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# Development of 1,2,3-Triazole Based Ionic Liquid Doped Sulfonated Polysulfone (SPSU) Electrolytes for Anhydrous Proton Exchange Membrane Applications

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**Abstract:** In this study, triazole based ionic liquid doped sulfonated polysulfone (SPSU) composite membranes were evaluated for high temperature proton exchange membrane fuel cell (PEMFC) systems. SPSU obtained by sulfonation of aromatic polysulfone (PSU) polymer matrix was used in the preparation of composite electrolytes. Sulfonated polymer matrices were doped with three different triazole-based ionic liquids (TIL-1, TIL-2 and TIL-3) synthesized within the scope of the study and composite membrane series were formed. Structural, thermal and mechanical characterizations were performed by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), respectively. Proton conductivities were measured over a wide temperature range (380-450 K) and the effectiveness of composite membranes in high temperature PEMFC systems was evaluated. As a result of TGA analysis, all triazole based ionic liquid doped membrane series exhibited high thermal resistance. It was observed that the proton conductivity of the composite structures was greatly improved with high temperature proton conductivity measurements (8.05 mS/cm for SPSU; 58.1 mS/cm for SPSU/TIL-3(1.0)) and the obtained membranes could be an alternative in high temperature PEMFCs.

**Keywords**: Triazole, Ionic liquid, Polymer electrolyte, Polysulfone, Proton conductivity

# Susuz Proton Değişim Membran Uygulamaları için 1,2,3-Triazol Esaslı İyonik Sıvı Katkılı Sülfone Polisülfon (SPSU) Elektrolitlerin Geliştirilmesi

**Öz:** Bu çalışmada triazol esaslı iyonik sıvı katkılı sülfone polisülfon (SPSU) kompozit membranlar, yüksek sıcaklık proton değişim membran yakıt hücresi (PEMYH) sistemleri için değerlendirilmiştir. Kompozit membranların hazırlanmasında, aromatik polisülfon (PSU) polimer matrisinin sülfonasyonuyla elde edilen SPSU kullanılmıştır. Yüksek sıcaklıklarda geliştirilmiş proton iletimi için kompozit elektrolitler, çalışma kapsamında sentezlenen üç farklı triazol esaslı iyonik sıvı (TIL-1, TIL-2 ve TIL-3) ile katkılanmış ve kompozit membran serileri oluşturulmuştur. Yapısal, termal ve mekanik karakterizasyonlar sırasıyla Fourier dönüşüm kızılötesi spektroskopisi (FTIR), termogravimetrik analiz (TGA) ve dinamik mekanik analiz (DMA) ile gerçekleştirilmiştir. Proton iletkenlikleri geniş bir sıcaklık aralığında (380-450 K) ölçülmüş ve kompozit membranların yüksek sıcaklık PEMYH sistemlerinde etkinliği değerlendirilmiştir. TGA analizi sonucunda, tüm triazol esaslı iyonik sıvı katkılı membran serileri, yüksek termal dayanım sergilemiştir. Yüksek sıcaklık proton iletkenlik ölçümleri ile kompozit yapıların proton iletkenliklerinin büyük ölçüde geliştirildiği (SPSU için 8.05 mS/cm; SPSU/TIL-3(1.0) için 58.1 mS/cm) ve elde edilen membranların yüksek sıcaklık PEMYH şartlarında alternatif olabileceği görülmüştür.

**Anahtar Kelimeler:** Triazol, İyonik sıvı, Polimer elektrolit, Polisülfon, Proton iletkenliği

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## 1. Introduction

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy with low pollutant emissions. The limited reserves and environmental damage of traditional fossil fuels increase the need for renewable and efficient energy converters such as fuel cells [1]. Proton exchange membrane fuel cells (PEMFCs), one of the most popular fuel cell types, stand out with their ease of adaptation to different applications. Polymer electrolyte membrane that provides proton conduction is the primary component affecting cell efficiency and performance in PEMFCs. Commercial Nafion membrane, which is the most widely used, shows high ionic conductivity in the temperature range of 60-80°C when it is fully saturated with water [2]. Therefore, temperature and water/humidity management and optimization are required for high and stable cell performance. The high proton conductivity of Nafion depends on absolute humidity, decreases in anhydrous conditions (>100°C) [2, 3]. The narrow effective operating temperature range and the dependence of ionic conductivity on humidity are limiting effects for PEMFC. These limiting effects can be overcome by development of alternative membranes which are highly conductive and thermomechanically stable at elevated temperatures and anhydrous cell conditions [4, 5].

The first approach in the synthesis of polymer electrolytes exhibiting high proton conductivity under anhydrous conditions is the addition of various inorganic fillers (such as titanium oxide, silicon oxide, and graphene oxide etc.) to Nafion structure. While these inorganic fillers increase thermal and chemical stability at high temperatures, they also slightly improve ionic conductivity [6, 7]. Another popular approach for the development of proton conductive membranes in anhydrous conditions is the use of aromatic polymer matrices such as polyether ketone (PEK), polyether ether ketone (PEEK) and polysulfone (PSU) etc. [8, 9]. In addition to the high temperature resistance and chemical stability of aromatic polymers, various processes such as sulfonation and chloromethylation are required to exhibit proton conductivity under anhydrous conditions. Moreover, proton conductivity can be improved by different organic-inorganic additives to polymer matrices functionalized by sulfonation or chloromethylation [10, 11].

