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Research Paper

Preparation and Physical Characterization of Sulfonated Poly (Ether Ether Ketone) and Polypyrrole Composite Membrane

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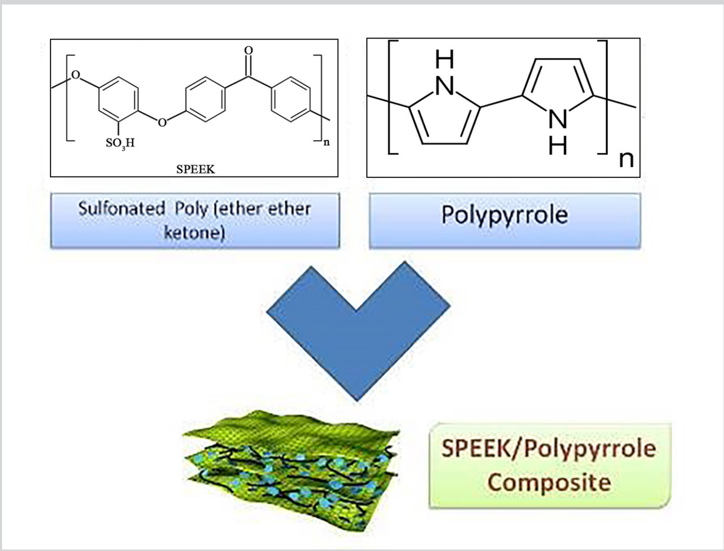
Highlights

- Synthesis of Polypyrrole with ferric chloride
- Sulfonation of poly (ether ether ketone) by sulfuric acid
- Composite of SPEEK/PPy with different ratios

Graphical abstract



Abstract

Sulfoanted poly(ether ether ketone) membranes were prepared by the sulfonating agent sulfuric acid. These membranes were modified by incorporating conducting polymer polypyrrole in order to increase the ionic conductivity and reduce the methanol transmission rate. The modified composite membranes were then compared on the basis of ionic conductivity, methanol transmission rate and thermal stability. Results indicated that the new membranes were thermally stable up to 300ºC and gave moderate ionic conductivity. Consequently, composite membranes show less water uptake and swelling. The composite membranes were then characterized by FT-IR spectroscopy, Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA), and ionic conductive properties were evaluated by Electrochemical Spectroscopy Impedance.

1. Introduction

Nowadays the research on renewable energy has been gained lots of attention due to increasing power demand, depletion of fossil fuel, and its rising price and environmental problems. Among the various renewable energy source, fuel cells have been become more popular due to their high-energy efficiency, near zero emission and variety of applications. A fuel cell converts the chemical energy into electrical with the help of electrolyte membrane [1]. Therefore, the electrolyte membrane is the heart of a fuel cell system. The role of the membrane between the electrodes is the conduction of produced proton from anode to cathode and acting as a barrier to crossover of fuel [2], [3]. Recently, the Nafion membrane has widely been used as PEM (proton exchange membrane) developed by Dupont, which exhibits excellent chemical and electrochemical stability as well as high proton conductivity at low temperature. However, the high cost, the low conductivity at high temperatures and the high methanol transmission rate across the PEMs are most important challenges that limit the use of Nafion membranes for DMFC (direct methanol fuel cell) [4]. In consequence, there are many materials studied for the development of alternative more economical non-perfluorinated PEMs.

In this work, a sulfonated poly(ether ether ketone)/polypyrrole (SPEEK/Ppy) composite membrane is investigated. Sulfonated PEEK is a low cost polymer which exhibits high thermal stability, mechanical strength, easy to handle and moderate proton conductivity. A validity of SPEEK membrane more than several thousand hours under fuel cell conditions was reported in the literature [5], which also demonstrated the microstructure advantages of SPEEK over Nafion as the PEM in DMFCs [6]. To increase the conductivity of the material, and reduce the methanol transmission rate the SPEEK support membrane is doped with a conductive polymer, in this case polypyrrole. It is already known that polypyrrole has been used to modify the Nafion

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membranes so they can be used in DMFCs [7].

