

Development of Proton Conductive Polymer Electrolytes Composed of Sulfonated Poly(Ether Ether Ketone) and Brønsted Acidic Ionic Liquid (1-Methylimidazolium Tetrafluoroborate)

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Research Article

Keywords: Solid polymer electrolyte, PEEK, sPEEK, Ionic liquid, Proton conductivity.

Posted Date: February 22nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-200865/v1>

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Abstract

This article relates to the synthesis, characterization and dielectric measurements of solid polymer electrolytes, derived from the ionic interaction of sulfonated poly(ether ether ketone) (sPEEK) and a Brønsted acidic ionic liquid (1-methylimidazolium tetrafluoroborate, [Hmim][BF₄]), for electrochemical applications. The efficiency of the interaction was examined by incorporating different amounts of ionic liquid (IL) with the sulfonated polymer matrices having three different degrees of sulfonation (DS). The composite electrolytes were systematically characterized with FT-IR, SEM, TGA and DMA analysis. Anhydrous proton conductivity and dielectric measurements were studied in detail as a function of temperature. The presented analyzes revealed that sPEEK_{1,0}-2 sample ($2.50\text{--}3.51 \times 10^{-1} \text{ Sm}^{-1}$ at 380–450 K) exhibited maximum proton conductivity and thermomechanical stability under anhydrous environment. Furthermore, sPEEK_{1,0}-2 composite membrane exhibited higher glass transition temperature and reasonable storage modulus value ($T_g = 157 \text{ }^\circ\text{C}$; $E' = 0.22 \text{ GPa}$) compared to IL doped sPEEK membranes presented in the literature. The work herein opens new prospects for the as-synthesized materials to use as a solid polymer electrolyte for electrochemical applications such as high temperature proton exchange membrane fuel cells (HT-PEMFC) in a wide temperature range.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) have been received as the most attractive fuel cell type due to rapid start-up, high energy efficiency and environmentally friendly operation conditions (no waste other than pure water). A typical PEMFC consists of electrodes, diffusion layers and a polymeric membrane that provides proton transfer. In literature, extensive research has been conducted on the production of potential membrane materials to improve proton transfer and cell performance [1–3]. Nafion® is the widely used commercial membrane in PEMFCs due to its high mechanical/chemical resistance and high ionic conductivity. The commercial Nafion® membrane shows high cell performance at low operating temperatures (60–80 °C) when fully saturated in water. On the other hand, it also struggles with problems as follows: the control of water saturation and humidity, the tendency of catalyst poisoning and high-pure hydrogen requirement, which are attributed to lower proton conductivity, lower performance and higher cost, respectively [4]. To improve these drawbacks for high-performance PEMFCs, research has been converged to develop alternative membranes with good conductivity in anhydrous conditions (above 100 °C) resulting in the elimination of water saturation/humidity management [5–7]. For this purpose, studies have primarily focused on the modification of commercially available membranes to enhance the water retention capacity of these membranes [8–11]. However, recently many studies have been carried out to develop polymeric membranes which can also maintain high proton conductivity, high chemical/thermal resistance, and electrochemical stability in anhydrous conditions. These studies targeting the development of high temperature PEMFC (HT-PEMFC) membranes are mainly based on three main approaches: i) modification of commonly used perfluoro sulfonic acid (PFSA) membranes with inorganic proton conductive materials [12, 13], ii) production of poly(ether ether ketone) (PEEK), polysulfone (PS), polybenzimidazole (PBI) etc. based polyaromatic and

sulfonated polyaromatic composite membranes [14–17], iii) production of acid-base interactive polymer membranes, such as phosphoric acid-doped PBI [18–21].

Ionic liquids (ILs) are ionic salts that have been commonly used for organic synthesis, separation processes, polymerization, and electrochemistry applications due to their high boiling temperatures (above 100 °C). In recent years, their superior characteristics such as ionic conductivity and good thermal stability have been gained attention to utilize them in electrochemical applications. While imidazole and pyridine groups are commonly known as cation, ILs containing tetrafluoroborate (BF_4^-), acetate (Ac^-), hexafluorophosphate (PF_6^-), trifluoromethanesulfonate (CF_3SO_3^-) as anion groups can be prepared depending on the desired application area [22, 23]. In literature, the usage of ILs in electrochemical devices such as dye sensitive solar cells [24], super capacitors [25], lithium batteries [26], electrochemical sensors [27] and the fuel cells [28, 29] have been extensively investigated. Approaches to the usage of ILs in the development of membrane electrolytes in fuel cells are also diversified in the literature as processes i) where ILs are used directly as electrolytes [30], ii) using membrane electrolytes obtained by the addition of ILs to the polymer backbone [31], iii) using functional polymer electrolytes obtained by polymerization of IL-soluble monomers [32] and iv) using electrolytes obtained by the polymerization of polymerizable ILs [33].

Recently, polymer materials such as poly(arylene ether ketone) (PAEK), polysulfone (PS), polyimide (PI), polybenzimidazole (PBI) and poly(ether ether ketone) (PEEK) have been presented as promising membrane materials for electrochemical applications due to their superior chemical/thermal strength and easy processability. Among aromatic hydrocarbon-based polymer electrolytes, PEEK has been reported as good membrane candidate in fuel cell applications due to its satisfactory conductivity, mechanical/chemical stability, and durability [34]. The properties of the PEEK polymer should be improved by various copolymerization processes or functional group additions to apply in PEMFC applications in terms of wide temperature range. One of the advantageous strategies is to sulfonate PEEK structure (sPEEK) for efficient membrane material [35–37]. In our previously published work, the effects of sulfonation degree on proton conductivity in standard fuel cell applications (60–80 °C) were investigated [38].

Herein, sPEEK/IL composite membranes with different degrees of sulfonation (DS) were prepared as polymer electrolyte with high ionic conductivity and thermal/mechanical stability for HT-PEMFCs. The synthesis was driven by the ionic interaction between the sulfone groups formed in the polymer chain by the sulfonation and the cations in the IL structure (1-methylimidazolium tetrafluoroborate, $[\text{Hmim}][\text{BF}_4]$). The composite membranes (sPEEK/ $[\text{Hmim}][\text{BF}_4]$) were diversified depending on the amount of IL. The structures of the sPEEKs, IL and sPEEK/ $[\text{Hmim}][\text{BF}_4]$ composite membranes were analyzed by FT-IR analysis. Thermal and mechanical properties of sPEEKs and composite membranes were investigated by TGA and DMA analysis, respectively. The proton conductivity and dielectric measurements of the composite membranes were determined and the effect of DS and IL addition on the proton conductivity and thermal/mechanical properties were discussed.

2. Experimental Details

2.1. Materials

Poly(ether ether ketone) (PEEK) was obtained from Röchling Sustaplast SE & Co.Kg. PEEK was dried at 65 °C for 24 hours before use. Sulfuric acid (H₂SO₄, 95–97%), sodium hydroxide (NaOH, ACS reagent, ≥ 97.0%, pellets) and sodium chloride (NaCl, BioXtra, ≥ 99.5%) were purchased from Merck and used as received. 1-methylimidazole (C₄H₆N₂, 99%), tetrafluoroboric acid solution (48wt.% in H₂O) and N,N-dimethylformamide (DMF, anhydrous, 99.8%) were also supplied from Aldrich and were not treated.