Ionic liquids are organic salts whose melting points are below room temperature. They have superior properties such as negligible volatility, non-flammability, high thermal and electrochemical stability, and superior ionic conductivity, even under anhydrous environment. Due to these unique properties, their use in many electrochemical systems including fuel cells has attracted attention in recent years [12]. Ionic liquids typically consist of asymmetric organic cations and inorganic anions. In this way, ionic liquids of different qualities can be prepared by using anion-cation pairs with different physicochemical and electrochemical properties. While the most known cation groups in ionic liquid structures are imidazole and pyridine, the most used anion groups are tetrafluoroborate ($BF_4^-$), hexafluorophosphate ($PF_6^-$), and trifluoromethanesulfonate ($CF_3SO_3^-$) [12, 13]. In recent years, it has been reported in many studies that imidazole-based electrolytes can meet the needs of new generation PEM fuel cells. Proton conductivities of ionic liquids with pyridine, piperidine, pyrrolidine and tetra alkyl ammonium cationic groups at room temperature are significantly lower than ionic liquids containing imidazole. For this reason, research is directed to the use of imidazole-based ionic liquids as electrolyte materials for improved proton conductivity and cell performance in high temperature fuel cells [14]. Imidazole is an aromatic heterocycle with two nitrogen atoms. It is thought that imidazole transmits protons through intermolecular proton transfer and therefore can replace water as a proton carrier at temperatures above 100°C. While high proton mobility is observed in imidazole-based materials, including ionic liquids, oligomers and polymers, the electrochemical stability of imidazole is sometimes considered insufficient for fuel cell applications due to the high electronic density of the imidazole ring [15]. Compared to imidazole ($T_{mp}$: 89°C, $T_{bp}$: 257°C), triazole ($T_{mp}$: 120°C, $T_{bp}$: 256°C) has a stronger temperature resistance depending on the density of hydrogen bonds in its structure. Since the cathode reduction and anode oxidation potentials of ionic liquids can be developed according to the carrier ion and cation to be selected, it is thought that triazole-based ionic liquids to be obtained with appropriate anion-cation pairs will show high potential, just like proton exchange membranes prepared with imidazole-based ionic liquids [15, 16].

Among the alternative polymer matrices, sulfonated polysulfone (SPSU) has attracted attention in recent years. This ionomer, synthesized by sulfonation of the PSU polymer backbone, stands out with its good film forming ability, low cost and excellent mechanical properties [17]. Cell performance of SPSU membranes is directly related to the degree of sulfonation (DOS). The high DOS increases the proton conductivity but weakens the mechanical strength due to the high swelling ratio [18]. In order to achieve this optimization, strategies that simultaneously improve conductivity and mechanical/thermal strength by incorporating various fillers and additives into the sulfonated polymer matrix have been presented in many recent publications in the literature [18-21].

In this study, triazole based ionic liquid doped polymer composite membranes were evaluated for high temperature PEMFCs. PSU, as an alternative aromatic polymer matrix, was sulfonated with sulfonation agent and SPSU membrane matrix with 15% DOS was obtained. Three different triazole-based ionic liquids (TIL-1, TIL-2, and TIL-3) were prepared for the composite membrane structure to improve proton conduction under anhydrous conditions, and composite membrane series were formed by adding ionic liquid in different molar ratios (n:0.5; 1.0; 2.0) Structural, thermal and mechanical characterizations of the membranes were performed by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), respectively. Proton conductivities were measured in a wide temperature range (380-450 K) and the effectiveness and usability of composite membranes in high temperature PEMFC systems were evaluated.

## 2. Experimental Method

### 2.1. Materials

Polysulfone (PSU) polymer matrix was purchased from Merck. Sodium ascorbate, copper sulfate, butyl alkyne, silver tetrafluoroborate and n-butylazide were supplied from Merck and used without further purification. Ethyl acetate, methyl trifluoromethanesulfonate, diethyl ether, trimethylsilyl chlorosulfonate were obtained from Aldrich. Ethanol, chloroform and 1-methyl 2-pyrrolidone solvents were purchased from Merck-Millipore and used as received.

### 2.2. Synthesis of 3,5-dibutyl-1-methyl-3H-1,2,3-triazolium Trifluoromethanesulfonate (TIL-1)

Sodium ascorbate (800 mg), copper sulphate (480 mg), and 20 mmol butyl alkyne were added to 20 mmol n-butylazide in 100 mL methanol and stirred at room temperature. Then, adding 500 mL of water to the mixture, it was extracted with 2 times 500 mL of ethyl acetate. The resulting organic phase was washed with brine and dried with sodium sulfate. After the solvent was evaporated in a rotary evaporator, the remaining oily phase [1,4-di (n-butyl) -1H-1,2,3-triazole] was removed. Methyl trifluoromethanesulfonate (0.11 mL, 1mmol) was added to oily triazole phase and stirred for 1 h. After the solvent had been evaporated off under vacuum, the product was washed with diethyl ether and again vacuum applied to yield 3,5-dibutyl-1-methyl-3H-1,2,3-triazolium trifluoromethanesulfonate (TIL-1) [22]. (Molecular Weight: 345 g.mol$^{-1}$; Yield: 99.1%; Theoretical:

C%: 41.74, H%: 6.38, N%: 12.17; Elemental analysis: C%: 41.87, H%: 6.34, N%: 12.21 )

### 2.3. Synthesis of 3,5-dibutyl-1-methyl-3H-1,2,3-triazolium Tetrafluoroborate (TIL-2)

The oily phase (1,4-di (n-butyl) -1H-1,2,3-triazole) obtained by the procedure applied in the synthesis of TIL-1 was treated with alkylating agent in dry acetonitrile. Then, $AgBF_4$ solution (15.4 mmol) in dry methanol was added dropwise. AgI precipitates were decanted from solution. After the solvent had been evaporated off under vacuum, the product was washed with diethyl ether and again vacuum applied to yield 3,5-dibutyl-1-methyl-3H-1,2,3-triazolium tetrafluoroborate (TIL-2) [22]. (Molecular Weight: 294.8 $g.mol^{-1}$; Yield: 97.9%; Theoretical: C%: 48.85, H%: 7.46, N%: 14.25; Elemental analysis: C%: 47.94, H%: 7.44, N%: 14.34)