Polypyrrole was reported to have high catalytic activity for the methanol oxidation and the Nafion/polypyrrole composite membranes showed extremely low methanol permeability [7–11]. Polypyrrole presents good environmental stability and it is chemically extremely resistant, being insoluble in many organic solvent. Compared with other polymers, Ppy has a high surface energy, also good electro-conductive and acid–base properties [12–14]. The synthesis of polypyrrole and sulfonation of PEEK and characterization of the new SPEEK/Ppy composite membrane are presented in this paper. The new material was characterized by FT-IR spectroscopy, TGA, DSC, water vapor transmission rate and the ionic conductive properties were evaluated by Electrochemical Impedance Spectroscopy.

2. Experimental

2.1. Materials

The raw materials used for this study of PEEK (KetaSpire KT-880 NL) was obtained from Solvay Specialty polymers. Sulphuric acid (98% abt) LR, *N*,*N*-dimethylformamide LR were obtained from S.D. fine-chem limited. Ferric chloride and Pyrrole extrapure purchased from SRL Pvt. Ltd.

2.2. Synthesis of polypyrrole

Polypyrrole was synthesized by chemical polymerization of pyrrole. Ferric chloride used as dopant as well as the oxidant. Pyrrole (0.01M) was taken in 25ml distilled water and ferric chloride FeCl3 (0.03M) was dissolved in 75 ml distilled water. The solution of pyrrole stirred one hour. After an hour dopant and oxidant solution of ferric chloride added drop wise to the pyrrole solution with vigorous stirring. The whole reaction carried out at 20ºC for four hours at stirring speeds 500 rpm. After addition of oxidant the solution turned black, indicating the onset of polymerization. The resulting black powder was filtered and washed abundantly with water, then with methanol, until the washings were free of any $FeCl_3$ solution color. The polymers were then dried in vacuum at 80°C for six hours.

2.3. Sulfonation of SPEEK

Concentrated sulfuric acid (98%) was used as the sulfonating agent. 5 g of PEEK was gradually added to 50 mL sulfuric acid in a three-necked round-bottomed flask. The flask was fitted with a mechanical stirrer. The reaction was carried out at room temperature for the 48 hrs while being vigorously stirred. The dissolved PEEK was a dark red, highly viscous solution. The sulfonation reaction was terminated by precipitating the polymer in cold water. The precipitated SPEEK formed white noodle-like strands. These were soaked in distilled water overnight and washed until the pH was neutral. The SPEEK polymer was dried at room temperature overnight and then in an oven at 60 °C for 24 hrs. For the preparation of SPEEK/PPy composite membrane.

2.4. Preparation of composite membrane

Composite of SPEEK/PPy membranes were prepared by solution casting using solvent evaporation technique. Solution was prepared by dissolving SPEEK in DMF to make 20 %w/v solution and stirred about 2 hrs. Then 5 wt% PPy added to the solution and stirrer overnight in order to obtain complete homogenization mixture at ambient temperature. The resulting solution was then cast onto a glass plate (Petri dish), dried about 80ºC in an oven for 8 hrs to remove the solvent, and annealed at 100ºC for 4 hrs. After cooling to room temperature, the resultant membrane was peeled from the glass in distilled water.

2.5. The Characterizations of membrane samples

2.5.1. Fourier Transform Infra-Red Spectroscopy Analysis (FTIR)

The synthesized samples along with raw material were analyzed using an OPUS-ALPHA Spectrum One spectrometer. The transmission mode was used to obtain the IR of the samples. The scan range used was 4500 cm^{-1} to 500 cm^{-1}. The FTIR of SPEEK/PPy composite was done to confirm expected structure of composite membrane.

2.5.2. Ion exchange capacity

IEC is a measure of the number of counter ions exchangeable in SPEEK membrane. IEC is defined as the milliequivalents of H^+ per weight of the dry polymer. The prepared SPEEK membranes and composite membrane were stored in 1 M HCl for 24 hrs to bring the sample into complete SPEEK-H^+ form. Membranes were then rinsed in DI water and equilibrated in 1 M NaCl solutions for three days to completely exchange the cations and achieve SPEEK-Na+ form. The ion exchange capacity was measured using the back-titration method as described in several previous paper[15],[16]. The NaCl solution was back titrated with 0.1 M NaOH using phenolphthalein as an indicator to determine the cations exchanged. The IEC was calculated as the ratio of total charge by dry weight of the membrane sample [17].

$$IEC = AB/m\ dry \tag{1}$$

where *A* is the concentration of the NaOH solution used, *B* is the volume of NaOH solution consumed in the titration and *m* dry is the dry weight of the membrane.

