Tensile Mechanical Properties of Sulfonated Poly(Ether Ether Ketone) (SPEEK) and BPO_4/SPEEK Membranes

A. Reyna-Valencia, S. Kaliaguine, M. Bousmina

Department of Chemical Engineering (CREPEC), Laval University, Ste-Foy, QC., G1K 7P4 Quebec, Canada

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ABSTRACT: A study to evaluate the tensile mechanical properties of sulfonated poly(ether ether ketone) (SPEEK) and BPO_4/SPEEK composite membranes has been carried out. It is aimed to give an assessment of these materials for applications in proton exchange membrane fuel cells. The stress–strain response of the membranes was measured as a function of the degree of sulfonation (DS) and the filler–matrix ratio. In addition, the effects of immersion in water at various temperatures were explored in situ by means of a homemade testing chamber fitted to the tensile analyzer. The results indicate that the DS has an important influence on the final mechanical behavior of the membranes. The introduction of the BPO_4 solid filler leads to deterioration in mechanical performance compared to unfilled SPEEK. A general picture of the microstructural features influencing the mechanical properties of SPEEK and BPO_4/SPEEK membranes is proposed. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2380–2393, 2005

Key words: poly(ether ether ketone) (PEEK); SPEEK; proton exchange membranes (PEM); mechanical properties

INTRODUCTION

During the past decade, proton exchange membrane fuel cells (PEMFC) have become the focus of very active research. The huge patent interest in this energy conversion technology arises mostly from promising applications in zero-emission vehicles and portable power generation, which could help address future environmental and energy-supply challenges. The PEMFC operation relies on a proton exchange membrane (PEM), which plays a decisive role as an electrolyte medium for proton transport from the anode to the cathode and as a solid barrier to avoid direct contact between fuel and oxygen. Consequently, PEM must fulfill the following performance features: good proton conductivity, high resistance to electrons, impermeability to fuel and oxidants to avoid diffusion and leakage, long-term chemical and thermal stabilities, and good mechanical properties.

Membranes manufactured from perfluorinated ionomers (PFI), such as DuPont's Nafion, have shown high proton conductivity and good chemical and mechanical stabilities during PEMFC operation. In fact, they remain the only commercially available high-performance PEMs. PFI membranes are, however, not wholly useful in direct methanol fuel cells due to high methanol permeability. Moreover, their production process is expensive and toxic, and their temperature operation range is limited because proton conductivity drops above 80 °C. Therefore, new materials are required to make PEMFC technology technically and economically competitive.

To date, various routes have been proposed to develop effective and low cost PEMs based on nonfluorinated polymers. For instance, electrophilic sulfonation of aromatic thermoplastics such as polyethersulfone, polybenzimidazole, polyimides, and poly(ether ether ketone) (PEEK) gives them some proton conductivity, thus making them suitable for PEM applications.[1–5] In this way, sulfonated PEEK (SPEEK) has been demonstrated to be a very promising alternative for PEMFC.

Characterization studies of SPEEK have mainly focused on conductive properties.[5–12] There is no agreement about the conductivity values as a function of temperature reported for samples with the same degree of sulfonation (DS), which vary from 10^{-5} to 10^{-2} S/cm for membranes with DS above 50%. Indeed, the conductivity is a complex property that depends on several factors besides DS, namely the pretreatment of the membrane, the hydration state, the ambient relative humidity, and the casting solvent used during membrane manufacturing.[13,14] It has been concluded,

Correspondence to: M. Bousmina (bousmina@gch.ulaval.ca).
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however, that this material has a strong potential for PEMFC applications.

During fuel cell operation, PEMs are subjected to saturated environments at elevated temperatures; consequently, the effects of temperature and moisture on membrane performance must be considered. In general, thermal stability studies of SPEEK evidence that degradation temperature decreases with increasing sulfonation level, but it has been found that the material is stable up to 250°C,[7,10,12] which is enough for PEMFC requirements.

Water uptake is an important parameter because PEMs must be saturated to achieve their proton conducting function. The moisture uptake increases with DS, thus improving the conductivity of the hydrated membrane.[10,12] However, highly polar water molecules act as a plasticizer, undermining the electrostatic interactions between SPEEK molecular chains and causing swelling and loss of mechanical stability. Xing et al.[12] measured SPEEK swelling following water sorption as a function of DS and reported that the dimensional changes varied from low values near 2% at around 50% DS to complete solubility at high DS. Moreover, water uptake, swelling, and conductivity are further enhanced by temperature in all cases.

In conclusion, proton conductivity and mechanical properties of SPEEK membranes are closely interrelated, in such a way that an increase in the degree of sulfonation improves water uptake and conductivity, but has a negative effect on the mechanical performance, thus reducing the long-term stability of the membrane in the fuel cell.

The principle of composite materials has been applied as an alternative route to overcome this difficulty. SPEEK has been used as a polymeric matrix for proton-conducting composite membranes. Conductive fillers have been added to the SPEEK matrix with the purpose of enhancing the conductivity with minimum sacrifice in mechanical properties. Several fillers have been employed, namely zirconium phosphate compounds,[9] silica,[9] heteropolyacids,[10] and boron orthophosphate (BPO_4),[15] among others.

Various studies have been concerned with the investigation of the properties of BPO_4/SPEEK composite membranes.[15–17] BPO_4 is an inorganic acid, typically a white microcrystalline powder that behaves as a proton conductor under certain circumstances. The incorporation of high loads of BPO_4 increases both water uptake and swelling of the inherently hydrophilic SPEEK matrices. Consequently, the composite membranes exhibit better conductivity values than the corresponding pure SPEEK matrices, depending on the BPO_4 contents and the DS and increasing with the temperature in all cases. It has been observed that they even display high conductivity values up to temperatures of 100–150°C. Results on conductivity and moisture uptake reported by Wang[17] are summarized in Table I.

TABLE I
Characteristics of BPO_4/SPEEK Composite Membranes (from Ref. 17)

SPEEK DS (%)	BPO_4 content (wt %)	Water uptake (wt %)	Conductivity (S/cm) (at 25 °C)
60	0	22.1	3.6×10^{-3}
	25	32.4	5.0×10^{-3}
	40	38.1	6.0×10^{-3}
	50	41.0	6.5×10^{-3}
70	0	29.5	5.0×10^{-3}
	25	35.1	6.9×10^{-3}
	40	42.1	7.2×10^{-3}
	50	48.3	8.5×10^{-3}
	60	59.5	9.8×10^{-3}
83	1	41.5	7.8×10^{-3}
	25	50.5	8.1×10^{-3}
	40	55.1	9.2×10^{-3}
	50	72.0	1.4×10^{-2}
	60	95.1	1.6×10^{-2}

This research was motivated by the need to investigate the mechanical behavior of SPEEK and BPO_4/SPEEK membranes to obtain a better comprehension of their properties in relation to fuel cell application conditions. This work focuses on the uniaxial tensile properties of the membranes as a function of the DS and the filler–matrix ratio. The effect of immersion in water at different temperatures was studied in situ by means of a homemade testing chamber fitted to the tensile analyzer. It is the aim that, based on the obtained results, a first general picture of the relationships between factors affecting mechanical performance of SPEEK and BPO_4/SPEEK membranes can be drawn.