2.2. Preparation of sulfonated poly(ether ether ketone) (sPEEK)

Sulfonated polymer matrices were synthesized according to the procedure given in our previously published work [38]. Primarily, 1 g of dried PEEK was dissolved in 10 mL of H₂SO₄. The suspension was then subjected to sulfonation at 60 °C for 80 min. The resulting solution, which was a dark red viscous solution, was slowly dropped to a 1 L distilled water/ice mixture to remove the heat and terminate the reaction. The final product was washed with distilled water to pH 5–6, and subsequently dried at 65 °C for 48 hours. The resultant sulfonated polymer was coded as sPEEK-1. In order to determine the effect of the sulfonation time, the same procedure was used to sPEEK-2 and sPEEK-3, which were assigned to 120 and 180 min, respectively.

2.3. Preparation of IL (1-methylimidazolium tetrafluoroborate, [Hmim][BF₄])

1-Methylimidazole (7.5 g, 92 mmol) was placed in a cold-water bath (0–2 °C) and tetrafluoroboric acid (12.29 ml, 92 mmol, 50% solution in water) solution was added dropwise (over 30 minutes) under vigorous stirring. The mixture was then further stirred for 2 hours. In the rotary evaporator, the aqueous solution was removed in vacuum (60–70 °C) to obtain the ionic liquid (yield: 98.7%, elemental analyses, wt; theoretical: C%: 32.82, H%: 4.42, N%: 16.31, experimental: C%: 32.73, H%: 4.31, N%: 16.30) [39].

2.4. Preparation of composite membranes (sPEEK_n-(1–3))

IL doped sPEEK composites were prepared with solution casting method. A certain amount of sPEEK was firstly dissolved in DMF and the solution was stirred for 2 hours. The required amount of IL was added to the polymer solution and mixed at room temperature for 4 h. Then, the as-obtained mixtures were poured into glass petri dishes for 48 hours at 40 °C to remove solvent. The prepared membrane material was coded sPEEK_n - (1–3), where n represents the mole ratio of HSO₃/imidazolium. In this study, two ratio values were set as 0.5 and 1. The composition of the as-obtained polymers and composite samples are presented in Table 1.

Table 1
sPEEK and sPEEK/[Hmim][BF₄] composite membranes, sulfonation times and their HSO₃/IL compositions.

Sample	t (Sulfonation time, min)	n (mol ratio, HSO ₃ /IL)
PEEK	-	-
sPEEK-1	60	-
sPEEK-2	120	-
sPEEK-3	180	-
sPEEK _{0.5} -1	60	0.5
sPEEK _{1.0} -1	60	1.0
sPEEK _{0.5} -2	120	0.5
sPEEK _{1.0} -2	120	1.0
sPEEK _{0.5} -3	180	0.5
sPEEK _{1.0} -3	180	1.0

2.5. Characterizations

The ion exchange capacity values (IEC) of the sulfonated polymer structures to be used as polymer matrices were calculated. For the determination of IEC, 0.1–0.2 g of dried sPEEK samples were left in 50 mL of saturated NaCl solution at 50 °C for 48 hours in order to allow the displacement of H⁺ and Na⁺ ions in the sulfonic acid groups. The solution was then titrated with 0.1 N NaOH to obtain the ion exchange capacity with the following equation, Eq. (1):

$$IEC = (V_{NaOH} \times N_{NaOH}) \div W_p \quad \text{Eq. (1)}$$

(V_{NaOH} = NaOH consumption, N_{NaOH} = NaOH normality, W_p = dry weight of membrane or polymer after ion exchange)

Degrees of sulfonation (DS) of the sulfonated polymers were also calculated by using the obtained IEC values by following formula, Eq. (2) [40]:

$$DS(\%) = [(288 \times IEC) \div (1000 - 103 \times IEC)] \times 100 \quad \text{Eq. (2)}$$

where 288 gmol⁻¹ is the mass of the unit of the initial polymer (PEEK), and 103 gmol⁻¹ is the molar mass of the SO₃Na group.

Fourier transform infrared spectroscopy (FT-IR) measurements were used to characterize the prepared IL, sulfonated polymers, and composite proton exchange membranes. The analysis was performed with the Perkin Elmer Spectrum 100 instrument containing the ATR unit, at a wavelength range of 650–4000 cm⁻¹ and at room temperature.

Scanning electron microscopy (SEM) analysis of the solid polymer electrolytes were obtained by Carl Zeiss 300VP system.

Thermogravimetric analysis (TGA) was performed to determine thermal behavior of sPEEK samples and the as-obtained composite membranes. The analysis was carried out with a SEIKO TG/DTA 6300 instrument in nitrogen flow, in the temperature range of 25–800 °C at a heating rate of 10 °C/min.

Dynamic mechanical analysis (DMA) tests were carried out to examine the mechanical properties of composite proton exchange membranes due to the addition of ionic liquids in a wide range of temperature and frequency ranges. The analysis was performed with the SEIKO DMS 6100 device at a heating rate of 2 °C/min and in tension mode.

Proton conductivity measurements were measured using Agilent 4284A LCR Meter system in the frequency range of 20 Hz to 1 MHz and in the temperature range of 380–450 K. Before the measurements, the membrane samples were cut to required dimensions and their surfaces were coated with silver paste to form electrodes. The proton conductivity values of all membranes produced in the study were calculated using the following formula:

$$\sigma \text{ (S/m)} = \omega \times C_p \times d \times \tan \delta / A \quad \text{Eq. (3)}$$

($\omega = 2\pi f$ = angular frequency, where f = frequency; C_p = capacitance of the sample; d = thickness of sample; $\tan \delta$ = dielectric loss factor; A = effective surface area of sample)

3. Results And Discussion

Sulfonation reactions were carried out at different reaction times (60, 120, 180 min) to produce three different polymer matrices with different DS. Sulfonation processes formed sulfonic acid groups in the PEEK polymer backbone. The effect of IL amount on proton conductivity and thermal/mechanical behavior was investigated by adding IL to the formed sulfonic acid groups in equimolar and doubling ($n = 1.0$ and 0.5). The basic idea in the use of sPEEK and IL is that the ionic interaction between the sulfone groups in the polymer matrix and the cation group imidazole in the IL structure improves proton conductivity. The ionic interaction between the sulfone groups and imidazole also prevents the migration of IL observed in blend membranes to which IL are doped [39].

After the sulfonation processes, IEC values were determined to calculate the DS of sPEEK materials depending on the way mentioned above. The relevant results are depicted in Table 2.

Table 2
Ion exchange capacity (IEC) and degree of sulfonation (DS) values of sPEEK samples [38].

Sample	t (Sulfonation time, min)	IEC (Ion exchange capacity, meq/g)	DS (Degree of sulfonation, %)
PEEK	-	-	-
sPEEK-1	60	1.00	32.10
sPEEK-2	120	1.72	60.20
sPEEK-3	180	2.19	81.44

As seen in the table, the IEC values of sPEEK-1, sPEEK-2 and sPEEK-3 polymer matrices were determined as 1.00, 1.72 and 2.19, respectively, indicating that the capacity enhanced with sulfonation time. The improvement in the IEC values resulted in increasing DS. The highest DS (81.44%) was achieved with the three-hour sulfonation process. That is to say, the amount of the sulfonic acid groups attached on PEEK backbone increased with longer reaction time [38].

3.1. Fourier transform infrared spectroscopy (FT-IR)

In order to confirm the chemical structures and functional groups of the as-obtained sPEEK, IL and sPEEK/IL composites, the samples were characterized by FT-IR spectroscopy and the spectrums are illustrated in Fig. 1a-b.