2.5.3. Water uptake and Swelling ratio

The samples was cut approximately 2 cm × 2 cm were dried in an oven at 60 ºC overnight and then weighed and measure the dry weight and dry length. These samples kept in distilled water for 24 hrs after that wet weight and wet length determine. The water uptake and swelling ratios were determined by the following equations.

$$\text{Water uptake} = [(\text{wet weight} - \text{dry weight})/\text{dry weight}] \times 100\% \tag{2}$$

$$\text{Swelling} = [(\text{wet length} - \text{dry length})/\text{dry length}] \times 100\% \tag{3}$$

2.5.4. Methanol Transmission Rate

The methanol transmission rate was determined by using a cell basically consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol 1M was placed on one side of the cell and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using a NETEL Chrome Lite GC 3000A chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol transmission was calculated according ref.[18]

2.5.5. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurement was performed using (Q 100 DSC, TA instruments Ltd., India) under flowing N_2 with about 1 to 5 mg of polymer for each thermogram determination. This Characterization was done to investigate the glass transition (T_g) behavior of the samples.

2.5.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of sample was carried out by loading between 5–10 mg of a sample into a pan and placing into a SDT Q600 from TA instrument. TGA was done to study the thermal stability of the sample.

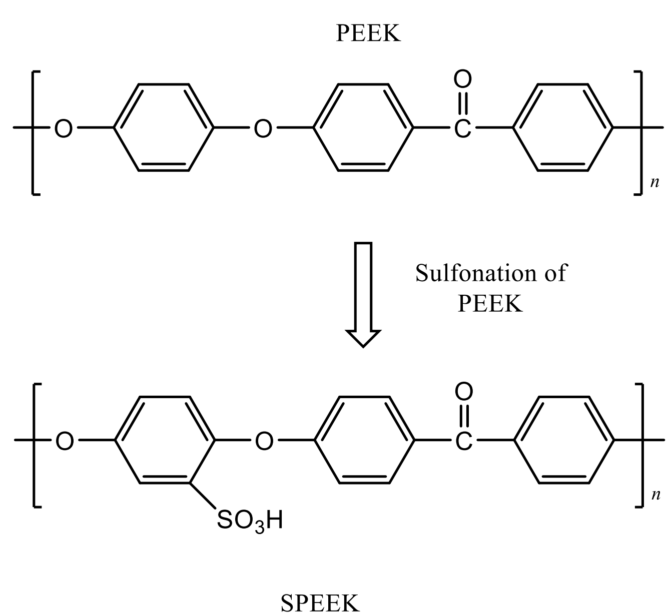

Fig. 1. Schematic representation of sulfonation of PEEK.

2.5.7. Ion Conductivity

Electrochemical impedance spectroscopy (Versa studio v 1.33.3462 AMETEK) was done to determine the impedance of sample. The resistance of sample was measured at room temperature by 1M NaCl in a frequency range from 10 to 100 kHz with an oscillating voltage of 10mV amplitude, then sample resistance based on the electrical resistance measurement, the conductivity (Scm^{-1}) was calculated according to Equation.

$$\sigma = L/(Rmem)A \quad (4)$$

where, Rmem is the resistance of sample, L is the thickness of sample (cm), and A is the effective area of the sample (cm).

3. Results and discussion

The SPEEK/PPy composite membrane was prepared by solution casting method. Due to the presence of polypyrrole in composite structure which can impose good thermal and chemical stability and resistance, the resultant composite material is insoluble in many organic solvents. The solution was cast onto a glass plate (petri dish) to obtain the SPEEK/Ppy composite membrane samples. In this paper, the membranes obtained with different weight ratios of the polypyrrole to SPEEK (5, 10 and 15%), are named SPEEK/Ppy-5, SPEEK/Ppy-10 and SPEEK/Ppy-15, respectively.

