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PREPARATION AND CHARACTERIZATION OF BROMINATED POLYPHENYLENE OXIDE MEMBRANES

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Abstract

In present research work, three different ratios of brominated polyphenylene oxide (BPPO) membranes were prepared by mixing with dimethyl form amide (DMF) as a solvent with the help of magnetic stirrer. The possible structure of membrane was determined by using Fourier-Transform Infrared spectroscopy (FT IR). In addition, the ion exchange capacity of each membrane was investigated by Mohr titration method. The resistance of the membrane was determined by Multimeter at the Department of Physics, Mandalay University. The morphology of the membranes was studied by Scanning Electron Microscopy (SEM). The solubility of each membrane was determined by dipping the membrane in various solvents such as water, ethanol, chloroform, distilled water and sodium hydroxide. The characteristic peak C-Br of membranes appeared at 1018.15 cm^{-1} was determined by FT IR spectroscopy. In addition, the ion exchange capacity measurement informs that 45 % BPPO membrane gives 1.48 mmol/g which is in agreement with the anion exchange membrane (AEM) membrane that can be used for fuel cell. The resistance of the membrane was determined by Multimeter and 45 % brominated (BPPO) membrane showed the suitable resistance value of 6 MΩ before immersing in 1 M NaOH solution as well as it shows 4.5 MΩ after immersing in 1 M NaOH solution. Furthermore, the swelling ratio of 45 % BPPO membrane indicates that informs the more ion exchange group corresponds to greater swelling ratio and high solubility.

Keywords: membrane; morphology; poly phenylene oxide; resistance; characterization

Introduction

Poly (p-phenylene oxide) or poly (p-phenylene ether) (PPE) is a high-temperature themoplastic. It is rarely used in its pure form due to difficulties in processing. It is mainly used as blend with polystyrene, high impact styrene –butadiene copolymer or polyamide. PPO is a registered trademark of SABIC innovative Plastics IP B.V. under which various polyphenylene ether resin are

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sold. Polyphenylene ether was discovered in 1956 by Allan Hay, and was commercialized by General Electric in 1960. While it was one of the cheapest high-temperature resistant plastics, processing was difficult and the impact and heat resistance decreased with time. Mixing it with polystyrene in any ratio could compensate for the disadvantages. In the 1960s, modified PPE came into the market under the trademark.

PPE is an amorphous high-performance plastic. The glass transition temperature is 215 °C, but it can be varied by mixing with polystyrene. Through modification and incorporation of fillers such as glass fibers, the properties can be extremely modified. PPE blends are used for structural parts, electronics, household and automotive items that depend on high heat resistance, dimensional stability and accuracy. They are also used in medicine for sterilizable instruments made of plastic.

Alkaline fuel cells (AFCs, hydrogen fuel cells with an alkaline liquid electrolyte such as KOH(aq)) are the best performing of all known conventional hydrogen-oxygen fuel cells operable at temperatures below 200 ºC. This is due to the facile kinetics at the cathode and at the anode; cheaper non-noble metal catalysts can be used (such as nickel and silver), reducing cost. McLean *et al*. gave comprehensive review of alkaline fuel cell technology. The associated fuel cell reactions both for a traditional AFC and also for an AMFC are:

Anode :$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall: $2H_2O + O_2 \rightarrow 2H_2O$
Rovert C.T Slade and Jamine P.Kizewski (2017)

Aim and Objectives

Aim

The aim of this research is study the conductivity performance and the alkaline stability of polyphenylene oxide modified anion exchange membrane (AEM) membrane for fuel cell technology.

Objectives

- To combine the brominated polyphenylene oxide (BPPO) and dimethyl formamide (DMF) in different molecular weights
- To measure the resistance of BPPO membranes
- To determine the conductivity
- To study the swelling ratio
- To investigate the morphology
- To study the water uptake and to measure the tear strength

Materials and Methods

Materials

1. Poly(2,6-dimethyl-1,4-phenylene oxide)(PPO)
2. Dimethyl Formamide (DMF)
3. 45% brominated polyphenylene oxide (BPPO)
4. 35% brominated polyphenylene oxide (BPPO)
5. 30% brominated polyphenylene oxide (BPPO)
6. Sodium Hydroxide
7. Hydrochloric Acid
8. Deionized Water

Methods

1. Fourier Transform Infrared Spectroscopy (FT IR)
2. Water Uptake and Swelling Ratio Measurement by comparing the wet and dry weights of the membranes
3. Ion Exchange Capacity (IEC) by Mohr titration method
4. Resistance Measurement by Multimeter
5. Scanning Electron Microscopy (SEM)

Determination of Resistance of Brominated Polyphenylene Oxide Membrane

Resistance of brominated polyphenylene oxide membranes were determined by Multimeter (Figure 1) at the Department of Physics, University of Mandalay.