Figure 1a confirms the presence of sulfonic acid groups in the sulfonated polymers, resulting successful sulfonation process. The spectrums of sPEEK materials were observed a wide peak at 3400 cm^{-1} corresponding to the vibrations of O-H groups. This broad band of the sPEEK polymer matrix appearing at 3400 cm^{-1} could be assigned to O-H vibration from sulfonic acid groups interacting with molecular water. The peaks observed in the wavelengths at 1020 and 1312 cm^{-1} , reflecting the presence of S-O bonds in the structures. Besides, the signals at 1080 and 1218 cm^{-1} demonstrated the presence of S = O and O = S = O bonds. Additionally, the vibration detected at 1640 cm^{-1} was attributed to the presence of the carbonyl group present in all samples [41]. The active groups of the as-synthesized IL sample were depicted in Fig. 1b. The highest intensity was observed at 1048 cm^{-1} , indicating the stretching vibration of the BF_4^- anion in the IL structure. The peak at 840 cm^{-1} was assigned to the C-N stretching. Moreover, the peaks occurred at 2957 and 2880 cm^{-1} , which were attributed to the symmetric and asymmetric stresses of CH_3 , respectively. The characteristic peaks of C = N and C = C stretching modes were observed at 1590 and 1633 cm^{-1} , respectively. In addition, the peaks attributed to C-H plane bending and symmetric C-H stretching vibration were placed at 760 cm^{-1} and 3156 cm^{-1} [42, 43]. Then, as mentioned above sPEEK/[Hmim][BF_4] composite membranes of each polymer matrix were produced with different mole ratios of HSO_3 /imidazole ($n = 0.5$ and $n = 1.0$) depending on the purpose of the study. The formation of sPEEK/IL composite membrane was controlled with the FT-IR technique of sPEEK_{1.0}-1 and the

spectrum were given in Fig. 1 a. As seen in the figure, the peak observed at the wavelength of 3150 cm^{-1} was attributed to the amide groups of the imidazolium structure. Furthermore, the peak at about 2980 cm^{-1} indicated the presence of aliphatic methyl vibration of the [Hmim][BF₄]. The vibration at 1064 cm^{-1} evidenced the presence of the anion groups of IL (BF₄⁻). Additionally, the absorption bands at 1486, 1590 and 1640 cm^{-1} showed the presence of aromatic rings in the sPEEK structure. All results statements showed that sPEEK polymer matrices, IL, and sPEEK/[Hmim][BF₄] were successfully synthesized in this study.

3.2. Scanning electron microscopy (SEM) analysis

The morphological structures of sulfonated polymer matrix and composite polymer electrolytes formed with IL additive were performed by SEM analysis. In Fig. 2, cross-sectional micrographs of the sPEEK-2 polymer matrix and composite membranes prepared by SPEEK-2 (sPEEK_{1,0}-2 and sPEEK_{0,5}-2) are given.

As seen from Fig. 2a the honeycomb micro-voids were formed in the membrane cross section with sulfonic acid groups formed in the pure PEEK backbone with the sulfonation process. Chain mobility in the polymer backbone increases as the IL contribution increases (Fig. 2b-2c). Branched structures are more concentrated in IL-doped polymer electrolytes compared to sulphonated polymer matrix. This functional mobility also enabled the IL-doped membranes to be more flexible, soft and mobile. In addition to sulfonation, these increasing branching and mobility increase the distance between polymer chains, and thus the proton conductivity.

3.3. Thermogravimetric analysis (TGA)

One of the important criteria for polymeric membranes to be used in fuel cells is the thermal resistance. In addition, it has been desirable that the membranes produced in this study have high thermal resistance at high temperatures (above $100\text{ }^{\circ}\text{C}$). For that, TGA analysis of sPEEK polymer matrices and sPEEK/[Hmim][BF₄] composite membranes were performed in the temperature range of $25\text{--}800\text{ }^{\circ}\text{C}$ under the nitrogen atmosphere. Considering to sPEEK products, the TGA results are presented in Fig. 3 and Table 3.

As shown in Fig. 3, the pristine PEEK membrane showed the single polymer main chain degradation behavior, while the sulfonated membranes showed three degradation steps. In terms of the pure PEEK, the only thermal decomposition phase starting at $550\text{ }^{\circ}\text{C}$ was attributed to the degradation of the polymer master chain. In case of the sulfonated PEEK products, the initial weight loss was observed at about $100\text{ }^{\circ}\text{C}$ due to the evaporation of adsorbed moisture in the polymers. Moreover, the second weight loss zone of sPEEKs occurred in the temperature range of $150\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$, corresponding to the degradation of the sulfonic acid groups in the composite membrane structure. Additionally, the third weight loss starting at $450\text{ }^{\circ}\text{C}$ was assigned to the degradation of the PEEK polymer main chain. Notably, it can be said that the increase in the DS promoted the formation of different degradation phases and the initial temperature of the thermal decomposition phase where the second weight loss was seen decreases as the DS increased [41, 44].

5%, 10% and 50% weight loss of pure PEEK and sPEEK products were presented in Table 3.

Table 3
Thermal degradation values of pure PEEK and sulfonated PEEK polymer matrices (sPEEK-1,2,3).

Sample	T ₅ (°C)	T ₁₀ (°C)	T ₅₀ (°C)
PEEK	571	578.4	790.3
sPEEK-1	188.8	228.2	575.9
sPEEK-2	171.5	215.9	524.4
sPEEK-3	164.7	215.8	541.4

T₅: The temperature where 5 wt.% weight loss has occurred; T₁₀: The temperature where 10 wt.% weight loss has occurred; T₅₀: The temperature where 50 wt.% weight loss has occurred.

The weight loss of 5% in the pure polymer was observed at very high temperature values (above 570 °C). At the same time, 50% weight loss of the pure polymer was observed at about 800 °C. As the DS increased, the weight loss carried out at lower temperature values. The weight loss of the sPEEKs was close to the observed temperatures. The weight loss of 5% was recorded in the temperature range of 165–190 °C while the 50% weight loss was observed in the 540–580 °C temperature range for sPEEKs.

In terms of sPEEK/[Hmim][BF₄] composite membranes, the TGA spectrums are shown in Fig. 4. Obviously, more than one degradation step was observed in all membranes like the sulfonated polymer matrices.

The first degradation step starting at around 100 °C could be attributed to the deterioration of the moisture trapped on the membrane structures. Degradation steps starting at ~ 200 °C were attributed to sulfonic acid groups in composite membrane structures. Furthermore, the thermal stabilities of IL doped composite membranes prepared from sPEEK-1 product (sPEEK_{0.5}-1 and sPEEK_{1.0}-1), which have the lowest DS values, were higher than that of other membranes. It can be therefore indicated that the increase in sulfonic acid groups and DS in membranes reduced the thermal resistance of the membranes. Regarding the effect of IL amounts, it was observed that the addition of the excess amount IL decreased thermal strength. This could be due to the IL residues which remained without binding to the sulfone groups. In Table 4, 10% and 50% weight loss of sPEEK/[Hmim][BF₄] composite membranes are presented.

Table 4
Thermal degradation values of sPEEK/IL composite polymer electrolytes.

Sample	T ₁₀ (°C)	T ₅₀ (°C)
sPEEK _{0.5} -1	238.9	552.6
sPEEK _{1.0} -1	240.3	556.8
sPEEK _{0.5} -2	225	359.3
sPEEK _{1.0} -2	223.1	519.9
sPEEK _{0.5} -3	204.7	355.8
sPEEK _{1.0} -3	187.6	419.2
T ₁₀ : The temperature where 10wt.% weight loss has occurred; T ₅₀ : The temperature where 50wt.% weight loss has occurred.		

