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RESEARCH ARTICLE

SYNTHESIS OF POLYMER ELECTROLYTE MEMBRANES BASED ON IONIC LIQUID DOPED SPEEK

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ABSTRACT

The sustainable and environmentally benign energy demand of the world has been increasing. Among the various options, proton exchange membrane fuel cell is an attractive choice for energy supply due to its high efficiency and application conditions without waste. In this research, triazole-based ionic liquid doped sulfonated polyether ether ketone (SPEEK) composite membranes were presented for proton exchange membrane fuel cell (PEMFC) applications. Composite membranes were prepared by incorporating 1,2,3-triazole-based ionic liquids (TIL 1-2-3) into poly(ether ether ketone) (PEEK) matrices. The mechanical, structural, and thermal properties of both composite membranes and the triazole-based ionic liquids were thoroughly characterized using dynamic mechanical analysis (DMA), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The performance and viability of composites for PEMFC applications that involve elevated temperatures were conducted by proton conductivity test across a broad range of temperatures (30-180 °C). High-temperature proton conductivity was measured as 1.73×10^{-2} S/cm for SPEEK/TIL-3(1.0). According to the proton conductivity test results, it was concluded that the composite membranes may exhibit improved performance in PEMFC applications due to increased proton conductivity values.

Keywords: Proton conductivity, Proton exchange membrane, Triazole, Ionic liquid, Polyether ether ketone

1. INTRODUCTION

The high dependence of traditional energy sources on fossil fuels has led to the emergence of energy demand and environmental pollution problems [1-3]. The ecological and economic issues resulting from the consumption of fossil fuels have increased the need for new technologies for energy production based on alternative energy sources. Polymer electrolyte fuel cells are a promising new technology for generating clean, efficient, and sustainable electricity. Due to these characteristics, the polymer electrolyte fuel cell is presented as an efficient and environmentally friendly energy source that eliminates the CO_2 emission problem of traditional internal combustion engines.

The membrane fuel cell contains a solid polymeric electrolyte that provides proton conductivity and separates the cathode and anode from each other [4]. The efficiency of a polymer electrolyte membrane fuel cell is mainly determined by its proton exchange capacity. PEM is a critical part of the fuel cell module designed for improved proton conduction performance. PEM should resist the harsh environment inside the fuel cell to provide efficient proton conduction. The good thermal, mechanical, and oxidation properties of PEM depend on its hydrophilicity [5]. Among widely used PEM for PEMFC, Nafion is the most preferred due to its high stability and proton conductivity. However, due to reasons such as high production costs and low proton transmission capacity at high temperatures, the need to evaluate alternative materials for PEM has arisen [6].

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Alternatively, aromatic thermoplastics such as polyether-ether-ketone (PEEK) are suitable for application as polymer electrolyte membranes owing to their thermal resistance, oxidation resistance, easy processing, and low cost. The sulfonation process could increase the conductivity of aromatic thermoplastics exhibited by protons. The sulfonated polyether-ether-ketones have superior structural properties than Nafion due to their hydrophilic structure and wide separation between -SO₃H groups. Although their hydrophilic capacity determines the proton conductivity of sulfonated polymeric membranes, they have high conductivity values for their aromatic structure in low humidity and high-temperature conditions [7]. The high sulfonation degree of aromatic thermoplastics provides high proton conductivity values (at s z 10^2 S/cm, 25 °C in fully hydrated media). On the other hand, the high sulfonation degree of aromatic membranes results in low structural stability and solubility [8].

In recent years, ionic liquids have drawn significant attention for their superior thermal, physical, and electrochemical characteristics, environmental safety, and low vapor pressure [9–11]. Ionic liquids are preferred in many application areas because they have adjustable cationic and anionic functions [12]. Combining anion-cation pairs with a wide variety of physicochemical and electrochemical properties increases the diversity of synthesized ionic liquids. The most preferred anion groups for ionic liquid synthesis are tetrafluoroborate (BF4-), hexafluorophosphate (PF6-), trifluoromethane sulfonate (CF3SO3-), and cation groups are imidazole and pyridine [13, 14].

The application of imidazole-based ionic liquids as electrolytic material in PEMFCs has been investigated owing to its enhanced conductivity and cell performance. Triazole-based ionic liquids are believed to be an alternative to imidazole since they have high thermal stability because of intense hydrogen bonding in their structures. 1,2,3 triazole-based ionic liquids have high stability, variety, and versatility of polymer design. Triazole-based ionic liquids obtained from appropriate anion-cation combinations, demonstrate a significant potential for utilization in proton exchange membrane (PEM) applications [15, 16].

