

Short communication

Mechanical properties of hybrid proton conducting polymer blends based on sulfonated polyetheretherketones

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Abstract

The mechanical properties of polymer blends made from sulfonated polyetheretherketone and sulfonated and/or silylated polyphenylsulfone (PPSU) are reported. Elastic modulus and maximum strength of membranes increase strongly by addition of silylated PPSU, whereas sulfonated PPSU softens the materials. A correlation is established between the water uptake coefficient measured after immersion in water and the elastic modulus of the membranes. The relation with membrane swelling during fuel cell operation is discussed.

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1. Introduction

The proton conducting polymer membrane is the heart of proton exchange membrane (PEM) fuel cells. It must simultaneously be impermeable to reactants, maintain good proton conductivity, and be chemically, thermally and mechanically stable under the fuel cell operation conditions.

Fully aromatic thermoplastic polymers, such as polyetheretherketone (PEEK) and polyphenylsulfone (PPSU), are widely studied as replacement of currently utilized Nafion membranes, because they seem to meet these requirements and are readily available and cheap [1,2]. They can be easily functionalized, for example by sulfonation to create proton-conducting polymers (S-PEEK and S-PPSU). However, a relatively high degree of sulfonation is necessary for good proton conductivity, but degrades the morphological stability of the polymer in presence of water: polymers with a high degree of sulfonation tend to important swelling and, finally, become even water-soluble and useless for PEM application [3]. Problems with membrane

«swelling» are due to interfacial regions between hydrophobic polymer backbone and hydrophilic percolating nanodomains, where sulfonate groups are situated [4]. It has been suggested recently that a correlation exists between this change of morphology and mechanical properties of the polymer; higher water uptake has been related to lower tensile strength of the polymer matrix [5].

We have in recent years presented new hybrid organic–inorganic polymers, based on sulfonated PEEK, in which inorganic silanol groups were added in order to improve thermal stability, water uptake and morphological stability [6–8]. In this work, we go a step further by investigating composite blends of a majority ionomer component, S-PEEK (93 w%), which should maintain high proton conductivity, and a minority component, PPSU (7 w%), in pure, sulfonated and/or silylated form (Si, S-PPSU), which should keep mechanical stability. The mechanical properties of these composite materials were measured and confronted with water uptake coefficients determined after 1 h full immersion in water. The objective is to reveal correlations of mechanical properties with chemical composition of the secondary phase and with water uptake of the composite polymer. Final objective would be to predict, and possibly avoid, polymer membrane swelling under fuel cell operation conditions.

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2. Experimental

2.1. Membrane synthesis

Sulfonated PEEK (S-PEEK) was prepared by reaction of PEEK (Victrex 450P, MW = 38,300 [9]) with concentrated sulfuric acid at 50 °C for 5 days [10]. 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 ^1H NMR [11] and by titration with according results: DS = 0.9.

Silylated and sulfonated PPSU (SiS-PPSU) was synthesized in two steps: (i) metallation reaction with butyl-lithium (BuLi), followed by electrophilic substitution by phenyl-trichlorosilane (PhSiCl_3), (ii) hydrolysis and reaction with concentrated sulfuric acid [12].

For silylation, the original polymer PPSU (Solvay, MW = 46,173) was added in nitrogen atmosphere to anhydrous tetrahydrofuran. The solution was stirred at room temperature for 1 h 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 (97%) was added and the solution was slowly warmed to room temperature, then kept at reflux for 2 h. The precipitate formed is Si-PPSU; 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 kept stirring at 50 °C for 5 h, then it was poured in ice-cold water. The precipitate was filtered, washed with water to neutral pH and dried under vacuum for 5 h. Elemental analysis for SiS-PPSU and S-PPSU gave in both cases a high DS = 2.

The procedure for membrane preparation was solution casting using dimethylacetamide (DMAc). In a typical experiment, around 250 mg of sample (93 w% S-PEEK + 7 w% substituted PPSU) 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 complete solvent removal.

2.2. Membrane characterization

The mechanical measurements were made on membrane samples of about 25 mm length, 5 mm width and 200 μm thickness, glued on aluminum sample holders, and using an ADAMEL Lhomargy DY30 traction machine at ambient temperature and humidity (around 50–60% RH).