3.1. FTIR analysis

The C=C stretching of the benzene ring appears at 1500–1400 cm^{-1}. The peaks at 1305 and 1643 cm^{-1} are induced by C-N and C=N stretching, respectively. As could be observed in Figure 2,with increasing the PPy content , the intensity of the absorption increased, which confirms the trend of the weight ratio of PPy in SPEEK membranes. The absorption bands at 1070 and 1044 cm^{-1} in the composite membranes can be referred to asymmetric and symmetric O=S=O stretching vibrations of the sulfonated groups. However, the related vibrations for the sulfonated groups in SPEEK are shown at 1070 and 1012 cm^{-1}.

3.2. Ion exchange capacity

The ion exchange capacity of the SPEEK/Ppy sample decreased after the addition of PPy particles into SPEEK matrix. The IEC of SPEEK is 1.42 meq/g, whereas, SPEEK/Ppy composite membranes show the IEC of 1.12, 1.04 and 0.98 meq/g, respectively, with the weight content of PPy increasing from 5 to 15%. However, the composite membrane shows decreasing trend of IEC. This can be considered as the incorporation of polypyrrole into the SPEEK matrix, resulting in the restricted mobility of the ionic clusters. The direct incorporated PPy in the SPEEK makes the structure of membranes more compact.

3.3. Water Uptake and Swelling Ratio

The water uptake and swelling ratio both have decreased as the PPy loading increased in the membrane composite. Results indicated that the SPEEK/PPy composite membranes exhibit lower water uptake when compared to the pure SPEEK sample. As could be observed in Figure 3, the water uptake for SPEEK was 29 %. While the PPy content increased in the SPEEK membrane, the water up reduced up to 17%. As could be observed in Figure 4, the swelling ratio decreased in the SPEEK due to the introduction of more PPy content. This can be due to the compact structure of the SPEEK/PPy composite membrane.

3.4. Methanol transmission rate

The membrane based on the SPEEK/PPY composite structure, in which conducting species, can be introduced into the polymer, which reduces methanol transmission rate, significantly. The PPy particles tighten the pores of the polymer, which inhibit the molecular migration of unwanted species through the membrane. It is observed that the increase of the PPy content in the SPEEK matrix the methanol transmission rate of the composite membrane decreasing SPEEK membrane shows 11.2×10^{-7} at room temperature whereas, the composite membranes, which contain 5, 10 and 15 wt% of Ppy particles show methanol transmission rate 6.82×10^{-7}, 4.92×10^{-7}, 3.20×10^{-7}, respectively.