As the DS increased in IL doped composite membranes, thermal strength limited depending on the density of sulfonic acid groups in the structure. It was observed that the excess IL (n = 0.5) significantly decreased the thermal resistance, and 50% weight loss was observed at 356 °C for IL doped composite membranes, having the highest DS (sPEEK_{0.5}-3). Similarly, the composite membrane (sPEEK_{1.0}-2) consisting of sPEEK and an equimolar IL with a DS of 60.20%, had a 50% weight loss at 520 °C, while the sample with an excess of IL (sPEEK_{0.5}-2) had a 50% weight loss at 360 °C. In the case of thermal endurance, this negative effect observed with an increase in the DS and the IL amount was not significant when considering the high temperature fuel cell operating conditions. All membranes showed sufficient thermal stability for HT-PEMFC operation (100–180 °C).

3.4. Proton conductivity tests

Proton conductivities of sPEEK and sPEEK/[Hmim][BF₄] composite was presented in Fig. 5. In terms of sPEEKs, it was indicated that the increasing DS improved the proton conductivity. This behavior showed that sulfonic acid groups formed in the membrane structure by sulfonation processes contributed to proton jumping zones [36, 45]. For sPEEK/[Hmim][BF₄] composites, it could be said that the addition of IL increased proton transfer, resulting higher conductivity. The motivation of the addition of IL to sPEEK matrices was to increase the ionic conductivity of the membranes at high temperature under anhydrous conditions. The doped IL was expected to behave as proton carrier media in the membrane instead of water in proton conductive membranes operated below 100 °C. That is, the addition of IL could provide proton jump zones leading to higher conductivity.

However, it was seen that the conductivity decreased in membranes where excess IL was used (n = 0.5), and the conductivity values were improved in products where imidazole was taken as equimolar to sulfonic acid at line with the studies [39, 46]. It was observed that IL doped membrane prepared with sPEEK-2 showed higher conductivity values than that of IL doped composite membranes prepared with

sPEEK-1 and sPEEK-3 polymer matrices. sPEEK_{1,0}-2 sample showed almost unchanged conductivity values ($2.50 \times 10^{-1} \text{ Sm}^{-1}$ – $3.51 \times 10^{-1} \text{ Sm}^{-1}$) at high temperatures, while surprisingly the conductivity decreased in all other samples. As stated in the literature, DS has a superior effect over temperature on sPEEK conductivity. Herein, sPEEK membranes having a DS of around 40% did not show any conductivity development by increasing the operating temperature, but rather decreased. Some examples showed that the conductivity of a sPEEK with DS (48%) could increase up to 85 °C and then sharply fell to very low values. In the meantime, for a DS about 70–75%, the sPEEK membrane showed an increase in conductivity and it was indicated to decrease gradually only was observed in anhydrous conditions [35, 47]. With the addition of equimolar IL to the sulfonic acid groups of sPEEK-1 membrane matrix (sPEEK_{1,0}-1), the conductivity was increased, and higher values were observed in the excess IL addition (sPEEK_{0,5}-1). These results are compatible with the motivation of the work. With the addition of equimolar IL in the sPEEK-2 membrane matrix (sPEEK_{1,0}-2), the conductivity increased and displayed the highest conductivity values among all samples. In the case of IL excess (sPEEK_{0,5}-2), the conductivity was even lower than the membrane without IL (sPEEK-2). A similar trend was observed in the samples with the highest DS (sPEEK-3). The decrease in conductivity of sPEEK-2 and sPEEK-3 samples with the excess amount of IL could be attributed to the self-condensation of the IL anion in the membrane matrix [48]. In future studies, DS, the type of IL (different anion-cation pairs) and the amount of IL should be optimized to obtain higher conductivity in HT-PEMFC applications, indicating that both temperature and DS play an active role in proton conductivity. In this study, it was seen that conductivity value of composite membrane prepared with DS of 60.20% was acceptable for HT-PEMFC applications ($3.40 \times 10^{-1} \text{ Sm}^{-1}$ – $3.51 \times 10^{-1} \text{ Sm}^{-1}$, at the temperature range of 420–450 K).

3.5. Dielectric constant (ϵ')

Following the proton conductivity measurements, dielectric constant measurements of the sPEEK_{1,0}-2 membrane series, which show the highest proton conductivity values, were performed. The dielectric curves of the related series are shown in Fig. 6a-c as a function of frequency at different temperatures (300–440 K).

As seen from Fig. 6a-c, higher ϵ' values were observed at low frequencies for all samples. As known, dipoles need much more time to orient themselves into the external electric field and high values of ϵ' at low frequency confirm this judgment. The dielectric values decreased sharply with increasing frequency and also showed slight decreases in the higher temperature range. This decrease in dielectric values observed under the effect of temperature can be explained by the rearrangement of the sulfonic acid groups with increasing temperature. It can also be concluded that decreases in dielectric constant with increasing temperature are relatively less effective in applying external electric field at higher frequency [49, 50].

As mentioned before, as the temperature increased, the dielectric constant values of samples decreased. These reductions could be explained by the evaporation of molecular water attached to the sulfonic acid groups in the membrane structure and the restriction of the polymer chain movement by cross-linking by

sulfonation process. On the other hand, sPEEK_{1.0}-2 membrane has higher ϵ' values compared to other samples. When the amount of IL was equimolar to the sulfonic acid groups in the polymer structure, the plasticizing effect of the IL facilitated the orientation of the electric dipoles and consequently increased the dielectric constant values. When the amount of IL increased, the lowest dielectric constant values were seen in SPEEK_{0.5}-2 sample. This result can be explained by the fact that the excess IL remaining unbound to the sulfonic acid groups disrupts the dipole orientation.

3.6. Dynamic mechanic analysis (DMA)

The mechanical properties of sPEEK and sPEEK/[Hmim][BF₄] composite membranes were investigated by DMA. Proton exchange membranes used in HT-PEMFCs are expected to exhibit good mechanical strength with high proton conductivity and thermal stability. For this purpose, the storage (E') and loss (E'') modulus of sPEEK-2 and sPEEK_{1.0}-2 composite membranes were analyzed, and the DMA plots were given in Fig. 7.

As shown in Fig. 7, the storage (E') and loss (E'') modulus values of the sPEEK membrane were higher compared to IL doped composite membrane. This result could be due to the plasticizing effect of the presence of IL in the composite membrane structure. The IL could facilitate the chain segment movements of the polymer by reducing the viscosity of the composite membrane [39, 51]. The storage moduli of sPEEK-2 and sPEEK_{1.0}-2 composite membranes were found to be 1.50 GPa and 0.22 GPa, respectively. These maximum stress values are similar to those given in the literature with trifluoromethanesulfonate-based IL doped sPEEK membranes (2220.5 and 53.92 MPa for sPEEK and sPEEK/IL, respectively) [46]. When the sulfonated polymers and IL doped sulfonated polymers presented in the literature were considered, it could be said that the sPEEK-2 and sPEEK_{1.0}-2 products had reasonable maximum stress at high temperature values [51].

In Fig. 8, changes in $\tan\delta$ values of sPEEK-2 and sPEEK_{1.0}-2 composite membranes were illustrated depending on temperature. From the $\tan\delta$ graph, it is possible to determine the glass transition temperatures (T_g) of the products depending on the temperature values at which maximum $\tan\delta$ values are observed. Considering the statement, it was presented that T_g of the sPEEK-2 membrane was 188 °C while the sPEEK_{1.0}-2 composite membrane had a decreased T_g value of 157 °C with the addition of IL. Similar behavior was seen in the storage modulus trend. This behavior could be explained by the disruption of polymer chain regularity due to the plasticizing effect of the IL. In case of T_g values, it was observed that the T_g of the sPEEK-2 membrane was similar to the other studies presented in the literature, whereas in this study, the high proton conductive composite membrane obtained by IL doping process (sPEEK_{1.0}-2) showed a higher T_g value than the IL doped membrane electrolytes presented in the literature (~ 70–90 °C) [51].