Figure 1: Multimeter

Determination of Thickness of Membrane

The thickness of brominated polyphenylene oxide membranes were determined by Micrometer (Figure 2) at the Department of Physics, University of Mandalay.

Figure 2: Micrometer

Determination of Solubility of Membrane

The solubility of each membrane was measured by immersing the membranes in 1 M sodium hydroxide solution, chloroform, ethanol, distilled water and water for 24 hours (Figure 3).

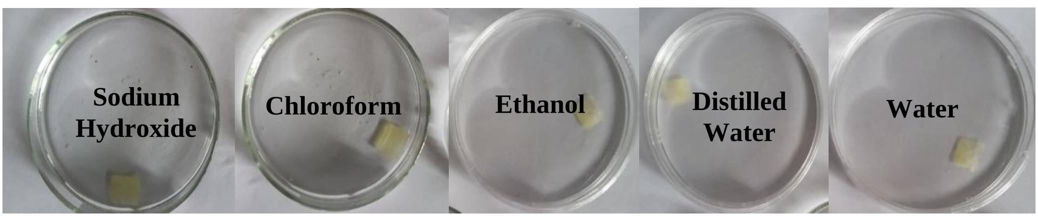


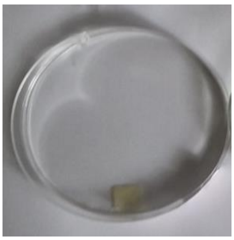
Figure 3: Solubility test of membrane in 1 M NaOH, $CHCl_3$, EtOH, distilled water and water

Identification of Brominated Polyphenylene Oxide Membrane by Fourier Transform Infrared Spectroscopy

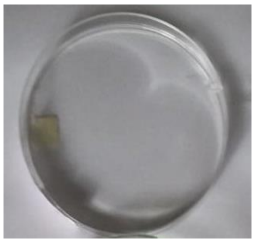
Brominated polyphenylene oxide membranes were identified by Fourier Transform Infrared Spectroscopy at Department of Chemistry, Monywa University.

Determination of Water Uptake (WU) and Swelling Ratio

The water uptake of brominated polyphenylene oxide membrane were measured by weight differences between the wet and dry weight of membrane. The membranes were soaked in water for 24 hours (Figure 4).



45 % brominated membrane



35 % brominated membrane

30 % brominated membrane

Measurement of Ion Exchange Capacity (IEC)

Ion exchange capacity (IEC) was determined by a back titration method derived from Slade and Varcoe (2013). The membranes were soaked in 1.0 M sodium hydroxide solution to exchange the bromide ion for hydroxide. And then the membranes were washed with deionized water and again dipped into this sodium hydroxide solution. After rinsing the membranes until neutral, they were dried in vacuum and immersed into 10 mL of 0.01 M hydrochloric acid. After soaking a day, the acid was titrated with 0.01 M sodium hydroxide. The ion exchange capacity of each membrane was calculated by the following equation:

$$IEC = \frac{C_{HCl}V_{HCl} - C_{NaOH}V_{Na}}{m_{dry}}$$

where C is the concentration of acid or base, V is the volume of the acid or base, and m_{dry} is the dry weight of the membrane after ion exchange.

Procedure for 45 %, 35 % and 30 % Brominated Polyphenylene Oxide Membranes

Firstly, 0.25 g of 45 % brominated sample was placed in round-bottomed flask and 15 mL of dimethyl formamide (DMF) was added. The mixture was stirred with the help of magnetic stirrer at 80°C for 24 hours. After the mixture was dissolved in DMF, it was poured into petridished and dried in oven for 24 hours. Finally, 45 % brominated polyphenylene oxide membrane was obtained. Similarly, the same procedure was done for 35 % and 30 % brominated poly phenylene oxide membranes.

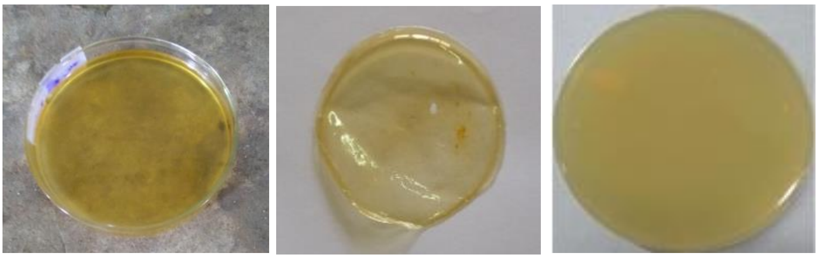


Figure 4: 45 % brominated polyphenylene oxide memembrane

Results and Discussion

Determination of Resistivity Value of 45 % Brominated Membranes

Table 1: The Resistivity Value of 45 % Brominated Membrane Before and After Immersing in Various Solvents

Solvents	Resistivity values before immersing in solvents M□	Resistivity values after immersing in solvents M□
Sodium Hydroxide	6	4.5
Ethanol	6	-
Chloroform	6	-
Distilled Water	6	-
Water	6	-

According to the experimental result, the resistivity value of 45 % brominated membrane immersing in sodium hydroxide responds the excellent value of 4.5 MΩ that is suitable for conductor. In other solvents such as ethanol, chloroform, distilled water and water, it was found that the resistivity values of 45 % brominated membrane couldn't be detectable.

