction.

The experiments show that composites with silylated PPSU have a high strength and tend much less to membrane swelling at RH above 50%. The mechanical reinforcement is related to the bulky phenyl-silanol groups in the silylated macromolecule. When membrane swelling is suppressed by addition of Si-PPSU, water uptake coefficients calculated after equilibration with water vapor at different RH are consistent with values calculated after immersion in liquid water. Water diffusion coefficients are in good agreement with previously reported values for other members of the S-PEEK family. Furthermore, they are a sensitive indicator of membrane swelling phenomena, given the dependence of chemical diffusion coefficients on the square of membrane thickness.

The concept of mechanically reinforced composite S-PEEK membranes by addition of a silylated PPSU minority phase is a promising step to master membrane swelling and develop proton exchange membranes suitable for intermediate temperature PEM fuel cell operation.

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