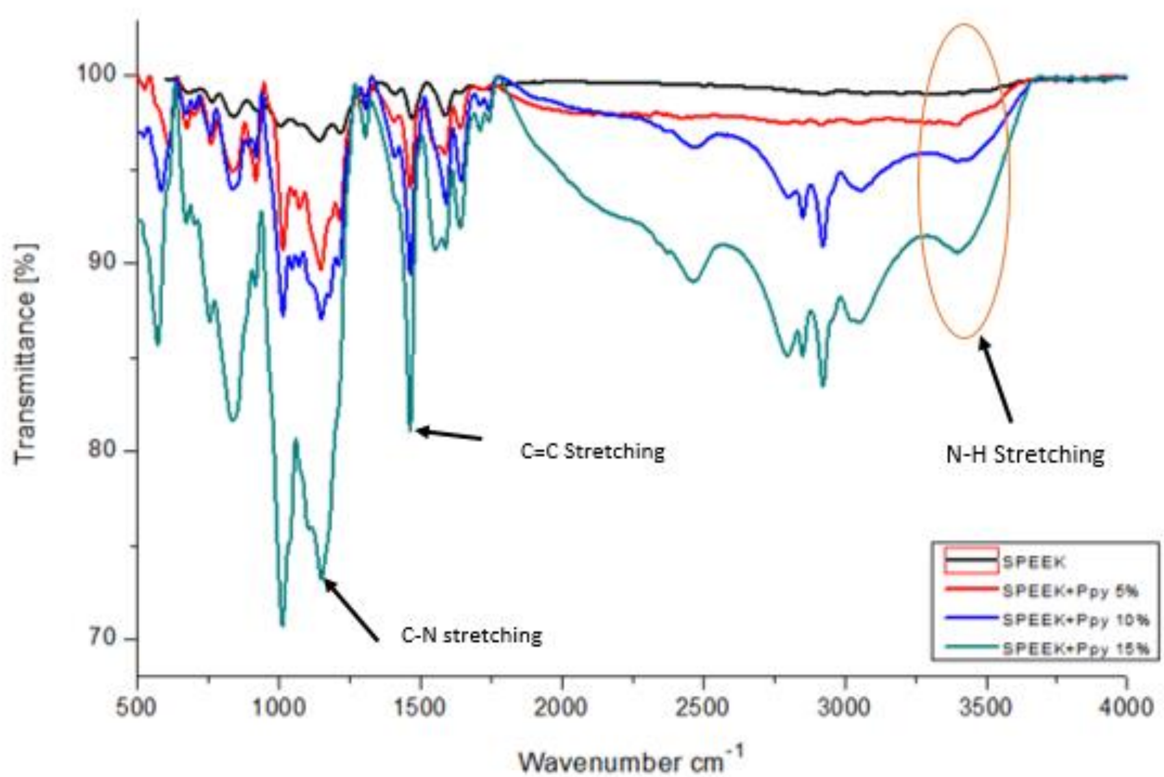

Fig. 2. FTIR spectrum of composite membrane.

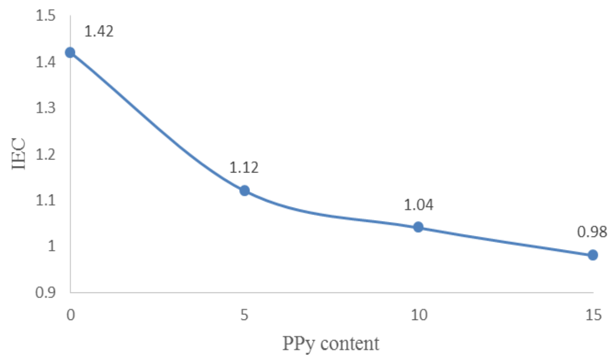

Fig. 3. IEC of composite membrane.

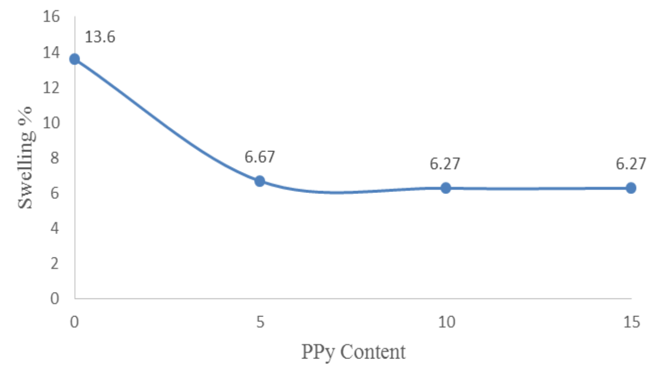

Fig. 5. Swelling ratio of composite membrane.

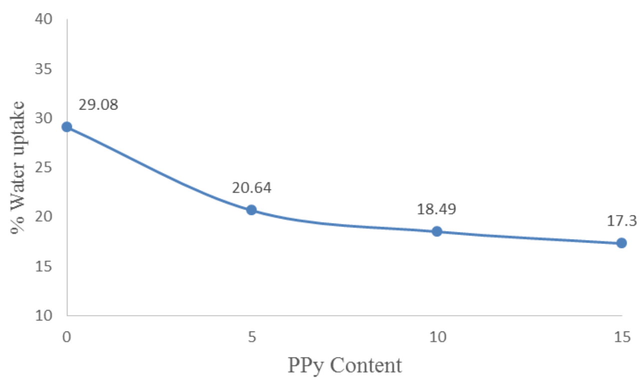

Fig. 4. Water uptake of composite membrane.