The water uptake coefficient λ (number of water molecules per sulfonic acid group) was measured after 1 h full immersion of the membranes in water at 25 °C. Excess water was removed with absorbing paper and the mass change was measured by double weighing before and after equilibration (EW is the equivalent

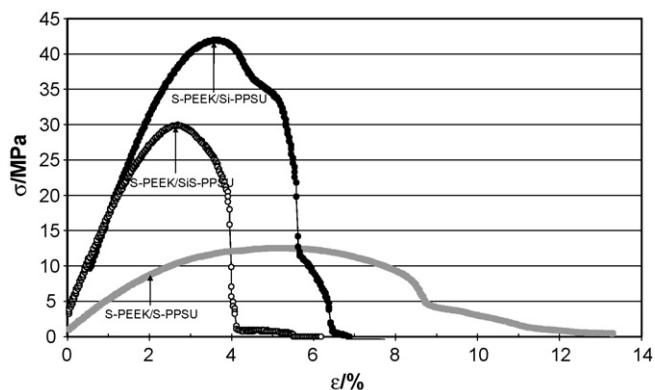


Fig. 1. Stress–strain curves for different sulfonated and/or silylated polymer blends.

weight, expressed in g/eq.).

$$\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}})}{18 \times W_{\text{dry}}} \times EW \quad (1)$$

Preliminary calculations of the optimized conformation of PPSU macromolecules were performed using a semi-empirical method (AM1) by the Hyperchem program [13]. Geometric optimizations were terminated when the energy difference was lower than 4.2 J mol^{-1} .

3. Results

Fig. 1 shows typical stress–strain curves obtained for three different silylated and sulfonated membranes. The corresponding mechanical properties, elastic modulus, maximum strength and elongation at rupture, are summarized for all investigated membranes in Table 1. Data for polymer blends with 5% and 10% SiS-PPSU are also reported [14]. Fig. 2 is a plot of maximum strength versus elastic modulus, showing a fairly linear relation. The relation between water uptake coefficient after 1 h of full immersion and the elastic modulus of different membranes in the S-PEEK family is plotted in Fig. 3.

4. Discussion

The stress–strain curves show a very strong influence of the secondary PPSU phase. Elastic modulus and maximum strength data are consistent: whereas sulfonation of PPSU softens the

Table 1
Elastic modulus E , maximum strength σ_{max} , elongation at rupture ε , and water uptake coefficient λ after 1 h full immersion for various membranes

Membrane	E (MPa)	σ_{max} (MPa)	ε (%)	λ
PEEK	3000	100	2.5 [9]	0
S-PEEK	600 ± 200	25 ± 1	4.9 ± 0.9	17
S-PEEK/7%S-PPSU	400 ± 100	10 ± 3	7.5 ± 1.0	17
S-PEEK/7%PPSU	1100 ± 200	35 ± 1	4.4 ± 0.3	15
S-PEEK/7%Si-PPSU	1500 ± 100	41 ± 2	3.6 ± 0.4	6
S-PEEK/5%SiS-PPSU	500	20	2.6	13 [14]
S-PEEK/7%SiS-PPSU	1200 ± 300	26 ± 4	2.9 ± 0.5	8
S-PEEK/10%SiS-PPSU	850	23	3.5	6 [14]

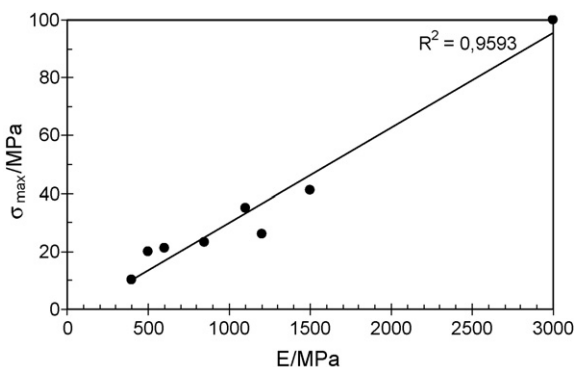


Fig. 2. Correlation between maximum strength σ_{\max} and elastic modulus E of investigated polymer membranes (see Table 1).

polymer, silylation of PPSU enhances the membrane strength considerably. It might be surprising that addition of such a small amount of silanol groups changes the mechanical properties of the membranes so strongly. Only 7 w% secondary phase is added, which contains furthermore only a small concentration of phenyl-silanol groups (only 5% of macromolecular units are silylated); in fact, the molar concentration of silicon is only about 0.3 mol%. However, it is well known that small additions of a second element can very strongly modify the mechanical properties of solids, the best known case being steel, where addition of about 1 mol% carbon hardens considerably the relatively soft iron matrix.