BACKGROUND

PEEK is a semicrystalline thermoplastic widely used as a high-performance material. Attractive characteristics include good abrasion resistance, low water absorption, good impact strength, and resistance to hydrolysis, wear, radiation, and high-temperature steam. It has a high glass transition temperature, T_g, of about 143°C, as well as an elevated melting temperature, T_m, in the range of 330 to 350°C. The crystallinity of PEEK varies from zero (amorphous) to around 50% depending on the thermal history and the conditions of crystallization.[18]

Mechanical properties of PEEK and its composites have been extensively investigated during the past two decades, evidencing the influence of structural parameters on mechanical behavior. Crystallinity has been considered the major factor affecting the mechanical response of the virgin material. However, morphology studies performed by differential scan-

ning calorimetry (DSC), infrared spectroscopy, wide-angle X-ray diffraction (WAXD), and electron microscopy have shown that the microstructure and, thus, the mechanical performances displayed by PEEK specimen, is complex and strongly dependent on the thermal history experienced by the samples. In fact, samples presenting the same crystallinity ratio but having experienced different thermal treatments exhibit different mechanical properties.[19] Moreover, it has been observed that the tensile behavior of PEEK depends not only on the original morphology but also on both the test temperature and the strain rate.[19–24]

PEEK is soluble in concentrated sulfuric acid, which causes the sulfonation of some of the phenyl groups. Several authors have studied the effects of sulfonation on the structure of PEEK.[7,10,12,15–17,25,26] It has been reported that the sulfonation degree (i.e., the number of sulfonic acid groups per repeat unit) can be controlled by reaction time, acid concentration, and temperature, which can provide a sulfonation range of 30–100% per repeat unit without chemical degradation or crosslinking reactions. In addition, it has been observed that SPEEK is heterogeneous with respect to the degree of sulfonation of individual repeating units. X-ray diffraction studies have shown that sulfonation strongly decreases the crystallinity of PEEK, even when the degree of sulfonation is quite low.[25] Introduction of $-SO_3H$ groups into the polymer alters the chain conformation and packing and thus causes loss of crystallinity. Furthermore, the T_g of SPEEK increases monotonically with the degree of sulfonation, because of the amplified molecular interaction by hydrogen bonding of $-SO_3H$ groups and the augmentation of the molecular bulkiness as well. Thermal stability of the highly heat-resistant PEEK is also affected. The main chain decomposition of PEEK occurs in one step at about 600°C. From thermogravimetric analysis it was found that the weight loss temperature of SPEEK drops and broadens with increasing sulfonation levels in comparison with the virgin material. The decomposition temperature of SPEEK is situated in the region of 250–300°C.[7,10,12,17,25]

Conversely to PEEK, the presence of sulfonic side groups causes SPEEK to be a hygroscopic material and enhances its solubility. Samples with a medium degree of sulfonation (above 30%) are soluble in hot dimethylformamide (DMF), dimethylacetamide (DMAc), and dimethylsulfoxide. Above 40% they are soluble in the same solvents at room temperature; the highly sulfonated polymer (above 70%) is soluble in methanol, and above 90% it becomes water soluble.[17,25]

On the other hand, characterization studies of BPO_4/SPEEK composite membranes have shown that, in general, the T_g of the membranes increased with the BPO_4 contents.[16] For example, the T_g value ranged from 210 °C for the pure matrix to 221 °C for the 60 wt % BPO_4/SPEEK membrane with a DS of 75%. These results may reflect a reduction in chain mobility caused by the presence of the solid particles. The images obtained by scanning electron microscopy (SEM) of the composite membranes evidenced that the solid filler was uniformly dispersed throughout the polymeric matrix.[16,17]

In view of the information presented above, it can be concluded that the mechanical response of SPEEK membranes is expected to be very different from that of the virgin PEEK due to the morphological modifications and the hydrophilic properties generated by sulfonation. In the same way, the addition of solid fillers to the polymeric matrix alters even more the mechanical behavior of the membranes. Thus, for comparison purposes, this study deals with SPEEK and BPO_4/SPEEK samples, and PEEK results are only presented for giving an overall idea of the extent of the changes induced.

TABLE II
Description of the Testing Samples

Degree of sulfonation (%)	Sulfonation time (h)	BPO_4/SPEEK ratio
63	96	15 : 85
		30 : 70
		50 : 50
		Blank (pure SPEEK)
69	65	15 : 85
		30 : 70
		50 : 50
		Blank (pure SPEEK)
83	140	15 : 85
		30 : 70
		50 : 50
		Blank (pure SPEEK)

EXPERIMENTAL

Materials

PEEK sheets were pressed from commercial powder (Victrex grade 450P). The dry material was then compression-molded between electrically heated ferrotype platens at 390°C under 10,000 ton for 10 min in a Carver Laboratory hot press. Afterward, air bubbles were removed by compression and release cycles. Cold water was used to cool the platens while maintaining full holding pressure and the mold was removed once the temperature had fallen below 20 °C. The films were 100–300 μm thick and only clear and smooth areas were used in subsequent tests.

SPEEK and SPEEK/BPO_4 composite membranes used in this study were prepared following the procedure reported in the Appendix. Table II shows the species selected for investigating the effect of the de-

gree of sulfonation and the filler-to-matrix ratio on the mechanical performance of the membranes. The membrane sheets (70–200 μm thick) were stored in plastic sealed bags. Before use, the test specimens were cut from the sheets and conditioned for 4 to 5 days in the oven at a temperature of 60–80°C under vacuum. The samples were then removed from the oven and kept in a desiccator at room temperature.

Crystallinity measurements

The crystalline fraction of PEEK membranes was measured by thermal analysis using a DSC Q1000 apparatus from TA Instruments operating at a heating rate of 20°C/min (130 J/g heat of fusion was assumed for the perfect crystal phase[18]). Samples weighing approximately 7 to 10 mg were tested under nitrogen atmosphere. The temperature and heat-flow were calibrated with pure standards of indium and zinc.

SPEEK membranes were analyzed by wide angle X-ray diffraction (WAXD). Measurements were performed with a Siemens/Bruker X-ray diffraction instrument using copper radiation. The apparatus consists of a Kristalloflex 760 generator, 3-circle goniometer, and Hi-Star bidimensional detector. The films were reduced to powder using a SPEX Certiprep 5100 Mill. The specimens were embrittled by immersion in liquid nitrogen and then impact-ground in a stainless-steel vial set, which was continuously chilled with liquid nitrogen. The resulting powder was encapsulated in 1-mm-diameter glass capillaries and analyzed at different temperatures by means of a heating plate.

Uniaxial tensile tests

Uniaxial tensile tests were carried out using an Instron 8821S servohydraulic test machine equipped with specially designed testing accessories and a static load cell of suitable capacity. To measure the tensile properties of the membranes while immersed in water, a homemade assembly consisting of a testing chamber and tensile grips was fitted for the Instron machine [see Fig. (1a)]. The testing chamber allows the recirculation of the liquid when coupled with a circulator bath, so that experiments can be carried out under several constant temperature conditions. Another important feature is that it was built in transparent Plexiglas, which provides a full view of the inside and permits the use of an optical extensometer with no negative effects on the accuracy of the measurements.

The experiments were divided into two parts depending on the moisture conditions. In the first part, tests were performed in air at 23°C and 30% RH. In the second part, the films were stretched while immersed in water at 23 and 40°C. All sets of experiments were carried out at a constant crosshead speed of 5 mm/min on dog-bone-shape specimens with the dimensions indicated in Figure 1(b). Load cells of 100*N* and 1 kN were used to match the loading requirements of the specimens to ensure accuracy and sensitivity: the former was used for SPEEK and composite membranes and the latter for tougher PEEK specimens. Specimen extension was followed through an optical extensometer (Instron Non-Contacting Type 3 Video Extensometer) with a field view of 50 mm. The gauge length (i.e., the distance between two marks on the specimen) was set at approximately 20% of the field of view.