### 2.4. Synthesis of 1-benzyl-3,5-dibutyl-3H-1,2,3-Triazolium Bromide (TIL-3)

The oily phase obtained by the procedure applied in the synthesis of TIL-1 [1,4-di (n-butyl) -1H-1,2,3-triazole] was refluxed with alkylating agent (Br) in benzyl alcohol and the solvent was evaporated under vacuum. The transparent oily ionic liquid was washed with diethyl ether. Applying vacuum again gave 1-benzyl-3,5-dibutyl-3H-1,2,3-triazolium bromide (TIL-3) [22]. (Molecular Weight: 352.1 $g.mol^{-1}$; Yield: 92.8%; Theoretical: C%: 57.94, H%: 7.38, N%: 11.93; Elemental analysis: C%: 53.16, H%: 7.19, N%: 14.23)

### 2.5. Preparation of SPSU/TIL-(1-3) Composite Membranes

Sulphonated PSU polymer matrix with degree of sulfonation of 15% was obtained by the procedure performed with sulfonation agent (trimethylsilyl chlorosulfonate). According to this procedure, firstly pure PSU was dissolved in chloroform at room temperature by stirring. Then trimethylsilyl chlorosulfonate was added and stirred for 24 h at room temperature to obtain PSU in the form of silyl sulphonate.

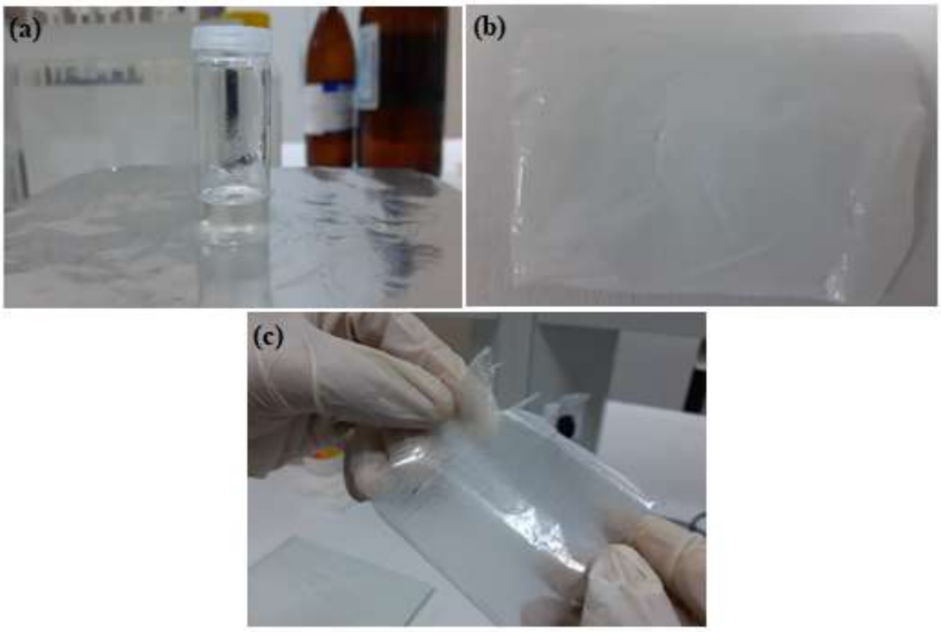

**Figure 1. (a)** Ionic liquid doped polymer solution, **(b)-(c)** SPSU/TIL composite membrane films.

Sodium methoxide was added to the mixture and mixed in order to cut the silyl sulphonate structures. The resulting sulphonated polymer solution was added dropwise into cold ethanol. The white polymer obtained as a precipitate was then filtered off, washed with distilled water and dried at 60°C for 24 h.

Pure SPSU and ionic liquid doped composite membranes were obtained by solution casting method. In ionic liquid doped membranes, ionic liquid was doped in 0.5, 1- and 2-times molar ratios (n) of sulfonic acid groups in SPSU structure. For this purpose, a certain amount of SPSU was weighed and dissolved in NMP and stirred for 2 h. Then, at room temperature, ionic liquid was added in the determined molar ratios and stirring was continued for 4 h. The composite polymer solutions poured on the glass surface were drawn with the applicator of the desired thickness and dried in the oven at 40°C for 24 h and membrane films were obtained by removing the solvent. Images of ionic liquid and composite membrane film are presented in Figure 1.

The compositions and nomenclatures of the proton exchange membranes prepared in this study are presented in Table 1.

**Table 1.** SPSU/TIL-(1-3) composite membranes and their composition.

| **Sample** | **Mol ratio (n; TIL/$HSO_3$)** |
|---|---|
| SPSU | - |
| SPSU/TIL-1(0.5) | 0.5 |
| SPSU/TIL-1(1.0) | 1.0 |
| SPSU/TIL-1(2.0) | 2.0 |
| SPSU/TIL-2(0.5) | 0.5 |
| SPSU/TIL-2(1.0) | 1.0 |
| SPSU/TIL-2(2.0) | 2.0 |
| SPSU/TIL-3(0.5) | 0.5 |
| SPSU/TIL-3(1.0) | 1.0 |
| SPSU/TIL-3(2.0) | 2.0 |

### 2.4. Characterizations

Structural characterization of ionic liquids and proton exchange membranes was carried out by Fourier Transform Infrared Spectroscopy (FT-IR). Analyzes were performed with the Perkin Elmer Spectrum 100 instrument containing ATR unit, in the wavelength range of 500-4000 $cm^{-1}$ and at room temperature. Thermal behavior of the prepared proton exchange membranes was examined by Thermogravimetric Analysis (TGA). Analyzes were carried out with SEIKO TG/DTA 6300 under nitrogen atmosphere, in the range of 25-800°C, with a heating rate of 10°C/min. Dynamic Mechanical Analysis (DMA) were applied to determine the mechanical properties of proton exchange membranes over a wide temperature range. Analyzes were performed with the SEIKO DMS 6100 device with a heating rate of 2°C/min. Proton conductivity measurements were performed by Agilent 4284A LCR Meter in a wide frequency range of 20 Hz-1 MHz at a temperature range of 380−450 K under anhydrous conditions.