In the present study, ionic liquid-based polymer composite membranes with high thermal resistance were produced for use in PEMFC systems. PEEK polymer matrix was sulfonated to have SPEEK structure as an alternative polymer electrolyte membrane. The proton exchange membrane was prepared by doping 1,2,3 triazole-based ionic liquids at varying mole rates. The structure of synthesized ionic liquids was analyzed. The proton conductivity of composites was measured between 30-180 °C, and their conformations in thermal-resistant fuel cell systems were evaluated.

To the best of our knowledge, there is limited research on producing composite materials comprising triazole-based polymer electrolyte membranes. This current investigation introduces a novel composite material with the potential for application as a proton exchange membrane in thermally resilient fuel cell systems.

2. MATERIALS and METHOD

2.1 Materials

Polyether ether ketone (PEEK) polymer matrix, copper sulfate, silver tetrafluoroborate, sodium ascorbate, butyl alkyne, and n-butylazide were obtained from Merck. Methyl trifluoromethane sulfonate, trimethylsilyl chlorosulfonate, diethyl ether, and ethyl acetate were obtained from Merck-Millipore. All reagents were used as reagent grade.

2.2 Synthesis of Ionic Liquids

Briefly, the synthesis method of ionic liquids involved combining n-butylated, sodium ascorbate, copper sulfate, and butyl alkyne in methanol, followed by the addition of water and extraction with ethyl acetate.

The organic phase was subjected to purification steps, including brine washing and reduction of water content. The resulting oily phase containing 1,4-di(n-butyl)-1H-1,2,3-triazole was further reacted with methyl trifluoromethanesulfonate to yield 3,5-dibutyl-1-methyl-3H-1,2,3-triazolium trifluoromethanesulfonate (TIL-1) [17].

The subsequent synthesis procedures for TIL-2 and TIL-3 were described in our previous study [18].

2.3 Synthesis of SPEEK/TIL-(1-3) Composites

Sulfonated polyether ether ketone was produced by the sulfonation process to be used in the synthesis of SPEEK/TIL-(1-3) composite membranes. Initially, a specific quantity of anhydrous pure polyether ether ketone was solubilized in H_2SO_4 . The red-colored viscous solution resulting from the sulfonation process was carefully added drop by drop into a mixture of 1 L of distilled water and ice to ensure the completion of the reaction while effectively dissipating the heat released during the process. The sulfonated polyether ether ketone was produced in the form of small droplets. Then, any excess sulfuric acid on the surface of the synthesized SPEEK polymer droplets was rinsed off using distilled water. The polymer matrices were dried in an oven at 65°C for a certain time. An appropriate amount of SPEEK was measured and dissolved in a suitable solvent (NMP) to prepare composite membranes with added triazole-based ionic liquid. The mixture was then stirred for 2 hours. Equimolar (n: 1.0) ionic liquids to the sulfonic acid groups in the structure were added to the resulting solution and agitated for 3 hours. The mixtures were transferred to glass petri dishes for solvent removal, and composites were obtained after 48 hours at 40°C.

The SPEEK matrix composite membranes prepared in the study are labeled with the notation SPEEK/TIL-'X'(n); where 'X' corresponds to the ionic liquid type and 'n' corresponds to the ionic liquid/HSO₃ mole ratio.

2.4 Characterizations

The structure determination of the ionic liquids and proton exchange membranes synthesized in the study was performed with the Fourier Transform Infrared Spectroscopy characterization method through wavelengths between 500-4000 cm⁻¹. The degradation temperatures of the polymer electrolyte membranes were determined with the Thermogravimetric Analysis (TGA, SEIKO TG/DTA 6300) method between the range of 25°C to 800°C. Mechanical features were determined by Dynamic Mechanical Analysis over a wide temperature range. Proton conductivity (σ) assessments were conducted using an Agilent 4284A LCR Meter system. These measurements were conducted over a frequency spectrum spanning from 40 Hz to 1 MHz and within a temperature range spanning from 30 °C to 180°C. In preparation for these measurements, membrane samples were appropriately dimensioned and then coated with silver paste to establish electrodes on their surfaces.

3. RESULTS and DISCUSSION

3.1. Elemental Analysis and Fourier Transformed Infrared Spectroscopy (FTIR)

FT-IR analysis was performed as a preliminary characterization to determine the molecular structure of materials and the structural interactions of these materials with each other. Firstly, prepared ionic liquids were characterized with elemental analysis and FTIR spectroscopy. C, H, and N ratios of TIL-1, TIL-2, and TIL-3 were presented in Table 1.