Prior to testing, each specimen was left for 5 min in the testing environment once it had been attached to the grips. An exception was made when testing the samples in warm water. Membranes markedly swell when they come in contact with warm water and this dimensional change damages the already clamped specimen, causing jaw breaks at the very beginning of the test. Consequently, the specimens in this case were soaked in water at the testing temperature for 5 min in a separate container and then clamped and tested within few minutes. It must be noted that the water absorption rates of SPEEK and BPO_4/SPEEK composite membranes were not measured in this study.

The following parameters were assessed during the experiments: the apparent elastic modulus E, the yield stress σ_y, the yield strain ε_y, the stress at break σ_b, and the strain at break ε_b. The load-elongation curves obtained experimentally were converted into engineering stress–strain plots. The apparent tensile modulus, E, was computed as the ratio of stress and strain in the initial slope of the stress–strain plot. Since some curves did not have a well-defined linear region, the secant modulus (which is the slope of the line that extends from the origin and intersects the curve at a given elongation) at 1% strain ($\varepsilon = 0.01$) had to be calculated. Velocity of elongation (crosshead speed), v, and initial sample length (gauge length) were used to estimate the strain rate, $\dot{\varepsilon}$. Stress versus strain curves were used to determine yield stresses and strains (σ_y, ε_y), as well as stresses and strains at break (σ_b, ε_b).

Five replicates were run for each set of experiments and only the mean values are reported here. Calculations of average percent standard deviation for each parameter yielded the following results: 16% for the modulus, 8% for the yield strain, 7% for the yield stress, 22% for the strain at break, and 12% for the stress at break. It must be kept in mind that reported curves illustrate the overall behavior observed and, consequently, some discrepancy might be found between results shown in figures and the average values summarized in tables.

RESULTS AND DISCUSSION

Crystallinity measurements

The DSC curves of the initial PEEK samples exhibited a single broad endothermic peak with a peak melting

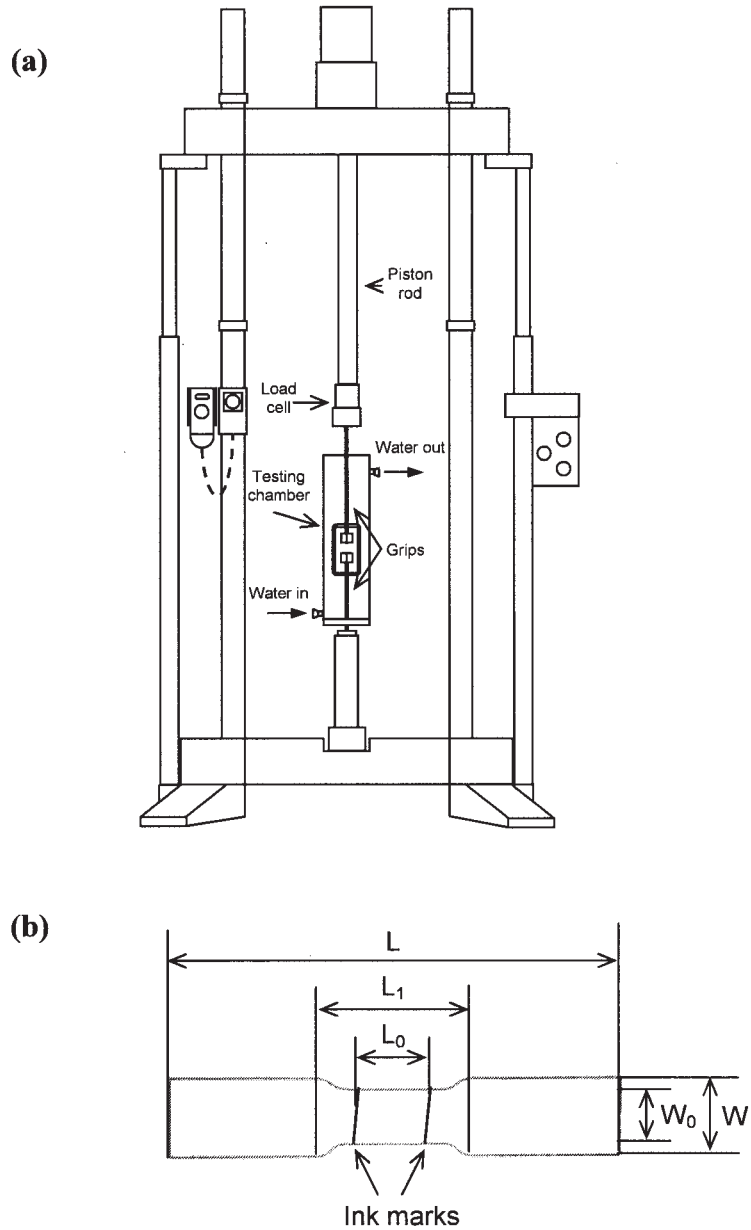

Figure 1 (a) Instron tensile analyser with testing accessories. (b) Tensile test specimen dimensions (in mm): overall length (L) = 60; length of calibrated section (L_1) = 20; gauge length (L_0) = 10; width of narrow section (W_0) = 7; overall width (W) = 10.

temperature of 338°C, from which a degree of crystallinity of about 28% was calculated. In contrast, the WAXD patterns of translucent SPEEK samples showed merely an amorphous halo. The composite membranes were not subjected to crystallinity studies.

Mechanical testing

SPEEK membranes

Table III summarizes the results obtained during the mechanical characterization of SPEEK membranes. Stress–strain behavior at room temperature and 30% RH is illustrated in Figure 2. PEEK specimens exhibit a rather brittle behavior, whereas SPEEK films display a ductile behavior characterized by a yield point followed by neck formation. This difference is basically explained by the fact that the sulfonated polymer was amorphous, while the virgin polymer specimens used in this study were semicrystalline. PEEK specimens withstood a stress of over 90 MPa before breaking at a low strain level of about 6% without necking. The brittle behavior of PEEK samples could be associated with the microstructural characteristics generated during film preparation conditions. Our previous re-

TABLE III
Effects of Degree of Sulfonation, Temperature, and Moisture Conditions on Mechanical Properties of SPEEK Membranes

DS (%)	Test temp (°C)	Moisture conditions	Modulus (MPa) (at 1%ε)	Yield strain (%)	Yield stress (MPa)	Break strain (%)	Break stress (MPa)
Pure PEEK	23	30% RH	3034	—	—	6	94.2
	23	30% RH	2404	5	62	50	51.5
63		In water	716	3	15.1	60	16.6
	40	In water	607	3	10.4	130	17.4
	23	30% RH	2258	6	61.9	90	55.8
69		In water	781	3	14.4	120	23.6
	40	In water	449	3	8.5	180	19.5
	23	30% RH	2599	5	66.8	80	59.2
83		In water	607	2	9.2	140	19.9
	40	In water	144	4	3.9	200	11.3

sults[27] suggest that, in the semicrystalline structure that develops when cooling from the melt, most of the amorphous regions are highly constrained between the crystallites, which act as crosslinking sites that pin the chains and cause failure shortly after yield.