## 3. Results and Discussion

### 3.1. FT-IR Analysis

FT-IR analyzes were carried out to characterize the chemical structures of ionic liquids and composite membranes and to determine the complexation between the ionic liquid-polymer structures formed. After the synthesis of ionic liquids, reaction yields were determined, and compositions of ionic liquids were verified by performing elemental analyzes. Reaction yields and elemental analysis results are presented with ionic liquid synthesis procedures given in the

'Experimental Methods' section. FT-IR graphs of ionic liquids (TIL-1 and TIL-2) are presented in Figure 2.

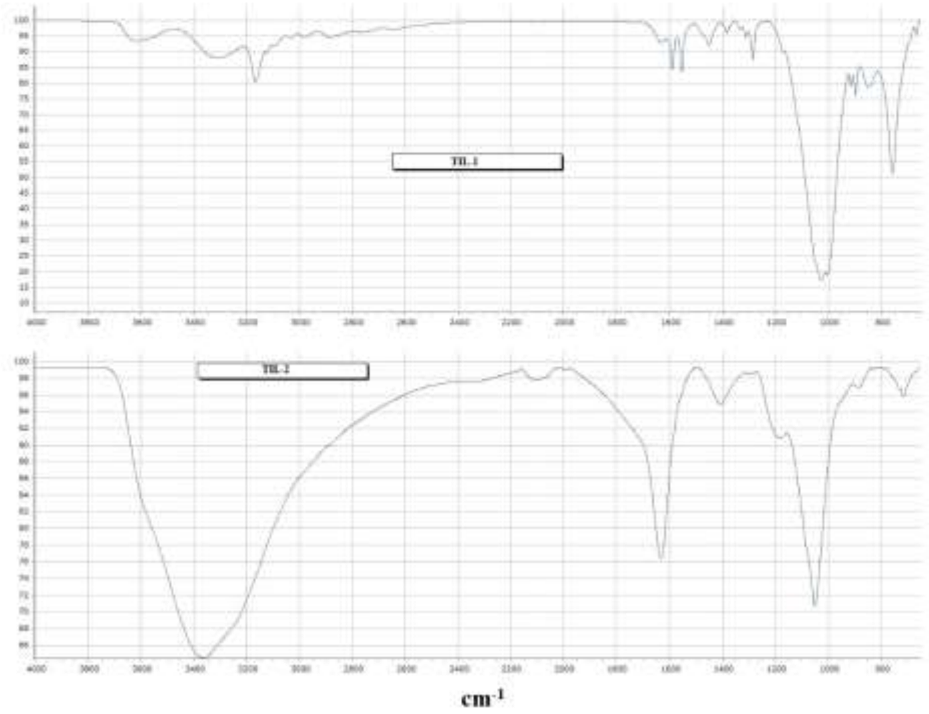

**Figure 2.** FT-IR spectra of TIL-1 and TIL-2 ionic liquids.

As seen in Figure 2, the band observed at 1048 cm$^{-1}$ shows the stress vibration of the $BF_4^-$ anion in TIL-2 ionic liquid structure, while the vibration at 1192 cm$^{-1}$ is attributed to C-N, C-H bonds. The wide bands observed at 3360 cm$^{-1}$ are attributed to NH stretching modes in ionic liquid structures. Vibrations of C-H plane bending and C=N tensile bonds are seen at 720 cm$^{-1}$ and 1633 cm$^{-1}$, respectively. The band at 1400 cm$^{-1}$ is attributed to C=C aromatic stretching modes [23, 24].