Ionic liquid	Theoretical			Elemental Analysis			Yield (%)	Molecular
	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)		Weight (<i>g mol</i> ⁻¹)
TIL-1	41.74	6.38	12.17	41.87	6.34	12.21	99.1	345
TIL-2	48.85	7.46	14.25	47.94	7.46	14.34	97.9	294.8
TIL-3	57.94	7.38	11.93	53.16	7.19	14.23	92.8	352.1

Table 1. Theoretical and experimental C, H, N ratios of ionic liquids

The bands observed at 1048 cm⁻¹ and 1192 cm⁻¹ in the FTIR spectrum of TIL-2 ionic liquid are attributed to BF4⁻ anion and C-N & C-H bonds, respectively (Figure 1). Characteristic broad bands of NH stretching vibrations of ionic liquid structures were observed at 3360 cm⁻¹. The absorption peaks at 720 cm⁻¹ and 1633 cm⁻¹ denote the bending in the C-H bonds and C=N tensions. The peak observed at 1400 cm⁻¹ ascribed to C=C to aromatic stretching vibrations [19, 20].



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

The broad spectral peak of sulfonated polyetheretherketone (SPEEK), derived from polyetheretherketone (PEEK) through sulfonation, is observed at 3400 cm⁻¹ (Figure 2). The presence of this distinctive peak can be attributed to the vibrations of hydroxyl (OH) groups within the sulfonic acid groups. The vibration bands of all composite samples and sulfonated polymer matrix at 1023 cm⁻¹ are due to S-O tensions. Also, the bands at 1080 and 1223 cm⁻¹ confirmed S=O and O=S=O stretching forces formed, respectively [20]. Observations revealed that the broad peaks associated with the hydroxyl (OH) groups of TIL molecules exhibited partial narrowing. The observed phenomenon can be defined by the interaction between TIL structure and sulfonic acid molecules in the polymer matrices, leading to a reduction in the concentration of hydroxyl (OH) groups. The presence of peaks detected at

3066 cm⁻¹ approved the tension of C-H bonds originating from the aromatic rings. The absorption bands observed at 1595 cm⁻¹ were associated with the presence of the triazolium cation within the composite membrane structures. Fourier Transform Infrared Spectroscopy characterization confirmed the successful production of all the samples in the present work [20, 21].



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

3.2 Thermogravimetric Analysis

The temperature resistance of the composite polymer membranes synthesized in the present work was characterized by TGA. Since polymer electrolyte membranes were synthesized for high-temperature fuel cell applications, they should have elevated temperature resistance. The TGA curve shows that the type of TIL structure has a significant effect on the degradation temperature of the final PEEK polymer.

In the Figure 3, the pristine polyether ether ketone structure has a single-step thermal degradation above 600°C. On the other hand, sulfonated polyether ether ketone structure and polymer electrolytes obtained by sulfonation indicated multiple degradation stages. The primary thermal degradation behavior under 100 °C is attributed to the evaporation of water attached to the membrane structures. The first degradation step of composite membranes and SPEEK polymer matrix at 150-200°C is on account of the degradation of the sulfonic acid group in the polymer structures [20, 22].

As observed in Figure 3, the thermal stability of the composite membranes is close to the thermal stability of the neat SPEEK polymer matrix. While SPEEK/TIL-1(1.0) and SPEEK/TIL-2(1.0) composite membranes exhibited poor performance due to both the removal of water at low temperatures and earlier degradation, the first degradation step of the SPEEK/TIL-3(1.0) membrane after the removal of water occurred at higher temperatures than the SPEEK membrane. Thermal resistance was slightly increased by the incorporation of TIL-3. While all composite membranes are effective at low temperatures, SPEEK/TIL-3(1.0) composite membrane is quite suitable for electrochemical processes at high temperatures (>200°C).



Figure 3. TGA curves of PEEK, SPEEK, SPEEK/TIL-1, SPEEK/TIL-2 SPEEK/TIL-3 composite membranes.

3.3 Proton Conductivity

Proton conductivity of SPEEK/TIL composite synthesized in this work was performed and the analysis results were determined by Equation 1.

$$\sigma = \frac{L}{RA} \tag{1}$$

The conductivity (σ) of the membrane is determined by its thickness (L) and the cross-sectional area (A) of the membrane. In Figure 4, The temperature variation is used as a parameter to present the proton conductivities of composite membranes fabricated using SPEEK.



Figure 4. Temperature-dependent proton conductivity values of SPSU/TIL-(1-3) composite membranes.