4. Conclusion

In this study, sulfonated poly(ether ether ketone) (sPEEK) and Bronsted acidic ionic liquid (1-methylimidazolium tetrafluoroborate) based polymer composite membranes were successfully synthesized and characterized for high temperature PEM fuel cells (HT-PEMFC). sPEEK polymer matrices were prepared to have three different degrees of sulfonation (32.10, 60.20 and 81.44%). Composite membranes were produced by the addition of ionic liquids (ILs) to the sulfonic acid groups of polymer matrices as equimolar and double ($n = 1.0$ and 0.5). The structures of sPEEK polymer matrices, IL and composite membranes were confirmed by FT-IR analysis. sPEEK_{1,0}-2 composite membrane showed increased proton conductivity values ($2.50-3.51 \times 10^{-1} \text{ Sm}^{-1}$) at a wide temperature range of 380–450 K. As a result of thermogravimetric analysis (TGA), it was observed that all composite membranes maintained their thermal stability above 180 °C. dynamic mechanical analysis (DMA) results showed that the glass transition temperature (T_g) of sPEEK_{1,0}-2 composite membrane was found to be higher than the sPEEK/IL based polymer electrolytes given in the literature and the composite membrane showed a high maximum stress in anhydrous environment (0.22 GPa). When all these results are evaluated, sPEEK_{1,0}-2 composite membrane can be presented as an alternative proton conductive polymeric membrane in HT-PEMFC applications.

Declarations

Acknowledgement

The author gratefully acknowledges Yalova University for financial support and thanks Assoc. Prof. Dr. Ufuk ABACI for proton conductivity and dielectric constant tests.

Ethical Approval

Ethics approval was not required for this study.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

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Funding This research has no funding.

Competing Interests

The authors certify that there are no known competing interests associated with this publication and they have no affiliation with or financial involvement in any organization.

Availability of data and materials

All data generated or analyzed during this research are included in this published article [and its supplementary information files].

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Figures

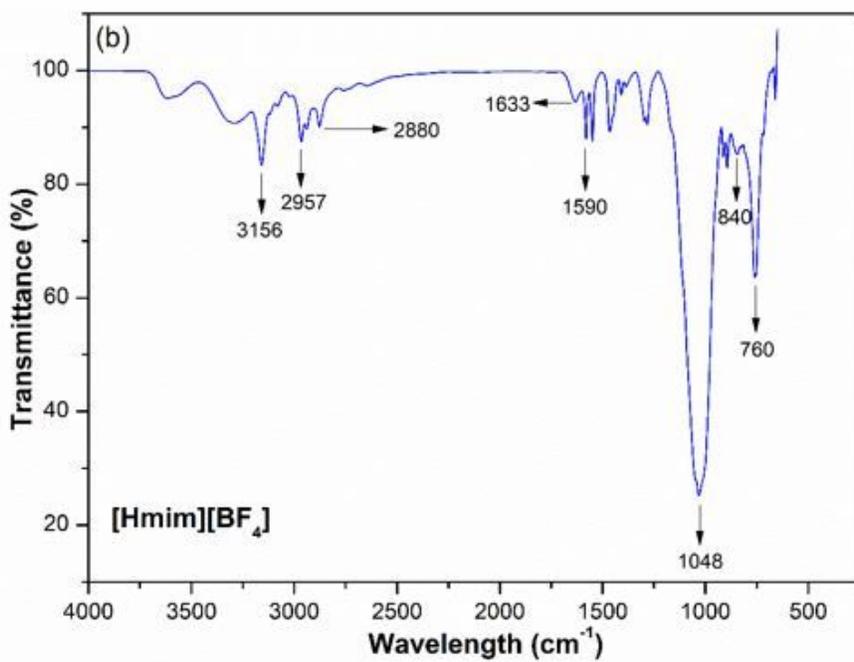
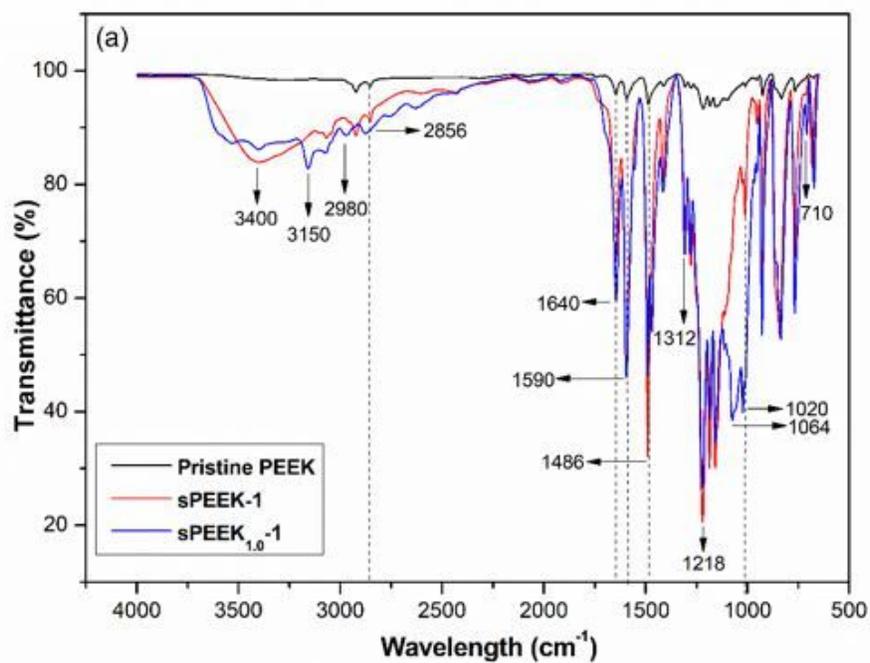


Figure 1

(a) FT-IR spectra of pure PEEK, sPEEK-1 and sPEEK/IL composite (sPEEK1.0-1) samples, (b) FT-IR spectrum of IL, 1-methylimidazolium tetrafluoroborate ([Hmim][BF₄]).