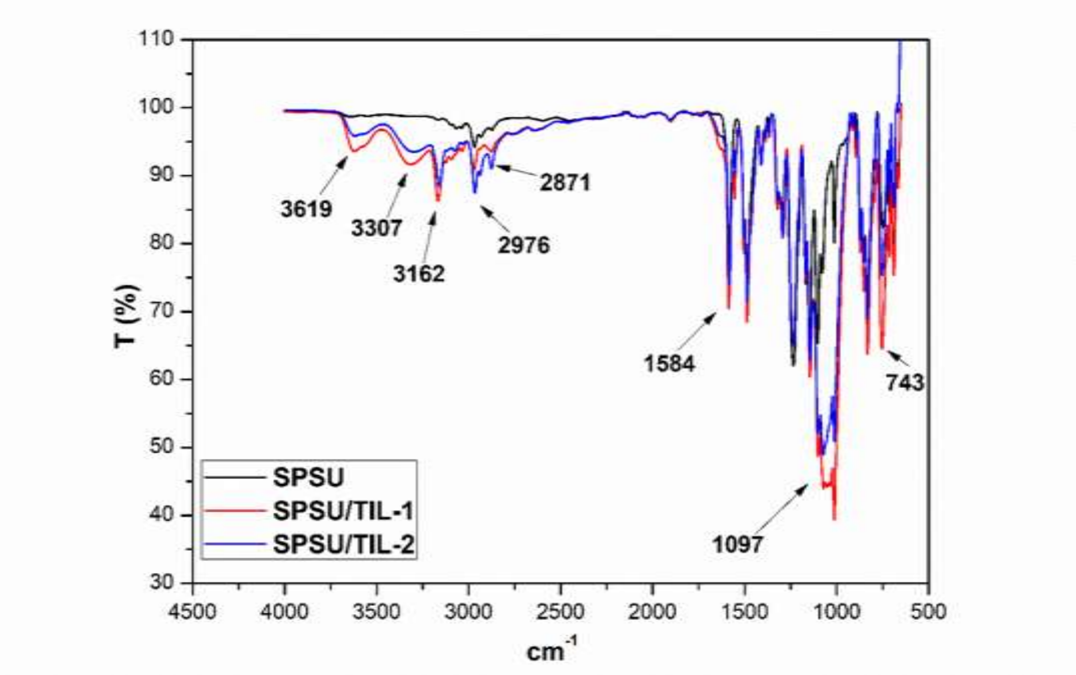

**Figure 3.** FT-IR spectra of SPSU, SPSU/TIL-1 and SPSU/TIL-2 composite polymer electrolyte membranes.

In Figure 3, FTIR spectra of pure SPSU and triazole based ionic liquid doped polymer electrolyte membranes (SPSU/TIL-1 and SPSU/TIL-2) are presented. While all the peaks attributed to the membrane matrices are seen as common, the membranes containing the triazolium cation show a clear shoulder, showing a vibration that is more intensified at 1584 cm$^{-1}$. In addition, the vibration seen at 3307 cm$^{-1}$ (not seen on the pure SPSU membrane) indicates the triazole groups in the structure of ionic liquid doped electrolytes [23, 25].

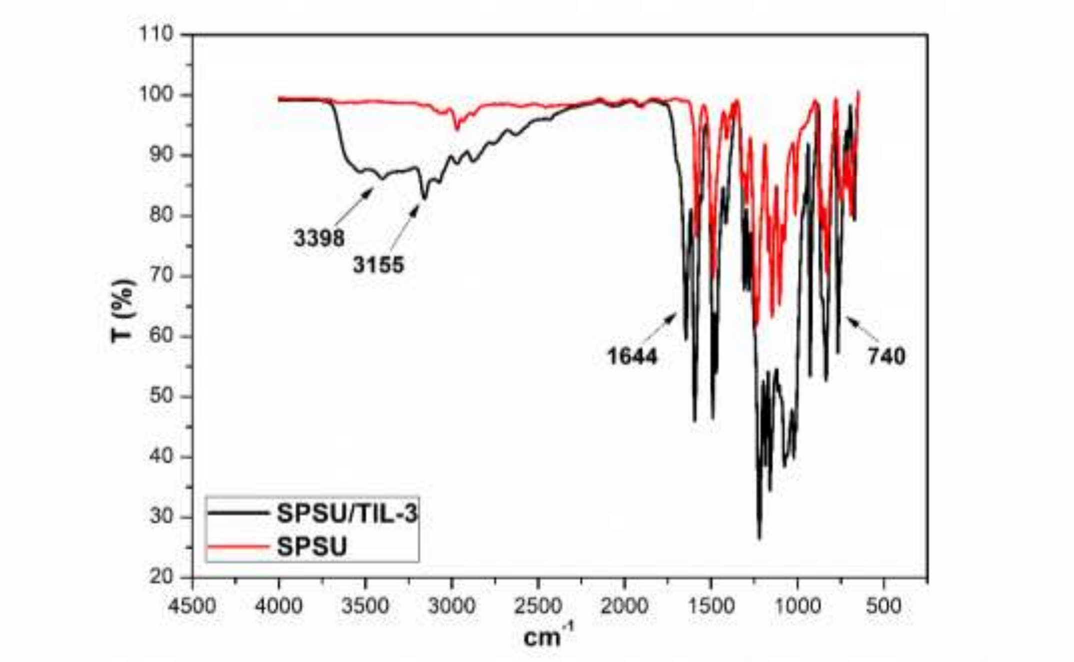

**Figure 4.** FT-IR spectra of SPSU and SPSU/TIL-3 composite polymer electrolyte membranes.

In Figure 4, FTIR spectra of composite membrane prepared with 1-benzyl-3,5-dibutyl-3H-1,2,3-triazolium bromide (TIL-3) and pure SPSU membrane are given. While the band observed at 1040-1050 cm$^{-1}$ in the composite membrane shows the stress vibration of the Br anion in the ionic liquid structure, the band observed at 3398 cm$^{-1}$ in the composite membrane without being seen in the SPSU structure is due to the NH stretching modes. The vibrations of the C-H plane bending and the tensile bonds of the C=N are seen at 740 cm$^{-1}$ and 1644 cm$^{-1}$, respectively. Vibrations common to both membranes at the range of 1400-1600 cm$^{-1}$ are attributed to the aromatic structures of polymer matrices [24, 25].

## 3.2. Thermogravimetric analysis (TGA)

TGA analyzes were performed for the thermal characterization of polymer composite membranes prepared within the scope of the study. Polymer electrolyte membranes to be used in high temperature fuel cells must have high thermal stability. In Figure 5a-c, TGA curves of TIL-1, TIL-2 and TIL-3 doped SPSU composite membranes are presented, respectively.

In Figure 5a, TGA curves are given in order to observe the effects of the ionic liquid molar ratio on the thermal resistance of the SPSU/TIL-1 composite membranes. As seen in the figure, there is no difference in the thermal behavior of the pure polymeric membrane and the ionic liquid doped membranes up to 150-160°C. While the first degradation at 150-200°C of the pure SPSU membrane is caused by the degradation of the sulfonic acid groups in the structure, the final degradation step starting at around 500°C is attributed to the decomposition of the polymer main matrix [26, 27]. The second degradation step was started and completed in the same temperature range for all samples. It is seen that the weight loss of ionic liquid doped membranes up to 250-280 °C is lower and their thermal resistance is higher than the SPSU membrane. As a result of thermal measurements, it is observed that this thermal behavior is sufficient and improved in terms of cell performance considering the high temperature fuel cell operating conditions (120-180°C) [24].