Determination of Resistivity Value of 35 % Brominated Membranes

Table 2: The Resistivity Values of 35 % Brominated Membrane Before and After Immersing in Various Solvents

Solvents	Resistivity values before immersing in solvents MΩ	Resistivity values after immersing in solvents MΩ
Sodium Hydroxide	9	8
Ethanol	9	-
Chloroform	9	-
Distilled Water	9	-
Water	9	-

Similarity, the resistivity value of 35% brominated membrane immersing in sodium hydroxide responds the excellent value of 8 MΩ that is suitable for conductor. In other solvents such as ethanol, chloroform, distilled water and water, it was found that the resistivity values of 35 % brominated membrane couldn't be detectable.

Determination of Resistivity Value of 30 % Brominated Membranes

Table 3: The Resistivity Values of 30 % Brominated Membrane Before and After Immersing in Various Solvents

Solvents	Resistivity values before immersing in solvents MΩ	Resistivity values after immersing in solvents MΩ
Sodium Hydroxide	9.6	10
Ethanol	9.6	-
Cholroform	9.6	12
Distilled Water	9 .6	64
Water	9.6	60

The resistivity value of 30% brominated membrane immersing in sodium hydroxide responds the resistivity value of 8MΩ , 12 MΩ in chloroform, 64 MΩ in distilled water and 60 MΩ in water that point out the resistivity values of 30 % brominated membrane are lower than their original value ie., before immersing in the solvents.

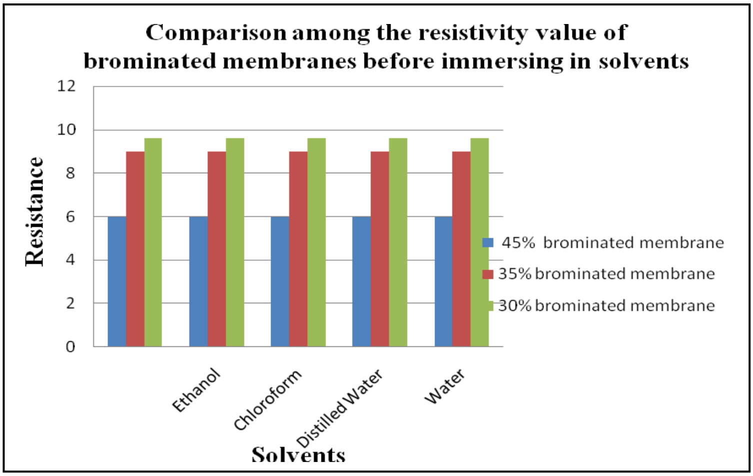


Figure 5: Resistivity values of brominated membranes before immersing in solvents

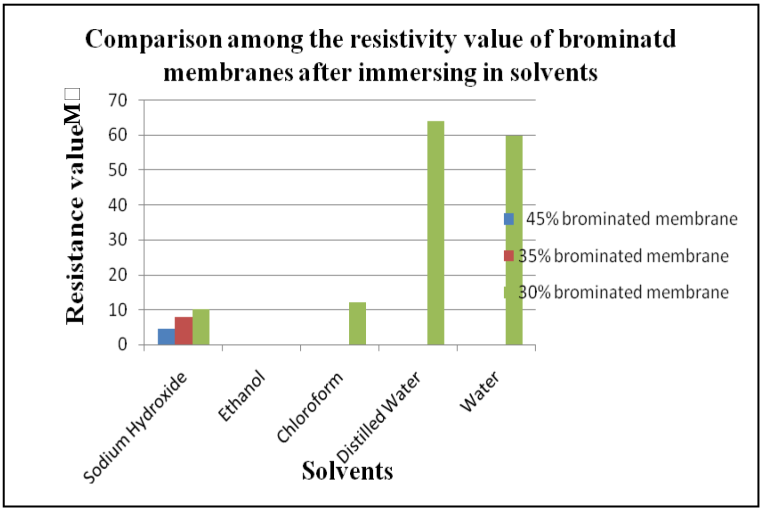


Figure 6: Resistivity values of brominated membrnaes after immersing in solvents

Determination of Thickness and Swelling Ratio of 45% Brominated Membrane

Table 4: The Thickness and Swelling Ratio of 45 % Brominated Membrane Before and After Immersing in Various Solvents

Solvents	Membrane thickness before immersing in solvents □m	Membrane thickness after immersing in solvents □m	Swelling Ratio %
Sodium Hydroxide	10	40	67
Ethanol	10	-	Undefined
Chloroform	10	60	34
Distilled Water	10	55	33
Water	10	60	20

From the result of the table, it was found that 45 % brominated membrane immersing in distilled water shows the highest swelling ratio.