3.5. Differential scanning calorimetry (DSC)

This Characterization was done to investigate the glass transition (T_g) behavior of the composite membrane. The endothermic peak shapes of the DSC curves are similar with the literature [19]. As could be observed, the endothermic peak is the T_g of the composite membrane, wherein SPEEK was about 192 °C. After incorporation of conductive polymer polypyrrole in the SPEEK membrane, the composite membrane shows significantly increase in T_g. The T_g of the SPEEK/PPy composite membrane was measured at 229, 234, 244 ºC, respectively.

3.6. Thermogravimetric analysis (TGA)

TGA of the composite membrane shows the thermal stability of the membrane. All the composite membranes contain two weight loss step. The first one at about 250–300ºC, which is associated with the decomposition of sulfonic functional group of the SPEEK. The second weight loss step at about 350-400ºC corresponds to the decomposition of the main polymer chain. The composite membranes and SPEEK membrane are all stable at about 300ºC, which is acceptable for proton exchange membranes. In addition, SPEEK lost about 50 wt% at 444ºC after thermal decomposition, while the SPEEK/PPy composite membranes lost only about 30% at the same temperature.

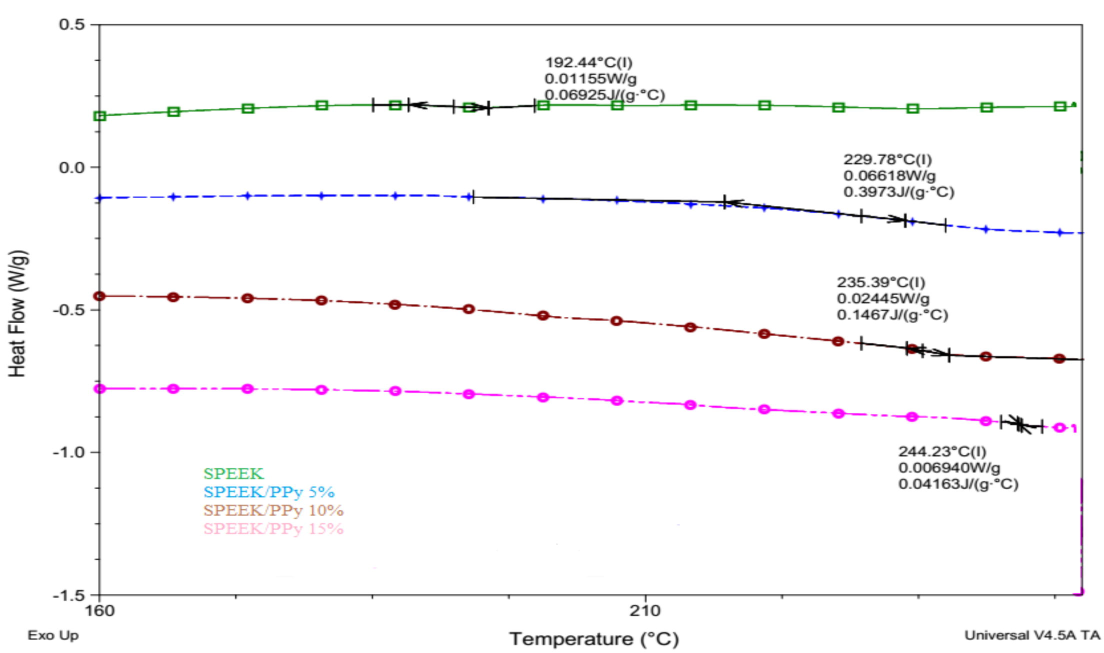

Fig. 6. DSC of composite membrane.

Table 1
Methanol transmission rate of composite membrane.

Membrane	Methanol Transmission Rate 10^{-7} (cm^2/sec)
SPEEK	11.2
SPEEK/PPy 5%	6.82
SPEEK/PPy 10%	4.92
SPEEK/PPy 15%	3.2

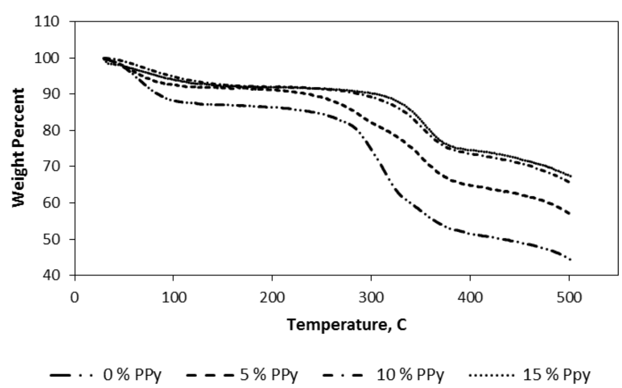

Fig. 7. TGA of composite membrane.