In contrast, SPEEK samples display a sharp yield point. The yield stress for the three samples shows little variation despite the difference in the degree of sulfonation, whereas the peak width somewhat broadens with increasing DS. After the stress drop, a neck forms and runs completely to the grips. For 63% DS samples drawing happens almost at constant stress, while 83% DS samples strain harden before failing; 69%DS films have an intermediate behavior. Even if the strain at break is strongly influenced by sample defects, there is a tendency to increase as a function of DS, from 57 to 90% for 63% and 83% DS, respectively, most likely because chain packing decreases, facilitating orientation of the amorphous structure and chain slippage. In addition, ambient moisture may act as a plasticizing agent in the hydrophilic SPEEK membranes.

As plotted in Figure 3, the modulus of the sulfonated polymer decreases with respect to that of the virgin polymer, showing an average reduction of 20%: there is not a clear tendency in modulus variation as a function of the sulfonation degree. The origin of these irregularities might be attributed to the preparation conditions of the samples. Figure 3 also shows the dramatic effects of moisture and temperature on the modulus of SPEEK membranes. When tested in water at 23 °C, a reduction of approximately 70% is observed in comparison with the values obtained at 30% RH and the same temperature conditions. An increase of

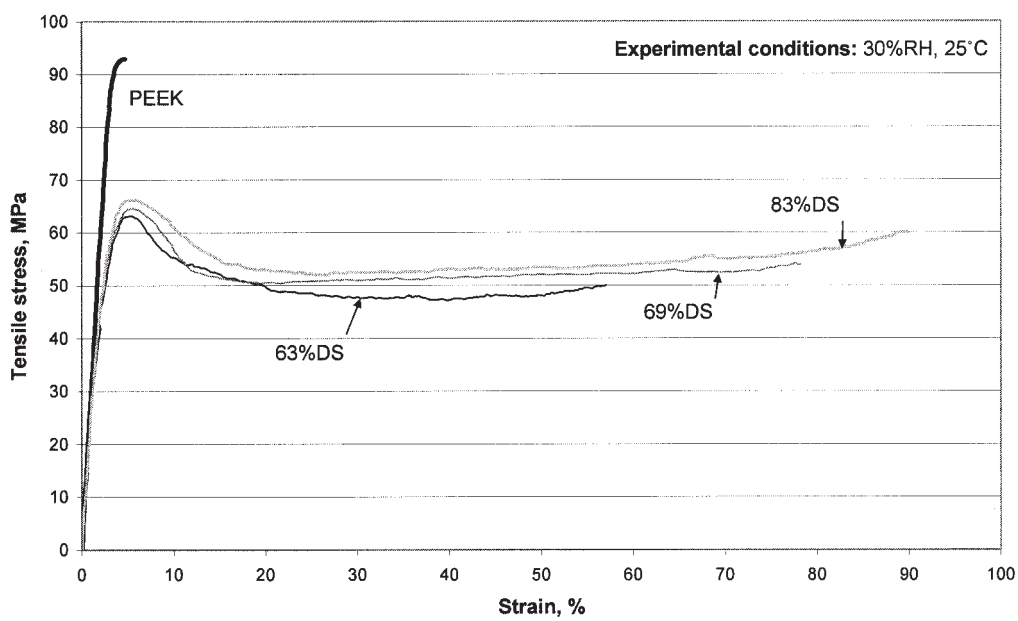

Figure 2 Stress–strain curves of PEEK and SPEEK films tested at 30% RH and 23 °C, illustrating the effect of DS on the tensile properties.

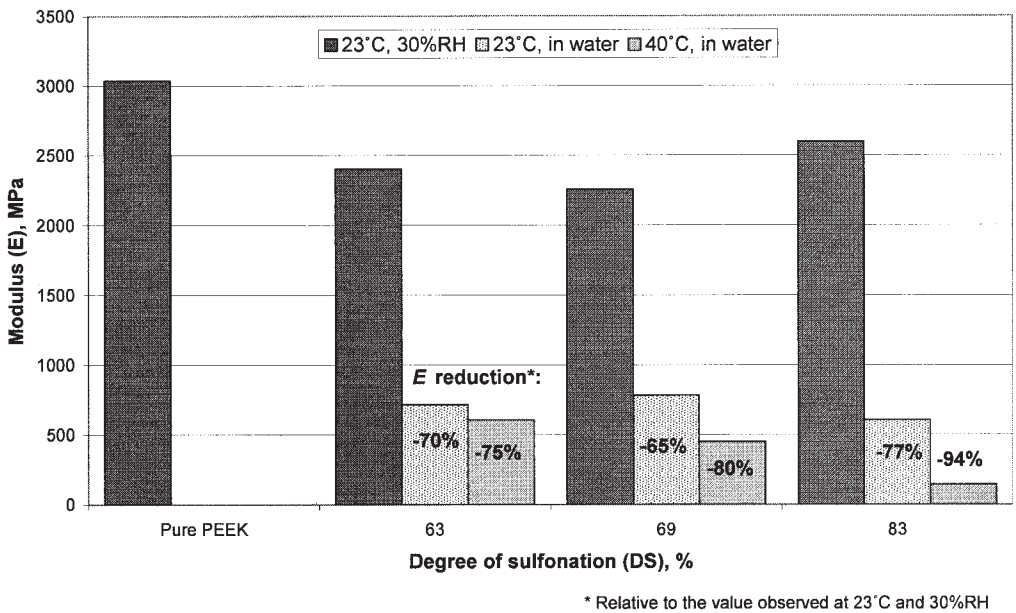

Figure 3 Tensile modulus of SPEEK membranes tested under different temperature and humidity conditions. Percentages in black indicate the modulus reduction relative to the values obtained at 23°C and 30% RH.

17°C in the temperature of water caused an additional modulus drop, in such a way that membranes lost 75 to 94% of their original stiffness depending on their degree of sulfonation.

Curves presented in Figure 2 may be used as rough indicators of the effect of sulfonation on the entanglement network structure of PEEK. The introduction of $-SO_3H$ groups increases chain bulkiness and hinders the entanglement formation. A reduction in the number of entanglements represents lesser topological constraints relative to chain motion in the glassy state. As a result, chains are more easily oriented in the stretching direction with increasing DS, resulting in upper strain hardening levels and higher breaking strain values at the failure point. Moreover, sulfonic groups may enhance chain stiffness and promote the creation of hydrogen bonds; these factors would be at the origin of the greater stress for yield required by 83% DS SPEEK samples compared to those with lower DS.

Figure 4 shows typical results of the tests performed under various moisture and temperature conditions for 69% DS SPEEK samples. These data illustrate the general trends also observed for the 63 and 83% DS SPEEK samples.

When SPEEK specimens are exposed to water at room temperature, the amorphous structure absorbs the liquid and swells. Solvent molecules plasticize polymeric chains, increasing their segmental mobility and affecting drastically their mechanical response, as reported in Table III. All the tensile parameters are very sensitive to the mobility of the chains (see Figs. 3 and 4). The modulus and the stresses associated with yield and neck propagation in the plasticized films are strikingly reduced with respect to the dry membranes. Furthermore, the enhanced chain orientation and slippage cause strain hardening and increase the strain at break.

It is well known that the incorporation of a plasticizer into a polymer disrupts the intermolecular forces between the macromolecules. Penetration of the amorphous regions occurs via the breakdown of intermolecular bonds and such an effect causes the glass transition temperature to be depressed. The glass transition temperature of the system, T_g, can be estimated by the Fox equation:[28]

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}. \quad (1)$$

A and B indicate the polymer and the plasticizer, respectively. T_g is the glass transition and W is the weight fraction of the components.