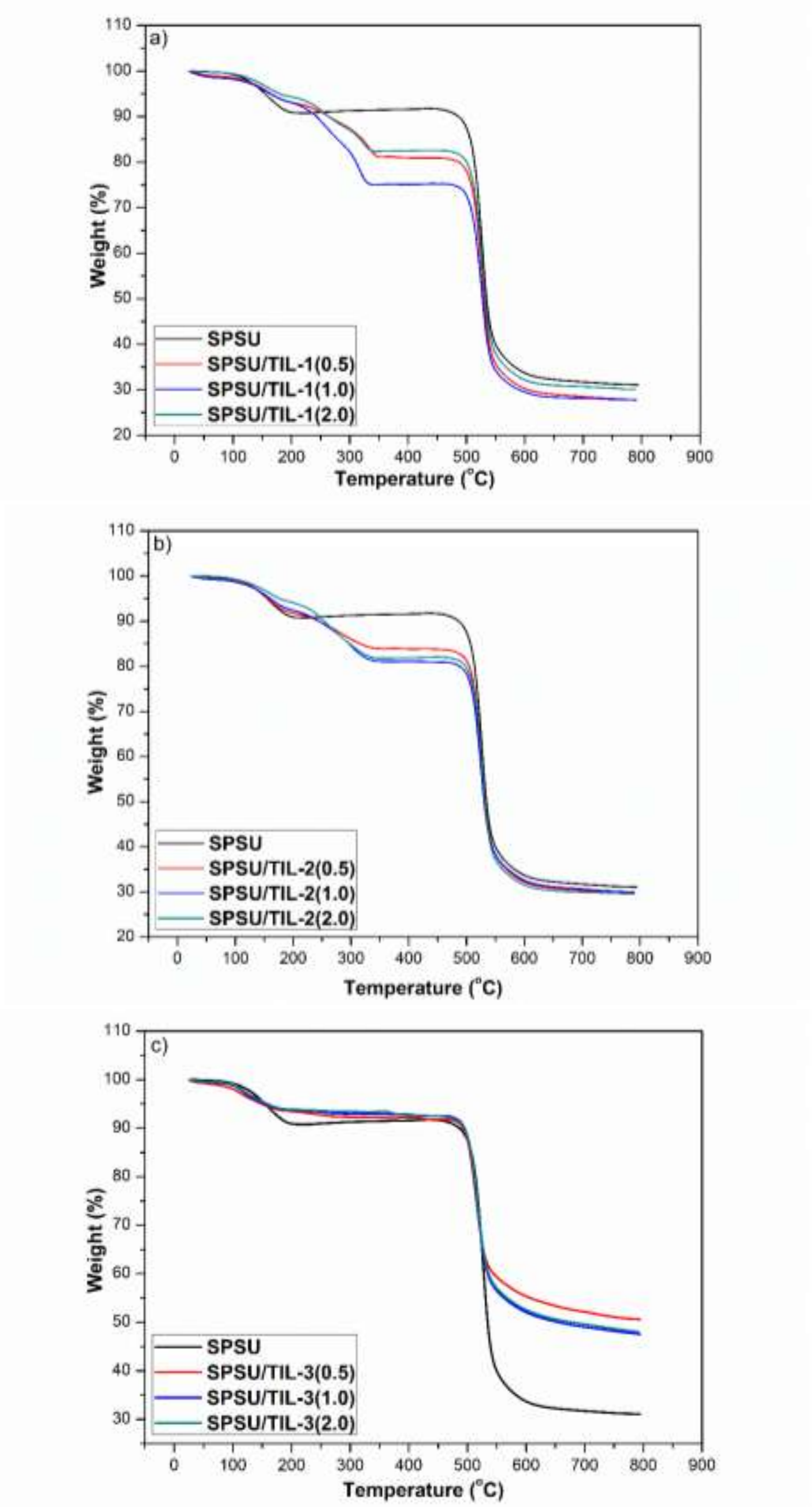

**Figure 5.** TGA curves of **a)** SPSU/TIL-1 composite membranes, **b)** SPSU/TIL-2 composite membranes, **c)** SPSU/TIL-3 composite membranes.

Similarly, TGA curves of TIL-2 doped composite membranes are given in Figure 5b. When the figure is examined, it is seen that the first degradation step, which is observed in all samples and attributed to the degradation of sulfonic acid groups, is completed at higher temperatures (300-350℃) in TIL-2 doped composite membranes as well as in TIL-1 doped membranes. It was concluded that the weight loss in all TIL-2 doped composite membranes up to 250℃ is lower compared to pure SPSU membrane and that composite membranes are sufficient with their improved thermal resistance compared to pure SPSU membrane under high temperature fuel cell operating conditions. The last degradation step, which is attributed to the degradation of the polymer main chain, occurred in the same temperature range (500-550 ℃) for all samples. TGA curves of polymer electrolytes prepared with TIL-3 ionic liquid with Br- anion are given in Figure 5c. As can be seen in the figure, all TIL-3 doped samples showed superior thermal resistance compared to pure SPSU polymer matrix. As with other membrane series, two degradation steps were seen, involving the degradation of the sulfonic acid groups and the polymer main chain. Unlike membrane series prepared with other ionic liquids (TIL-1, and TIL-2), at the end of the second degradation step, the pure SPSU membrane matrix loses a weight of 70%, while the weight loss at 800℃ is approximately 50% in TIL-3 ionic liquid doped membranes. These results showed that TIL-3 addition have significantly improved the thermal strength of TIL-3 based composite membranes compared to others. As a result, all triazole based ionic liquid doped membrane series displayed thermally stable behavior for high temperature fuel cell applications.