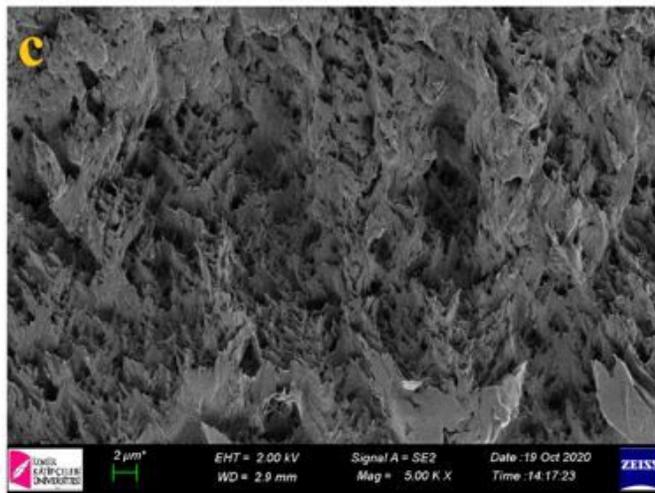
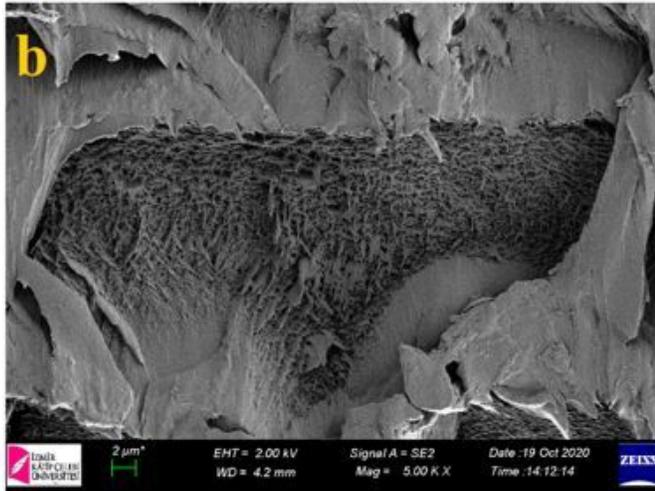
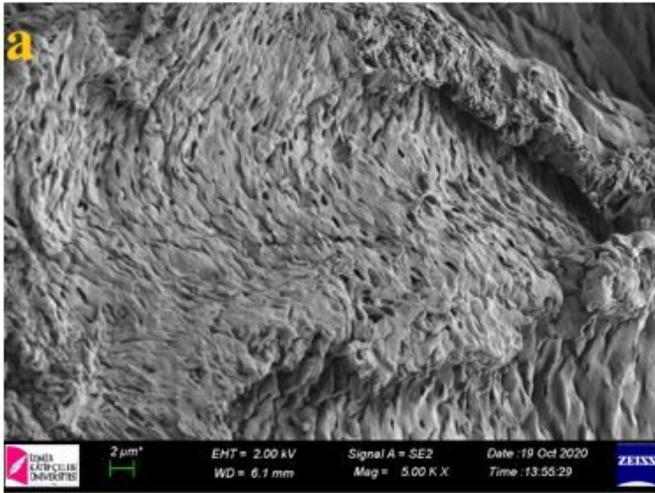


Figure 2

SEM micrographs of (a) sPEEK-2 (b) sPEEK1.0-2 and (c) sPEEK0.5-2

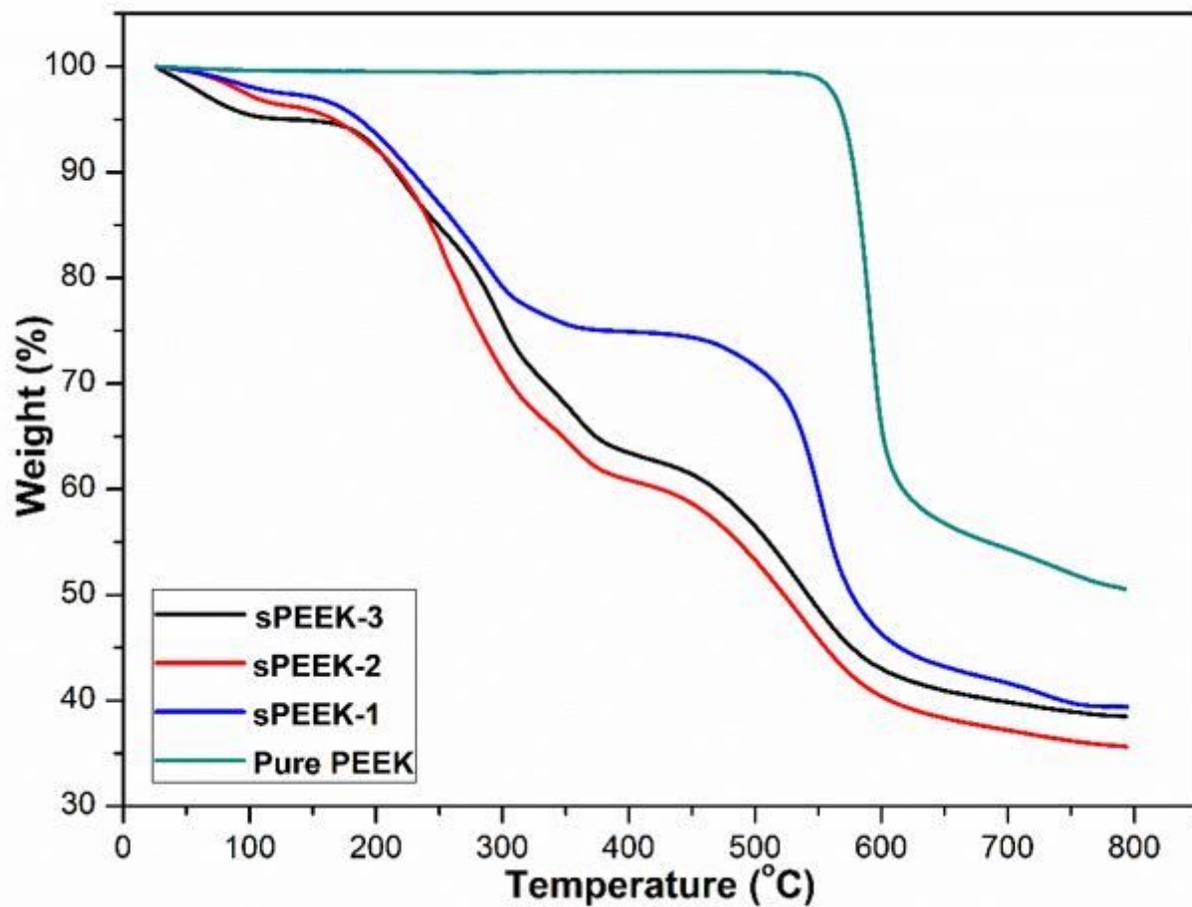


Figure 3

TGA patterns of pure PEEK and sulfonated PEEKs (sPEEK-1, 2, 3) [38].