The T_g of SPEEK specimens is located at about 220°C (493 K),[12] while the approximate value for water is 141 K. Using these data and an average value of 20 wt % estimated from the solvent uptake measurements of water in SPEEK reported in Ref. 12 gives a T_g of around 56°C for the water/SPEEK system. This result suggests that the experimental temperature of 23°C becomes closer to the T_g of the polymer; thus, the segmental mobility is highly increased as if the material were heated, shifting the drop in mechanical performance associated with the glass transition to lower temperature.

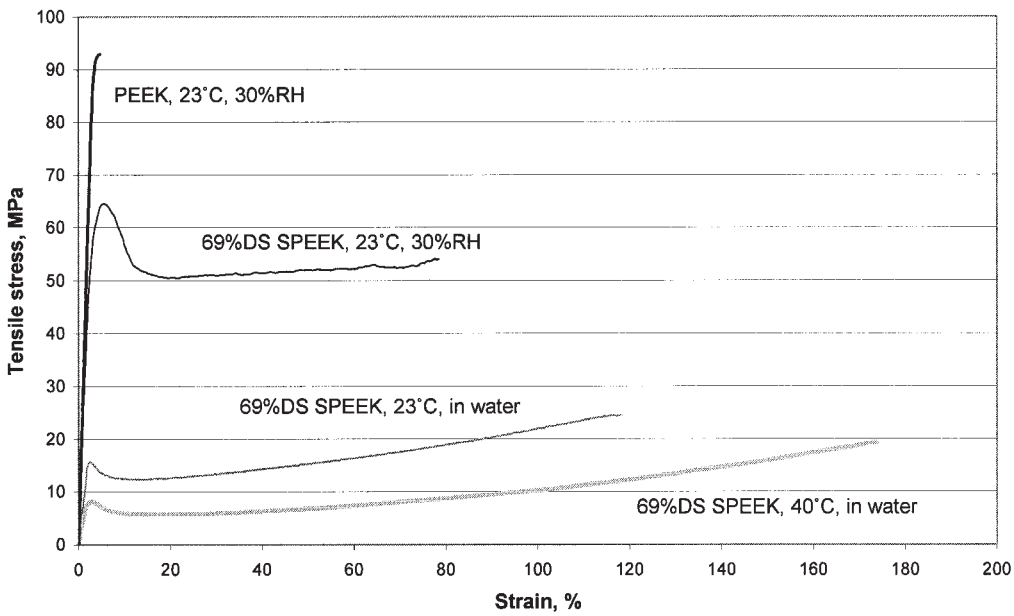

Figure 4 Stress–strain curves of PEEK and 69% DS SPEEK films, illustrating the effect of moisture and temperature on the tensile properties of the membranes. The testing conditions were as indicated.

Large-scale penetration and plasticization of the polymer is further enhanced by an actual increase of the temperature of the solvent, as occurs when the specimens are tested in water at 40 °C (see Figs. 3 and 4). The highly swollen structure displays rubbery behavior with very low values of modulus, a less pronounced yield point, and a substantial increase of the extensibility, reflected in the high strain-at-break values.

It should be mentioned that SPEEK membranes exposed to water become extremely deformed when dehydrated, indicating that the interactions between the polymeric structure and the solvent are strong. These observations confirm that solvent desorption causes chain orientation of SPEEK samples in the desorption direction, generating internal stresses in the structure that may influence material performance during operation.

BPO_4/SPEEK composite membranes

Tables IV to VI show the results of characterization of the composite membranes. Table V and Figure 5 evidence the effect of the incorporation of solid particles in the 69% DS SPEEK matrix. Tests carried out at room temperature and 30% RH indicate that the increase in filler concentration induces a transition from ductile to brittle behavior. The stress–strain trace for the unfilled matrix showed a sharp yield point and marked strain softening, followed by a lengthy plateau region char-

TABLE IV
Effects of Filler/Matrix Ratio, Temperature, and Moisture Conditions on Mechanical Properties of 63% DS SPEEK Membranes

BPO_4 : SPEEK ratio	Test temp (°C)	Moisture conditions	Modulus, MPa (at 1%ε)	Yield strain (%)	Yield stress (MPa)	Break strain (%)	Break stress (MPa)
Blank (63% DS SPEEK)	23	30%RH	2404	5	62	50	51.5
		In water	716	3	15.1	60	16.6
	40	In water	607	3	10.4	130	17.4
	23	30%RH	2600	—	—	8	64.41
15 : 85		In water	960	3	14.1	70	19.7
	40	In water	454	3	8.8	120	16.1
	23	30%RH	2624	—	—	8	56.6
30 : 70		In water	725	—	—	80	16.3
	40	In water	400	—	—	110	14
	23	30%RH	1887	—	—	3	32.8
50 : 50		In water	341	—	—	64	9.34
	40	In water	209	—	—	80	6.8

TABLE V
Effects of Filler/Matrix Ratio, Temperature, and Moisture Conditions on Mechanical Properties of 69% DS SPEEK Membranes

BPO_4 : SPEEK ratio	Test temp (°C)	Moisture conditions	Modulus (MPa) (at 1%ε)	Yield strain (%)	Yield stress (MPa)	Break strain (%)	Break stress (MPa)
Blank (69% DS SPEEK)	23	30% RH	2258	6	61.9	90	55.8
		In water	781	3	14.4	120	23.6
	40	In water	449	3	8.5	180	19.5
	23	30% RH	2020	6	51.1	31	45.8
15 : 85		In water	640	2	8.8	104	16.6
	40	In water	341	3	5.3	160	15.9
	23	30% RH	1518	—	—	8	35.5
30 : 70		In water	423	—	—	85	11.7
	40	In water	227	—	—	122	8.89
	23	30% RH	1800	—	—	4	24.8
50 : 50		In water	280	—	—	81	8.5
	40	In water	147	—	—	110	6.6

acterized by little strain hardening; specimen fracture occurred at approximately 80% strain and the breaking stress was lower than the yield stress. In comparison, the curve for 15 wt % filler exhibited a shallow yield point and cold-drawing with strain softening; the film formed a short neck that extended to about 30% strain and again the stress at break was situated below the stress at yield. The curve for 30 wt % filler displays an ill-defined yield point; the membrane was drawn to over 7% at constant stress before failure. Finally, the curve for 50 wt % filler showed brittle behavior with failure occurring at 2% strain. In all cases, these stress–strain curves show a downtrend in both yield and break stresses with growing filler concentration.

The response observed when the membranes were tested in water at 40°C is illustrated in Figure 6. The yield stresses are too much low by comparison to the values seen in Figure 5. However, similar effects are noted concerning the sharpness of the yield point, i.e., a gradual decline with increasing filler contents. Neck formation and strain hardening occur just above yielding. Moreover, breaking strain levels are quite elevated.

Figure 7 shows the changes generated by the filler concentration and the testing conditions in the modulus of the composite membranes. In general, the incorporation of the second phase deteriorates the initial modulus of the matrix. This reduction ranges from 11 to 33%, but the variation with the filler concentration remains ill defined. Similarly to SPEEK membranes, water and rising temperature have negative effects on the membrane resistance to stretching. In all cases, the gaps between the values observed at room temperature and 30% RH and those obtained in water at 23 and 40°C increase with higher filler loadings.