### 3.3. Proton Conductivity

Proton conductivities of SPSU/TIL based composite membranes prepared within the scope of the study were measured using the Agilent 4284A LCR Meter system at a frequency of 1MHz and a temperature range of 380-450 K. Proton conductivity values were calculated according to the following equation:

$$\sigma = \frac{L}{RA}$$

where σ is conductivity, L is the membrane thickness, and A is the cross-sectional area of the membrane. Figure 6 shows the proton conductivities of composite polymer electrolytes as a function of varying temperature.

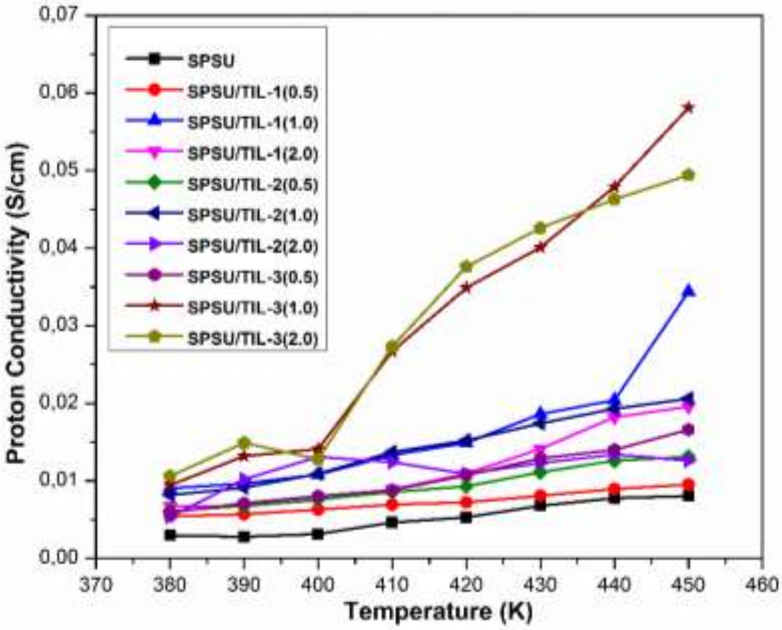

**Figure 6.** Temperature dependent proton conductivity values of SPSU/TIL-(1-3) composite membranes.

Proton conductivity values of SPSU membranes, which were presented in previous studies in the literature, vary between $10^{-6}$ and $10^{-2}$ S/cm, depending on their degrees of sulfonation and ion exchange capacities [26-28]. As can be seen in the figure, the pure SPSU polymer matrix prepared within the scope of the study (15%, DOS) exhibited proton conductivity values ($2.96 \times 10^{-3}$ - $8.05 \times 10^{-3}$ S/cm) increasing with temperature (380-450 K). At the same time, with increasing temperature, proton conductivity values increased for all TIL doped samples. This behavior indicates that proton transfer is facilitated by the increase in molecular mobility with the increasing temperature. Depending on the degree of sulfonation, compared to the values presented in the literature, the proton conductivity values of TIL-based composite electrolytes are higher than the conductivity value of pure SPSU membrane. This result shows that the ionic liquids prepared within the scope of the study form proton conduction paths that improve ionic conduction at high temperatures. Under anhydrous conditions, the TIL-3 doped SPSU/TIL-3(1.0) membrane sample has the highest proton conductivity ($5.81 \times 10^{-2}$ S/cm at 450 K). It was observed that the proton conductivity value of the SPSU membrane matrix was increased more than 7 times with the equimolar TIL-3 ionic liquid contribution. Incorporation of TIL-based ionic liquids into the polymer matrix leads to an increase in polymer chain mobility, which improves ionic mobility and facilitates proton transport within membranes [29]. Moreover, ionic liquids act as proton transport media in composite membranes, similar to water in water-swollen polymer electrolyte membranes [24].

Conductivity values are higher when the addition of ionic liquid is equimolar (n=1.0) to sulfonic acid groups in all membrane series. On the other hand, proton conductivity values are generally lower in cases where the ionic liquid is doped more or less (n=2.0; n=0.5). It is thought that the heterogeneous character caused by the excess ionic liquid remaining unbound to the sulfonic acid groups in the structure may have an inhibitory effect in the formation of proton conduction paths in some cases. Conductivity values of equimolar TIL-1, TIL-2 and TIL-3 ionic liquid doped samples at 450 K are $3.44 \times 10^{-2}$, $2.06 \times 10^{-2}$ and $5.81 \times 10^{-2}$ S/cm, respectively. When these values are compared with the proton conductivity of pure SPSU membrane matrix ($8.05 \times 10^{-3}$ S/cm), it is seen that the TIL ionic liquid doping significantly improves proton transport in all membrane series. Normally, hydration is the most important factor for the conductivity of Nafion commercial membranes. The conductivity increases linearly with the water content in Nafion based membranes and exhibits a maximum conductivity of $9 \times 10^{-2}$ S/cm at 100% relative humidity. In this study, the conductivity values of all TIL doped membranes are closer to this value even in anhydrous environment.

There are two main mechanisms that describe proton transport in proton conducting electrolytes: the Grotthuss mechanism and the vehicle mechanism. Generally, in ionic liquid doped composite membranes, the Grotthuss mechanism is expected to dominate the proton conduction. In the composite membrane structure, ionic liquids act as proton-conducting media, while the cation group of the ionic liquid interacts with the polymer matrix and then replaces the counter ions of the sulfonic acid group ($-SO_3H$). As a result, the anion group of the ionic liquid is attached to the polymer matrix [30]. This interaction creates a continuous proton transfer channel to improve conductivity. In the membrane series prepared within the scope of the study, it was observed that composite membranes prepared with Br-anionic ionic liquid (TIL-3) exhibited the highest proton conductivity values. According to the anion groups in the TIL-based ionic liquid structure, proton conductivities are also listed as $BF_4^- < CF_3O_3S^- < Br^-$. In addition to its thermal stability, the SPSU/TIL-3(1.0) composite membrane, with its superior proton conductivity in anhydrous environment, can be a good membrane electrolyte alternative under high temperature PEM fuel cell conditions.