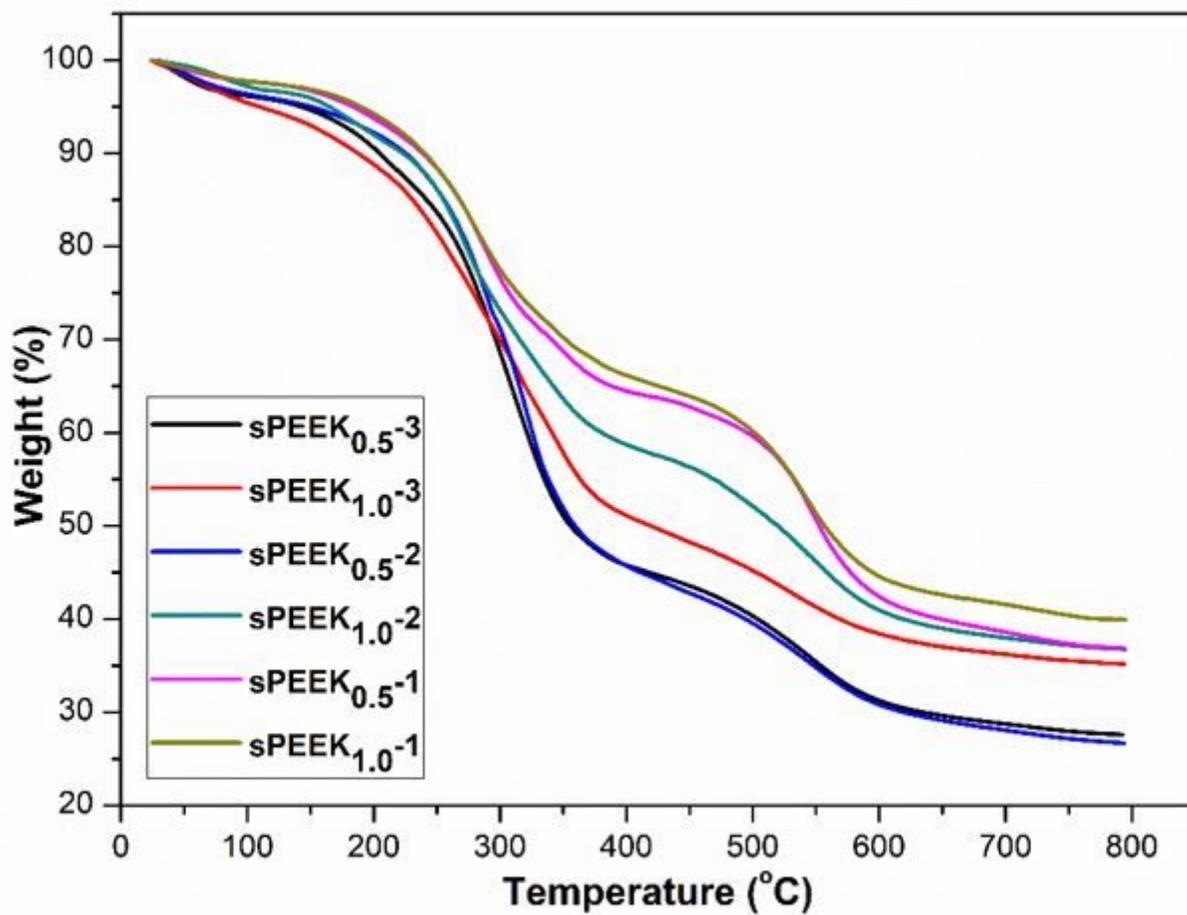


Figure 4

TGA curves of sPEEK/IL composite membranes.

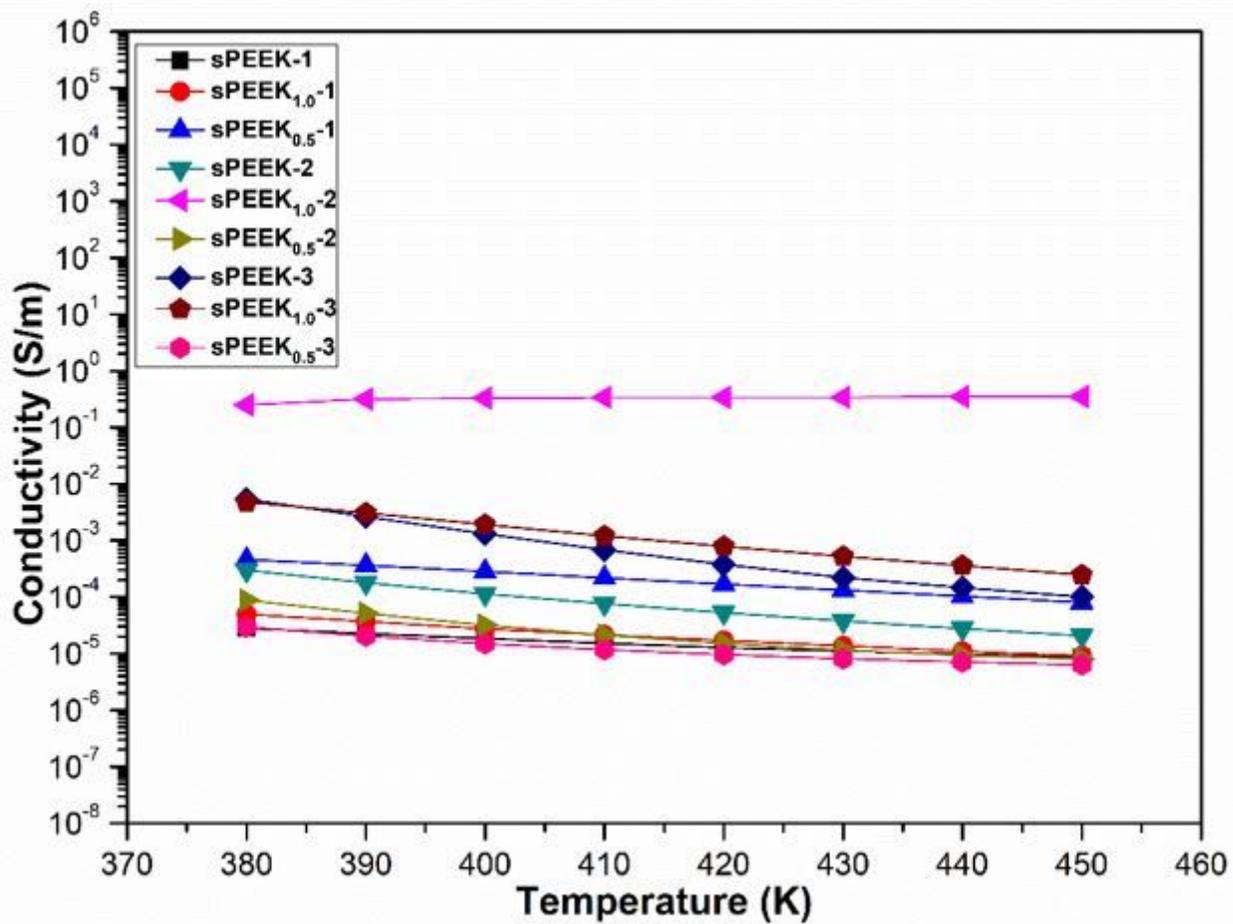


Figure 5

Proton conductivities of sPEEK and sPEEK/[Hmim][BF₄] samples (1 MHz).

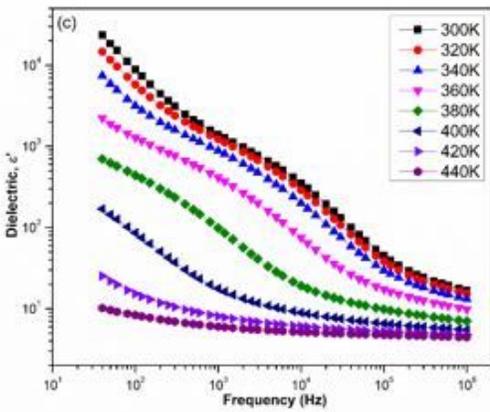
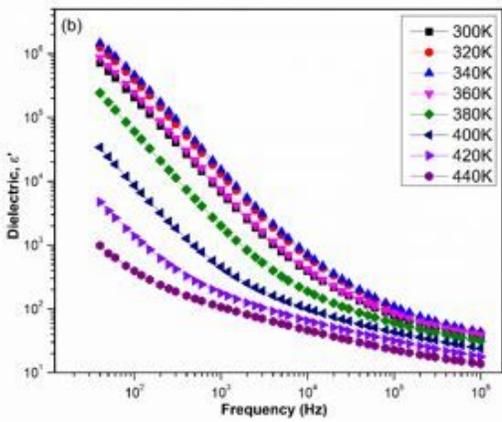
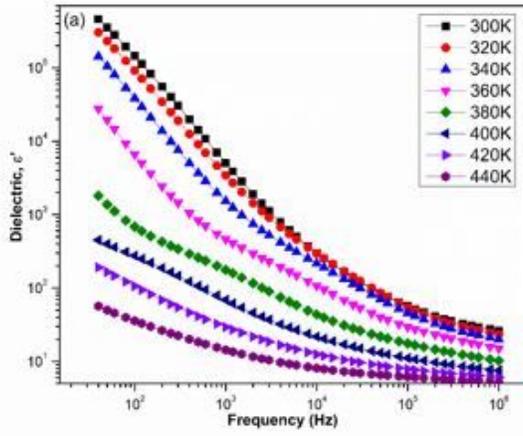


Figure 6

The variation of dielectric constant on frequency from 40 Hz to 1 MHz for (a) sPEEK-2, (b) sPEEK1.0-2, (c) sPEEK0.5-2.