By adding solid particles to the polymer matrix, one might expect to obtain a high-performance material, but Figures 5 and 6 evidence that the toughness of the composite membranes is inversely proportional to the filler–matrix ratio. In the same way, it is clear that the filler does not reinforce the initial modulus of the

TABLE VI
Effects of Filler/Matrix Ratio, Temperature, and Moisture Conditions on Mechanical Properties of 83% DS SPEEK Membranes

BPO_4 : SPEEK ratio	Test temp (°C)	Moisture conditions	Modulus (MPa) (at 1%ε)	Yield strain (%)	Yield stress (MPa)	Break strain (%)	Break stress (MPa)
Blank (83% DS SPEEK)	23	30% RH	2599	5	66.8	75	59.2
		In water	607	2	9.2	140	19.9
	40	In water	144	4	3.9	200	11.3
	23	30% RH	2668	5	50.7	23	43.6
15 : 85		In water	646	2	8.7	140	20.6
	40	In water	240	3	4.6	150	9.8
	23	30% RH	2172	5	46.2	25	40.6
30 : 70		In water	465	2	6.1	120	14.6
	40	In water	223	3	4.2	170	11
	23	30% RH	1415.5	—	—	20	24.4
50 : 50		In water	—	—	—	120	8
	40	In water	105	—	—	150	4.6

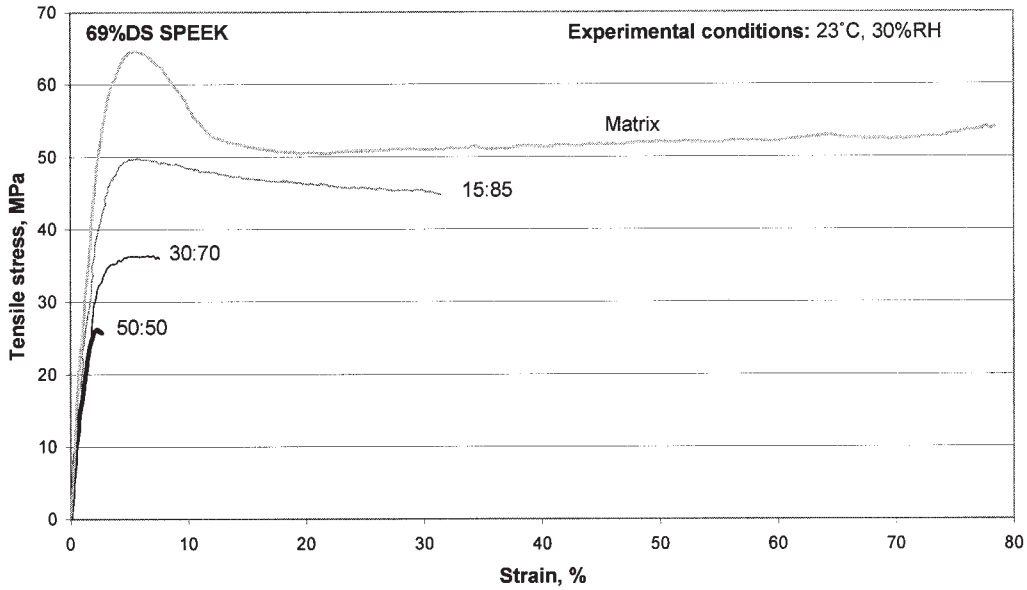

Figure 5 Stress–strain curves of BPO_4/SPEEK membranes, illustrating the effect of the filler to matrix ratio on the tensile properties of the membranes. Tests were performed at 23°C and 30% RH.

matrix, making the role of the second phase questionable.

Figure 8 illustrates the effects of moisture and temperature on the stress–strain response of 30 wt % filler composite membranes based on 69% DS SPEEK. These curves are in agreement with the information reported above relative to the plasticizing effects of water and rising temperature. Furthermore, these data indicate that the presence of solid filler does not preserve the mechanical stability of the material in the presence of moisture.

The low performance exhibited by the composite membranes might be due to poor or even nonexistent adhesion between the rigid particulate filler and the polymeric matrix. The stress is not transmitted to the filler by the polymer chains and, thus, the reinforcement effect is eliminated in the BPO_4/SPEEK composite membranes.

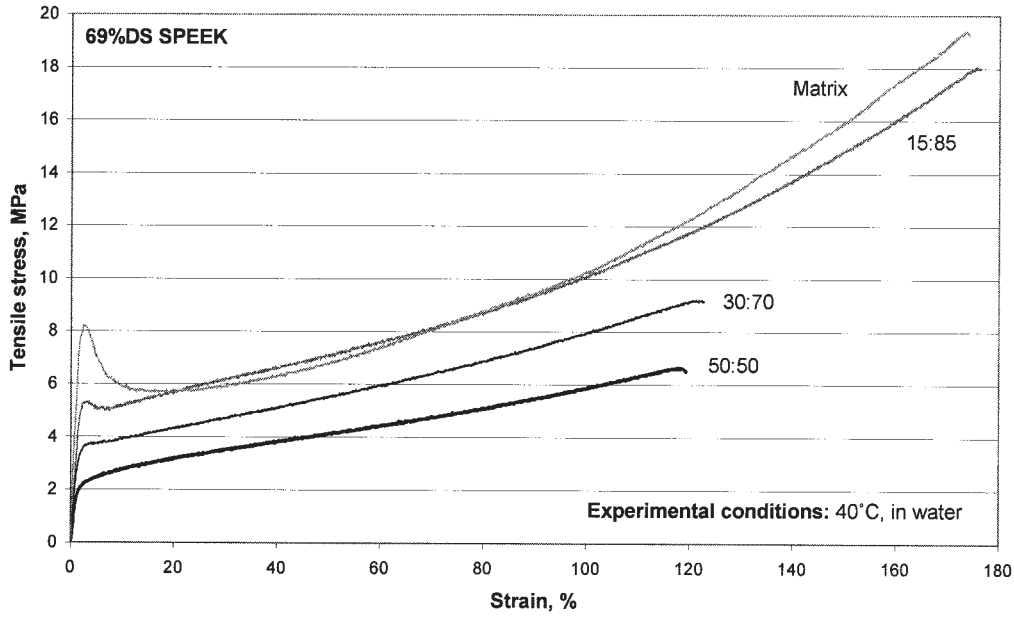

Figure 6 Stress–strain curves of BPO_4/SPEEK membranes, illustrating the effect of the filler to matrix ratio on the tensile properties of the membranes. Tests were performed in water at 40°C.