### 3.4. Dynamic mechanical analysis (DMA)

Mechanical properties of SPSU-based membranes prepared within the scope of the present study were examined by dynamic mechanical analysis (DMA). The peak maximum in the tanδ curves obtained by DMA analysis represent the glass transition temperatures ($T_g$) of composite membranes. In Figure 7, the change in tanδ values of SPSU membranes is presented depending on the temperature.

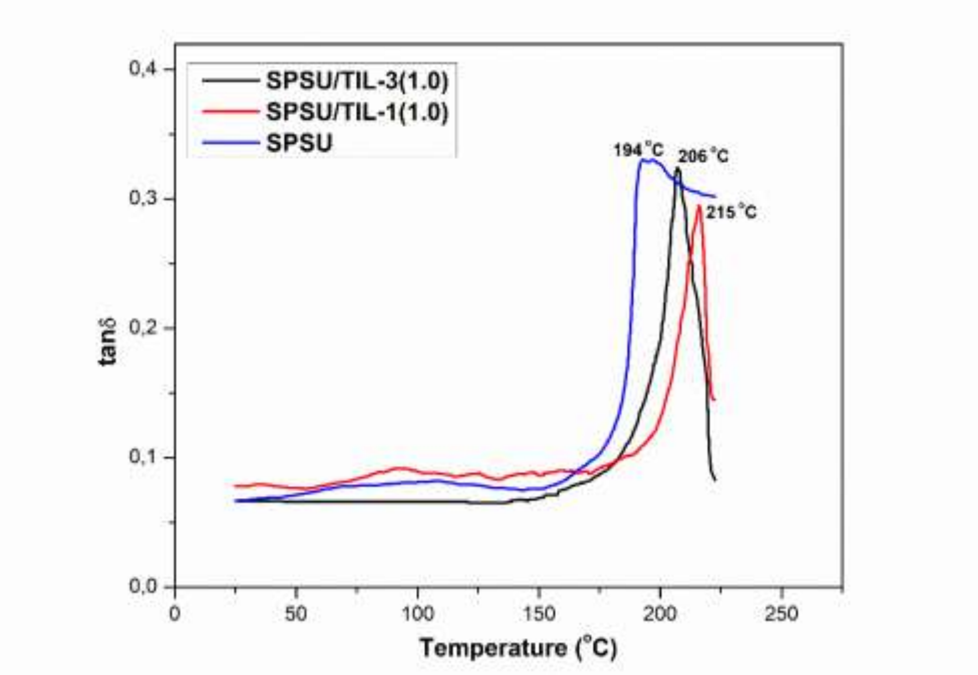

**Figure 7.** tanδ curves of SPSU, SPSU/TIL-1(1.0) and SPSU/TIL-3(1.0).

As seen in the figure, the maximum in tanδ curve of pure SPSU polymer matrix was observed at 194℃. This means, the glass transition temperature of the sulphonated polymer matrix with degree of sulfonation of 15% is 194℃ and this value is compatible with the values presented in the literature [31, 32]. While no significant changes were observed in the glass transition temperature with the ionic liquid addition, the glass transition temperatures were 215℃ and 206 ℃ for SPSU/TIL-1(1.0) and SPSU/TIL-3(1.0) composite membranes, respectively. Reducing the glass transition temperature with additional additives or processes in composite membranes causes an increase in molecular mobility and conductivity due to the increased amorphous character of the crystal structure. In contrast, this study shows that despite the slight increase in the glass transition temperature, proton conductivities in composite membranes are higher than pure SPSU polymer matrix. It is thought that the proton conduction pathways and electrostatic interactions created by TIL-based ionic liquid dopants are more dominant in proton conduction than molecular conduction arising from the chain mobility. When the glass transition temperatures of composite membranes are compared, it is seen that the glass transition temperature (206℃) of the SPSU/TIL-3(1.0) electrolyte with the highest proton conductivity values is lower than the glass transition temperature (215℃) of the SPSU/TIL-1(1.0) electrolyte. This behavior shows that the proton conductivity behaviors in composite membranes in the proton conduction mechanism are shaped by the increased chain mobility and molecular/electrostatic interaction in the polymer backbone [24, 31, 32].

## 4. Conclusions

In the present study, triazole based ionic liquid doped polymer composite membranes were evaluated for high temperature PEMFC systems. SPSU membrane matrix with 15% sulfonation degree (DS) was obtained by the sulfonation process of polysulfone (PSU) as an alternative aromatic polymer. Three different triazole-based ionic liquids (TIL-1, TIL-2 and TIL-3) were prepared for the composite membrane structure in order to improve proton conductivity in anhydrous conditions, and composite membrane series were formed by adding ionic liquids in different molar ratios (n:0.5; 1.0; 2.0).

As a result of TGA analysis, all triazole based ionic liquid doped membrane series exhibited thermally stable behavior for high temperature fuel cell applications. The glass transition temperature ($T_g$) of the SPSU polymer matrix was determined as 194 ℃. While there was no significant change in glass transition temperature with the addition of ionic liquid, $T_g$ values for SPSU/TIL-1(1.0) and SPSU/TIL-3(1.0) composite membranes were 215 and 206 ℃, respectively. Finally, proton conductivity measurements showed that the proton conductivity was greatly improved as predicted by the composite structures (8.05 mS/cm for SPSU; 58.1 mS/cm for SPSU/TIL-3(1.0)) and the obtained membranes could be a promising alternative in high temperature PEMFCs.

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## Author(s) Contributions

MY and ŞK performed test and analysis and wrote the article. Both authors read and approved the final version of the article.

## Conflict of Interest

The authors declare that there is no conflict of interest.

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