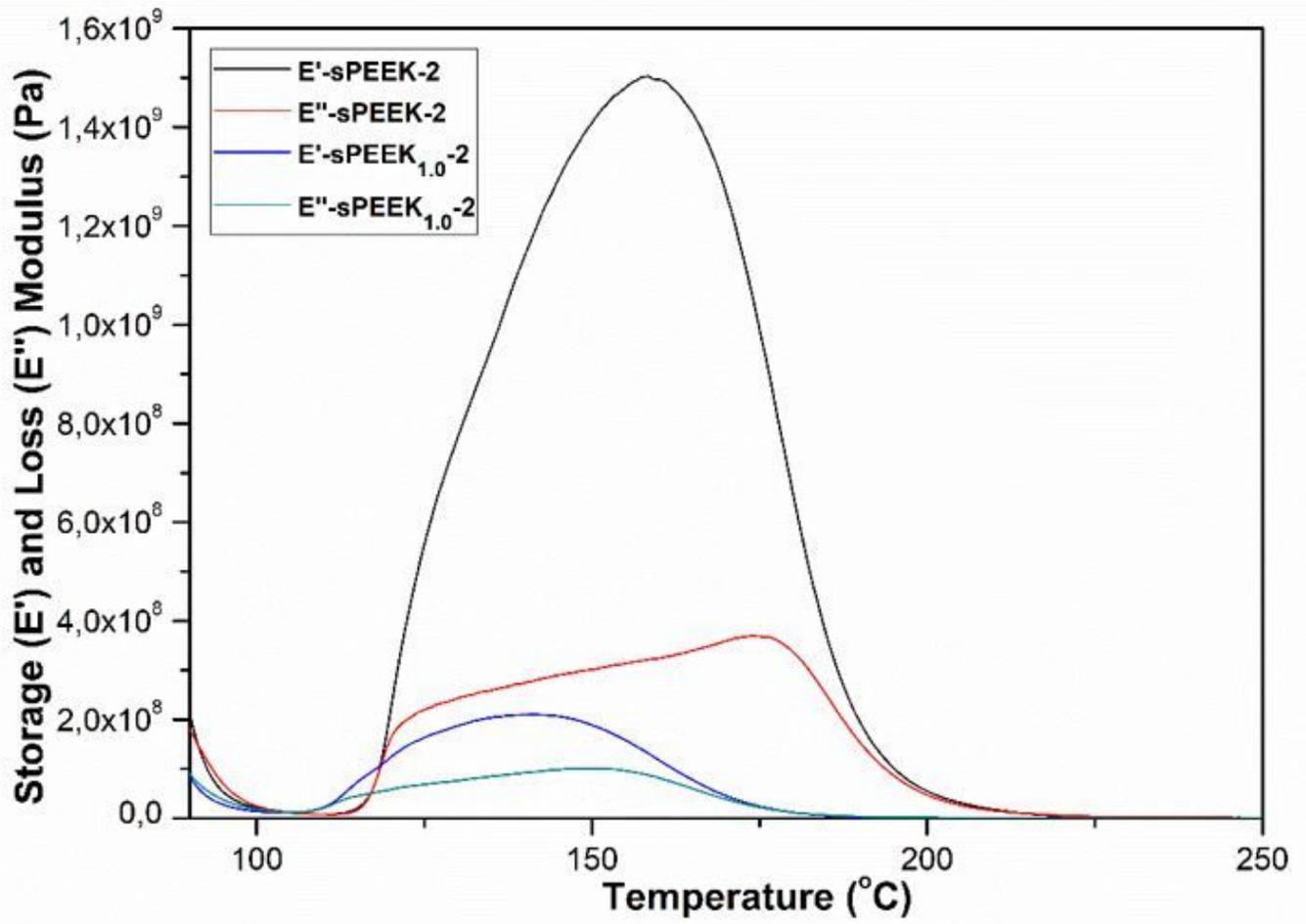


Figure 7

DMA graphs of sPEEK-2 and sPEEK1.0-2 samples.

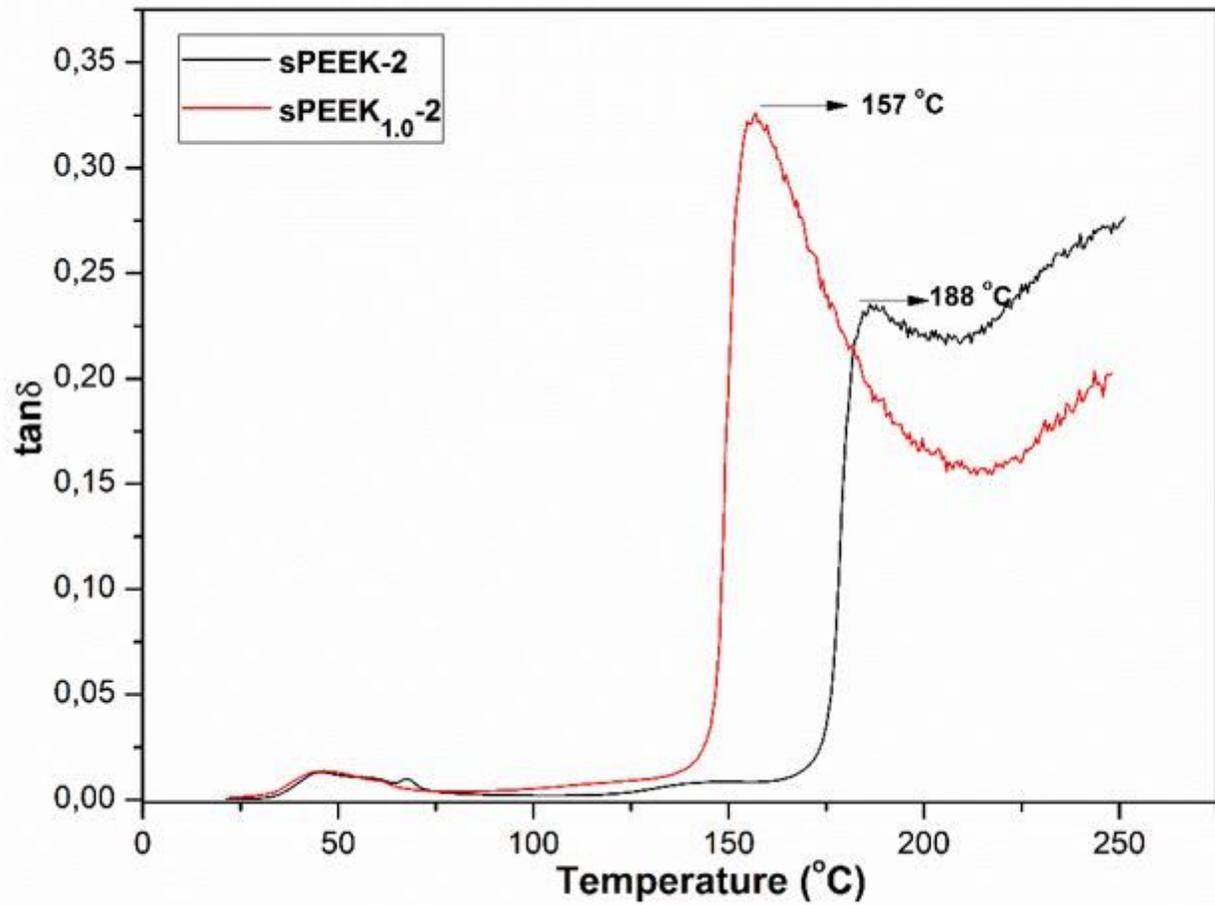


Figure 8

$\tan \delta$ graphs of sPEEK-2 and sPEEK1.0-2 samples.