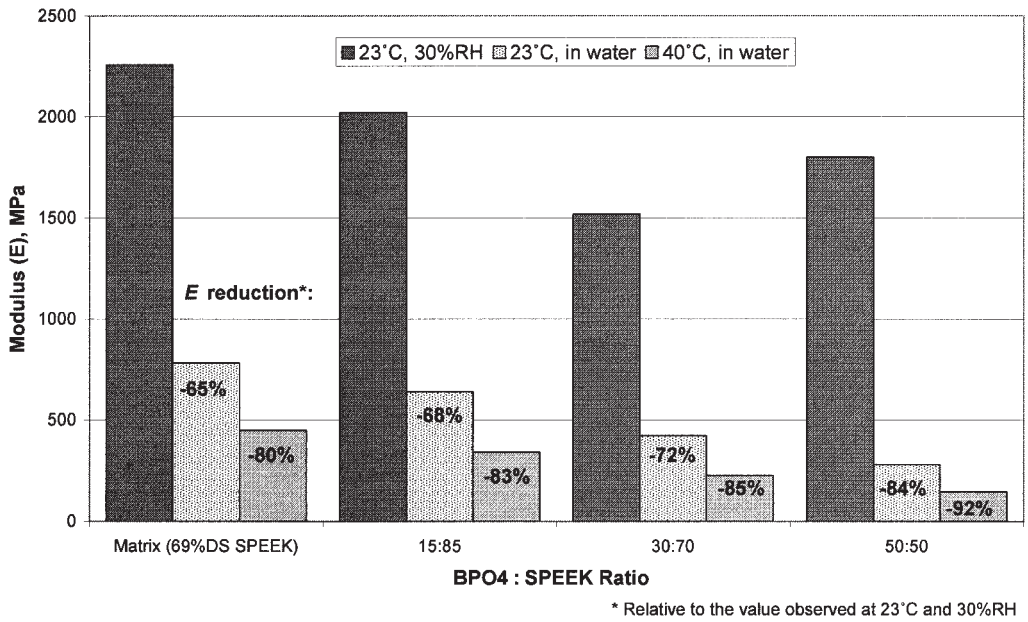

Figure 7 Tensile modulus of 69% DS SPEEK-based composite membranes tested under different temperature and humidity conditions. Percentages in black indicate the modulus reduction relative to the values obtained at 23°C and 30% RH.

The mechanical response exhibited by the membranes may be explained by the molecular inhomogeneities existing in their structure, which give rise to weak and strong regions.[29] The amorphous polymer matrix is thought to be significantly altered by the addition of rigid particles. Molecules surrounding the solid particle do not entangle with one another, thereby promoting the formation of weak points. In contrast, entanglements and chains oriented parallel to the stress direction located between the said weak domains act as strong points. On stretching, the weak regions are the first to break or pull apart to form many submicroscopic cracks and voids, while strong regions bear most of the load and become tight as they get oriented in the load direction. The balance between weak and strong regions, which determines the stress–strain behavior of the membranes, seems to be undermined by the solid filler. Debonded particles

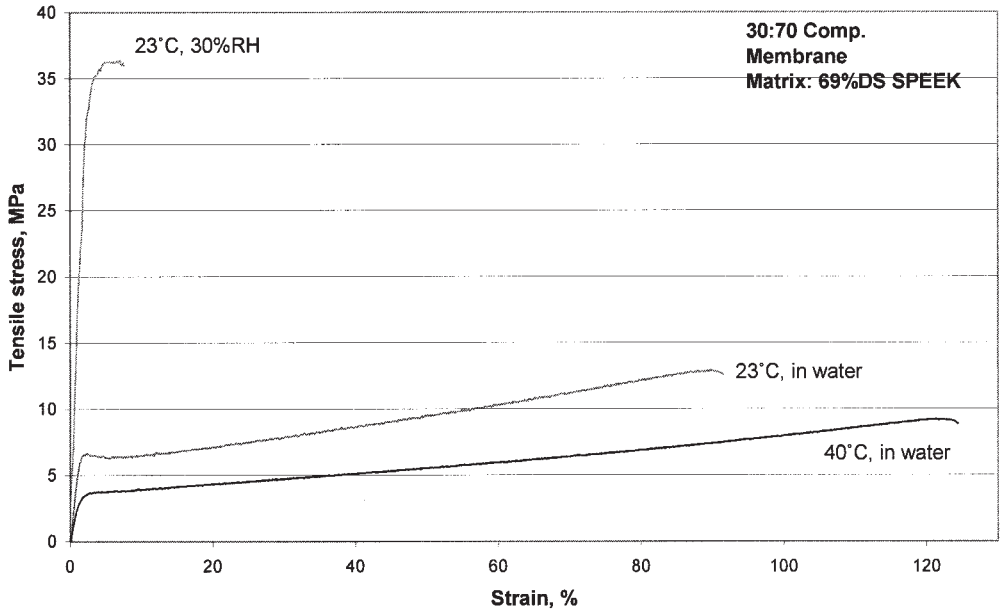

Figure 8 Stress–strain curves of BPO_4/SPEEK membranes, illustrating the effect of the temperature and the moisture conditions on the mechanical response of the 30 : 70 composite films.

TABLE VII
Composite-Membrane Weight Loss and Water pH Changes Caused by Membrane Immersion

DS (%)	BPO4/SPEEK ratio	w_0 (mg)	w_1 (mg) (after 24 h)	Average %w loss	pH_0	pH_1 (ca. 1 h later)	pH_2 (24 h later)
69	15 : 85	50.5	45.9	9	6	4–5	4
	30 : 70	48.1	41.8	13	6	4–5	4
	50 : 50	50.4	40.1	20	6	4–5	3–4
83	50 : 50	50.4	40.2	20	6	4–5	3–4

develop large interfacial voids that weaken the structure. Moreover, they act as physical constraints that prevent slippage in the chain orientation process, a mechanism necessary to relieve stress and delay rupture. Therefore, higher concentrations of filler mean more weak points and, accordingly, weaker tensile properties, as evidenced by results reported in Figure 5.

The decrease in the modulus and in the yield stress, as well as the long elongation at break observed when the membranes were tested in water, might arise from a strong interaction between the material and the solvent. First, solvent molecules penetrate more easily in the less entangled structure. Second, BPO_4 is a highly hygroscopic solid that improves water uptake and swelling.

It was also observed that specimens became opaque during stretching. In tensile testing, this "whitening" is caused by the formation of voids, which lead to major fluctuations in the refractive index in comparison with the bulk material and cause opaqueness due to the scattering of light.[30] This observation might suggest that the solid particles debond during deformation and dissolve in water.

With the aim of verifying this hypothesis, a number of specimens with different BPO_4 contents were dried, weighed, and immersed in deionized water. The acidity of the liquid was measured during the experiment. After 24 h, the membranes were dried and weighed again. It was found that membranes lost weight and that the water pH increased, implying that some of the inorganic acid had remained in the liquid. As reported in Table VII, the percentage weight loss increased with the filler-to-matrix ratio.

Consequently, the absence of rigid particles in the wet membranes may facilitate chain orientation and slippage, causing an increase in orientation hardening and in the elongation at break. The voids left by the particles collide during chain stretching and form longer cracks that result in fracture. Thus, the larger the number of voids, the sooner failure occurs. This would explain why membranes with higher initial filler loadings fail in first place.

Scanning electron micrographs of the composite membranes support the preceding discussion. The morphology of the tested specimens was frozen in liquid nitrogen and analyzed using a Jeol JSM-840A scanning microscope. The images shown in Figure 9 correspond to cross sections taken from the stretched regions near the fracture surfaces of 69% DS specimens, except for Figure 9(a), which pictures an undeformed specimen. The specimen tested in air at room temperature [Fig. 9(b)] shows no remarkable features. In contrast, membranes tested in water at room temperature and at 40°C (Fig. 9(c,d), respectively) exhibit an internal structure characterized by voids and increased roughness, suggesting that morphological changes occur more easily in the presence of water. Figure 9(e) is a zoom of a debonded particle observed in the specimen stretched in air.

In the particular case of BPO_4/SPEEK composite membranes, it would be very useful for design and material selection to model and predict the final mechanical properties. Nonetheless, this type of analysis was not feasible in the present study due to scatter in the experimental data and to the several factors affecting the structure of the composite.

On the other hand, although the analysis of the deformation and failure mechanisms of the PEM membranes is out of the scope of this work, some comments can be made on this subject. Naked-eye observations indicate that, during the uniaxial tensile deformation of PEEK films at room temperature, insignificant plastic flow resulted from low polymer chain mobility, as already discussed. Therefore, the nonoriented structure favored a brittle fracture.