It has been noted that the proton conductivity of composites doped with SPEEK and TIL decreases as the temperature increases in the absence of water, and this result is consistent with previous studies [20, 23, 24]. It is known that the conductivity of SPEEK matrix may decrease due to the crosslinking of -SO₃H groups at high temperatures. Furthermore, the decrease in conductivity can be attributed to the evaporation of the water in the polymer matrix and the TIL structure. The sulfonic acid groups of the sulfonated polyether ether ketone matrix exhibit insufficient conductivity and even become virtually inert under anhydrous conditions. Compared to the pure sulfonated polyether ether ketone polymer matrix, the proton conductivity of the composites increased with the contribution of TIL (1-3) under anhydrous conditions. The conductivity values for the SPEEK polymer matrix were measured in the range of 4.05×10^{-5} - 7.41×10^{-5} S/cm and within the determined temperature range. The incorporation of TIL into the matrix, contributed to the improvement of ionic mobility and thus facilitation of proton transfer across polymeric membranes [25]. Additionally, it is anticipated that TIL will create pathways for proton conduction within the composites, resembling the role of water in hydrated proton exchange membranes. [26]. The conductivity values for TIL-1 and TIL-2 doped composites were very close, and the maximum measured proton conductivity rate of composites was approximately $5x10^{-3}$ S/cm. The highest proton conductivity value was observed as 1.73 x 10⁻² S/cm for SPEEK/TIL-3(1.0). The result demonstrated that TIL-3 doped membranes exhibited higher conductivity values, indicating their potential as a viable substitute for electrochemical applications.

3.4 Dynamic mechanical analysis (DMA)

The DMA method was employed to evaluate the mechanical behavior of sulfonated polyether ether ketone composites in the conducted study. The peak values of the graph produced by dynamic mechanical analysis exhibited the glass transition temperature (Tg) of the composites. Figure 5 presents the temperature-dependent changes in tand values for both the SPEEK polymer matrix and the SPEEK/TIL-3(1.0) composite membrane. The increase in chain mobility of the polymer matrix creates electrostatic interactions between TIL and SPEEK structures, improving proton conductivity. The figure shows that Tg of the pure SPEEK membrane was measured as 172°C. However, the incorporation of TIL-3 ionic liquid resulted in a reduction in the glass transition temperature (Tg) of the membrane, which was measured to be 190°C. This change in Tg trends of pure SPEEK and TIL-doped composite membranes is consistent with the literature [20, 27, 28]. This decreasing trend is explained by the molecular Brownian motion that starts in the polymer structure due to Tg value [29, 30]. The decrease in the glass transition temperature (Tg) of the composite membrane, induced by different additives or treatments, leads to enhanced versatility and conductivity of molecules. This effect is attributed to the transformation of the crystalline structure into an amorphous structure. The electrostatic interactions between the TIL and SPEEK chains increase due to the mobility of the polymer matrix, and thus, the proton conductivity is further improved [31]. The storage (E') and loss (E") modulus of SPEEK-2 and SPEEK/TIL-3(1.0) electrolytes were presented with DMA plots in Figure 5b. As illustrated in the figure, the storage modulus (E') and loss modulus (E") values of the pure SPEEK membrane exceeded those of SPEEK/TIL3-(1.0). This result can be attributed to the plasticizing influence exerted by the presence of the ionic liquid (TIL3) within the composite membrane. The TIL3 ionic liquid has the capacity to enhance the mobility of polymer chain segments by reducing the viscosity of the composite membrane. Specifically, the storage moduli for the SPEEK and SPEEK1.0-2 composite membranes were determined to be 1.7 GPa and 1.3 GPa, respectively. In the context of sulfonated polymers and ionic liquid-doped sulfonated polymers reported in previous studies, it is evident that the SPEEK and SPEEK/TIL3-(1.3) electrolytes exhibit reasonable maximum stress levels at elevated temperatures.



Figure 5. a) tanδ curves of SPEEK and SPSU/TIL-3(1.0). b) The storage (E') and loss (E'') modulus of SPEEK and SPEEK/TIL-3(1.0) electrolytes

4. CONCLUSION

This study carried out three different ionic liquid syntheses based on triazole and ionic liquid doped sulfone polyether ether ketone synthesis. Composite electrolytes were prepared, including different ratios of ionic liquids to the SPEEK matrix obtained by the sulfonation process of PEEK polymer. Proton conductivity of sulfonated polymer matrices is greatly improved by ionic liquid doping. The proton conductivity of the SPEEK/TIL-3(1.0) composite electrolyte was determined as 1.73×10^{-2} S/cm). The polymer composites produced in this study have demonstrated their potential as alternative materials suitable for high-temperature PEM fuel cells. The thermal stability of the composites exhibited satisfactory ionic conductivity and temperature resistance under cell conditions (>200°C).

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Şeyda Karadirek: Formal analysis, Investigation, Writing - original draft, Visualization, Conceptualization. Mesut Yılmazoğlu: Formal analysis, Investigation, Writing - original draft, Visualization, Conceptualization.

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