In case of SPEEK membrane, TGA shows three stages of degradation with the increase in temperature. In Figure 7, first weight loss in the SPEEK membrane occurred at 87 ºC due to loss of absorbed water molecule. Second weight loss in the temperature region 287 ºC was due to the de-sulfonation process. Third weight loss in the temperature region 311 ºC was due to the decomposition of main chain of the polymer. SPEEK membrane shows 50% loss at 444 ºC. The curve of the SPEEK/PPy membrane showed broader weight loss step in comparison with the pure SPEEK membrane. This suggests that the incorporation of PPy can suppress the decomposition of the polymer chain. Veenit et. al reported that the decomposition temperature of polypyrrole showed two stage pattern 261 and 491 ºC [20].

Table 2
TGA weight loss of composite membranes.

Composite Membrane	10% wt loss Temperature (ºC)	20% wt loss Temperature (ºC)	30% wt loss Temperature (ºC)	Glass Transition Temperature (ºC)
SPEEK	86	287	341	192
SPEEK/PPy 5%	245	318	362	229
SPEEK/PPy 10%	291	354	463	234
SPEEK/PPy 15%	322	364	491	244

3.7. Ion Conductivity

In this work, the impedance of the composite membrane was observed through-plane conductivity. The impedance was measured by taking 0.1 M NaCl solution. As the PPy content increased, in the composite membrane the resistance also increased. The SPEEK/PPy 15% was high resistance 1.22 Ω/cm and the composite membrane SPEEK/PPy 5%, SPEEK/PPy 10%, and SPEEK shows 0.476, 0.339, 0.215 Ω/cm, respectively. When the polypyrrole content increases, the ionic conductivity of composite membranes decreases. This phenomenon can be explained based on two factors first. First, the decreased mobility of the ionic clusters despite the swell of clusters, and second, the dense structure by an ion-dipole interaction between the polypyrrole and SPEEK. Figure 8 shows the ionic conductivity of the composite membrane graph we can see that the as polypyrrole content increase in the SPEEK matrix the ionic conductivity reduced drastically. The 10% polypyrrole loading in SPEEK composite found intermediate conductivity.

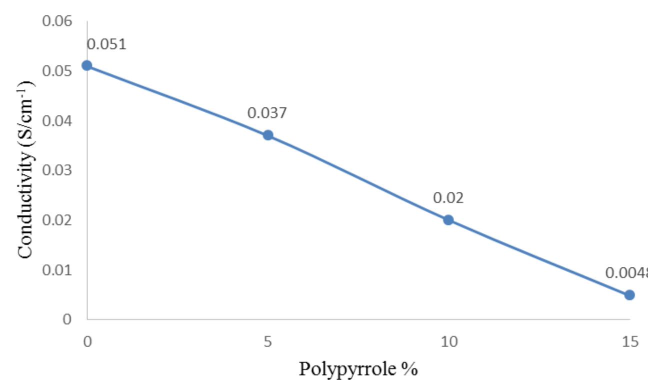

Fig. 8. Ion Conductivity of Composite Membrane.

4. Conclusions

SPEEK/PPy composite membranes with various weight ratios were prepared by solution casting method. The effect of PPy on the properties of composites was evaluated by FTIR, water uptake, IEC, and ionic conductivity. Thermal stability determined by DSC and TGA. In this paper, SPEEK/PPy 10% shows the intermediate properties with low water vapor transmission rate and moderate ionic conductivity as well as thermally stable up to 300ºC. The water uptake and swelling reduced drastically as the PPy loading increase in the SPEEK matrix. The above facts make that the SPEEK/PPy 10% composite membrane are the attractive candidate for proton exchange membrane.

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