The deformation of SPEEK and BPO_4/SPEEK membranes occurred by macroscopic plastic necking in all cases, and the failure mode was identified as crazing, characterized by banding perpendicular to the tensile axis and fibrillation in the edges. This mechanism was promoted by the presence of voids and defects, especially in the composite membranes. Indeed, defects incorporated in specimens during processing and/or use can act as critical flaws that cause or accelerate fracture.

Finally, the effects of thermal treatment previous to tensile testing were not explored in this work. It is known, however, that mechanical properties of polymeric materials are very sensitive to both the manufacturing method and the subsequent processing, in such a way that preparation and processing conditions largely determine the structural characteristics of the samples. SPEEK-based membranes are prepared by solution casting with solvent evaporation, as detailed in the Appendix. Our previous studies showed

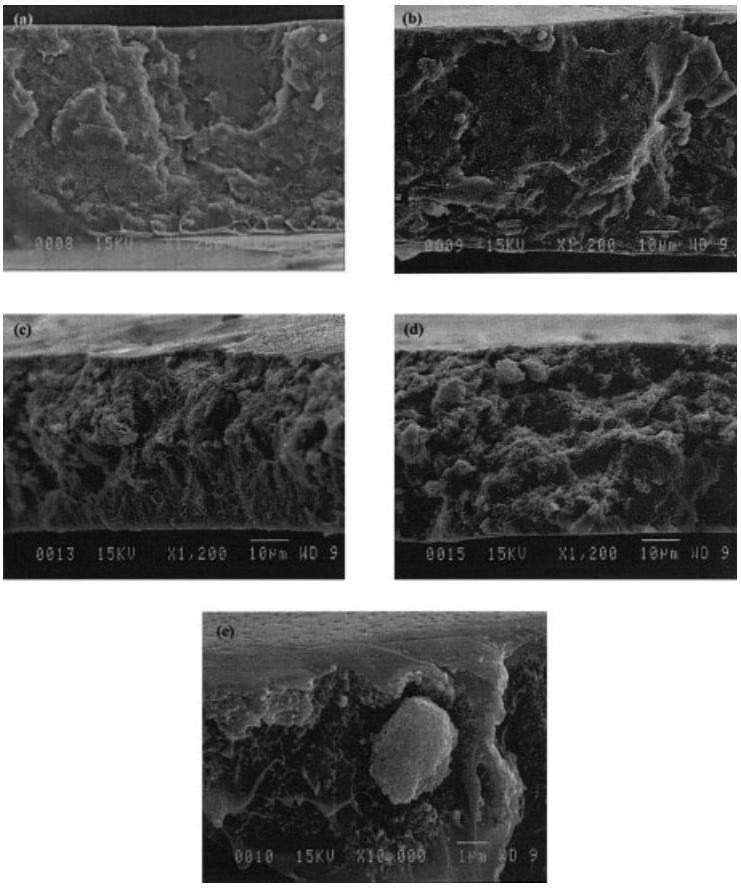

Figure 9 SEM pictures of 69% DS 30 : 70 BPO_4/SPEEK membranes: (a) unstretched, (b) tested in air at room temperature, (c) tested in water at room temperature, (d) tested in water at 40°C, (e) BPO_4 particle embedded in a specimen stretched in air.

that, in the drying step, solvent diffusion and evaporation lead to dissimilarities of thickness and molecular structural ordering between contiguous regions of the same film. These factors contribute to the development of residual stresses in the structure, which can only be released by heat treatment.

The structural features resulting from preparation as well as the effects of thermal treatment on SPEEK membranes were reported elsewhere.[27] Heating the membranes above the T_g leads to sulfonic-group decomposition at ~250°C, but thermal treatment at somewhat lower temperatures causes relaxation–orientation phenomena that certainly affect the mechanical response, at least at small deformations. The low degree of severity of this treatment is not likely to cause major changes in the structure that would have dramatic effects on tensile properties. Therefore, large-strain parameters such as tensile strength and elongation at break are not expected to reflect the rather minor microstructural changes generated by mild sample pretreatment.

CONCLUDING REMARKS

The tensile mechanical behavior of SPEEK and BPO_4/SPEEK membranes has been studied as a function of the degree of sulfonation and the filler–matrix ratio, respectively. The effects of moisture and temperature conditions have also been considered in an attempt to assess the mechanical performance of these materials under PEM fuel cell working conditions. This study gives an idea of the general mechanical behavior displayed by the membranes while tested at 30% RH and soaked in water at room temperature and at 40°C.

From the results reported above, it can be concluded that the membranes that showed the best performances are based on 69% DS SPEEK. As expected, the DS plays a major role in determining the mechanical properties of the membranes, which are severely affected by the coupling effects of water and temperature on chain mobility of the amorphous structure. Similar to the conductivity, the mechanical response is a complex property that depends on several interacting factors. Interaction of the polymer structure with solvent molecules is particularly important and should be the object of further studies focusing on chain orientation.

In addition, the presence of the BPO_4 solid filler in composite membranes has a detrimental effect on mechanical properties. Detailed morphological studies are required to understand the structure–property relationships of the composite system.

The trends observed in this study can be contradicted by differences in the preparation conditions and the quality of the specimens being compared. These data may, however, be useful in deciding on the applicability of the given materials.

APPENDIX

SPEEK and BPO_4/SPEEK membranes were prepared as reported in Ref. 17.

Sulfonation reaction

PEEK extruded pellets (from Victrex) were dried in a vacuum oven at 100 °C overnight. Then 25–35 g of polymer was dissolved in 400–500 mL of H_2SO_4 concentrated sulfuric acid under vigorous stirring for the desired time ranging from 48 to 230 h at room temperature. In some cases the temperature was increased up to 50–90 °C and the reaction time decreased to several hours. Then the polymer solution was gradually precipitated into a large volume of ice water under continuous mechanical agitation. The precipitate was collected by filtration and washed several times until the washing water became neutral. The product was dried at 30–50 °C under vacuum for 2 or 3 days. The degree of sulfonation was determined by titration: 1–2 g of polymer was immersed in 20 mL NaOH (0.5*M*) solution with occasional agitation for 1 day and then titrated with 0.5*M* HCl to the phenolphthalein endpoint. After titration, the membranes were rinsed with distilled water and dried under vacuum at 80 °C to constant weight.

Membranes preparation

The dry sulfonated polymer was dissolved (5–10%) in DMAc or DMF and cast onto a glass plate. The membranes were dried at room temperature for 1 day and then gradually heated under vacuum from 25 to 120 °C within 8 h and finally kept at 120 °C for 2 days.

The BPO_4 was ground and sieved through a 60-mesh sieve. Then, the powder was dried to remove any moisture and avoid precipitation in the polymer solution. The pure polymer SPEEK solution and inorganic solid powder BPO_4 suspension were prepared separately in DMF solvent. The SPEEK polymer was first dissolved in DMF to form a 5–10% solution and then the BPO_4 suspension was added to the polymer solution. The resulting mass was stirred for 24 h and heated gradually up to 100 °C. When the mixture became homogeneous, a certain amount of the solvent was evaporated; the suspension was cooled down to room temperature and subsequently outgassed under vacuum. The mixture solution was cast onto a glass plate. The cast membranes were first dried at room temperature overnight and then at 25–120 °C for 6 to 8 h and at 120 °C for 2 days.

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