Tentatively, one may attribute the hardening of the polymer matrix to the presence of the large phenyl-silanol side chains (Fig. 4) that will counteract the motion of majority S-PEEK

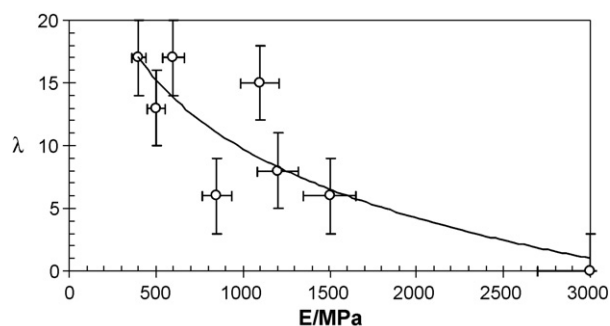


Fig. 3. Water uptake coefficient λ after 1 h full immersion as function of elastic modulus E of studied polymer membranes (see Table 1).

polymer chains, when a shear force is applied to the material. Furthermore, hydrogen bond interactions will be strong between the silanol groups and sulfonate groups of the S-PEEK matrix. This might explain the considerable hardening by addition of silanol groups.

Considering the water uptake properties of different membranes in the S-PEEK family, our data show unambiguously that the lower the elastic modulus, the higher the water uptake. Considering that too high water uptake leads to swelling of the membrane, the importance of elastic properties for membrane swelling under fuel cell operation conditions is underlined. On the other hand, given the relation between water uptake and proton conductivity of hydrated acidic polymer membranes, one must find a compromise between low membrane swelling and high proton conductivity, which should correspond to an optimum value of elastic modulus.

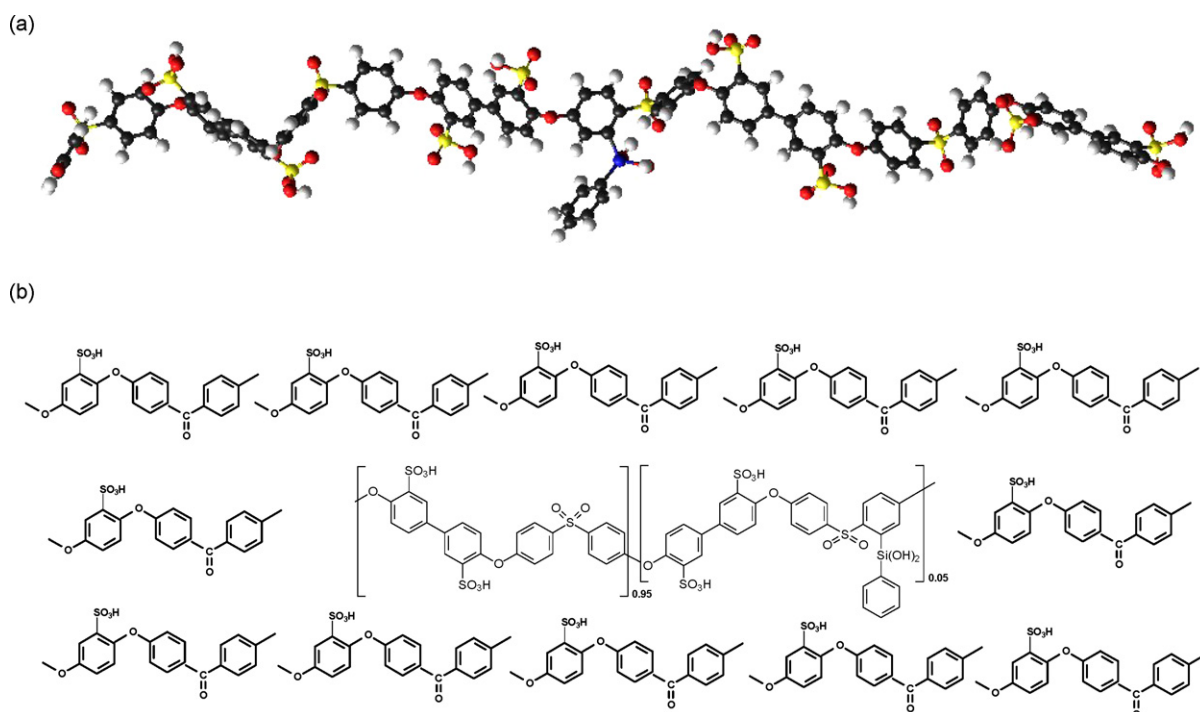


Fig. 4. (a) Calculated optimized conformation of a SiS-PPSU macromolecule. One notices the large phenyl-silanol group in the middle of the macromolecule. (b) Schematic model of composite blend.

5. Conclusion

In the quest for improved membranes, composite materials offer a supplementary degree of freedom for conception. We show in this study that introduction of phenyl-silanol groups strongly enhances the mechanical strength of composite polymer membranes, whereas sulfonation, as expected, reduces the elastic modulus. A clear correlation exists between the water uptake coefficient and the elastic modulus of the membranes. In order to reduce swelling during fuel cell operation, a membrane with sufficiently high elastic modulus must be chosen. The composite membrane with solely silylated PPSU appears particularly suitable from this point of view.

Acknowledgements

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