Determination of Thickness and Swelling Ratio of 35% Brominated Membrane

Table 5: The Thickness and Swelling Ratio of 35 % Brominated Membrane Before and After Immersing in Various Solvents

Solvents	Membrane thickness before immersing in solvents □m	Membrane thickness after immersing in solvents □m	Swelling Ratio %
Sodium Hydroxide	50	75	50
Ethanol	50	50	0
Chloroform	50	30	0
Distilled Water	50	45	33
Water	50	80	22

From the result of the table, it was found that 35 % brominated membrane immersing in distilled water shows the highest swelling ratio.

Determination of Thickness and Swelling Ratio of 30% Brominated Membrane

Table 6: The Thickness and Swelling Ratio of 30 % Brominated Membrane Before and After Immersing in Various Solvents

Solvents	Membrane thickness before immersing in solvents □m	Membrane thickness after immersing in solvents □m	Swelling Ratio %
Sodium Hydroxide	50	76	64
Ethanol	50	45	0
Chloroform	50	60	33
Distilled Water	50	60	33
Water	50	55	22

From the result of the table, it was found that 30 % brominated membrane immersing in distilled water shows the highest swelling ratio.

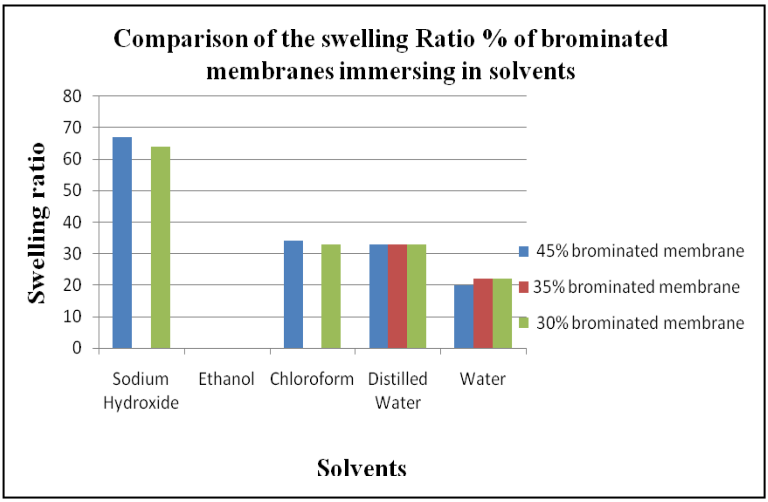


Figure 7: Swelling ratio % of brominated membranes immersing in solvents

Determination of Ion Exchange Capacity

Table 7: The Ion Exchange Capacity Value of Membrane

Membrane	IEC ($mmol/g^{-1}$)
45 % brominated membrane	1.48
35 % brominated membrane	1.22
30 % brominated membrane	1.05

The ion exchange capacity (IEC) value, water uptake, degree of swelling, and mechanical properties of the membranes are shown in table. The IEC represents the ion exchange capacity group in the membranes, and the IEC values can strongly interrlate to the water uptake, swelling ratio and hydroxide conductivity of the AEMs. Among the three membranes, 45 % brominated membrane has the highest IEC value of 1.48 $mmol/g^{-1}$.

The water uptake (Wu) value was found to be a reasonable amount associated with the IEC values. 35 % brominated membrane has the less amount of water content (50 %). Wu values of 45 % brominated membrane and 30 % brominated membrane were found to be (67 %) and (64 %), respectively. It was found that the modified membrane has a great thermal stability under boiling water. The water uptake and swelling ratio of three membranes were summarized in above tables. The influence of water uptake and swelling ratio of the membranes correspond to the hydroxide conductivity of the membrane. Wu value is measured by the weight difference between the wet and dry form of the membrane. These values indicate that the BPPO membrane has a good performance in the application of the membranes. The ionic exchange capacity (IEC) value is reliable to the capacity of membrane which may influence the power of AEMs in fuel cell application. The higher value of the water uptake and swelling ratio provide the greater power of hydroxide conductivity. But the thermal stability of the membrane can be decreased due to the higher value of water uptake. It was found that BPPO membranes have moderate amount of water content and swelling ratio. These attachments are the great performances of AEM membranes that are required for the satisfaction of ion exchange capacity.

Identification of Brominated Polyphenylene Oxide Membrane by Fourier Transform Infrared Spectroscopy

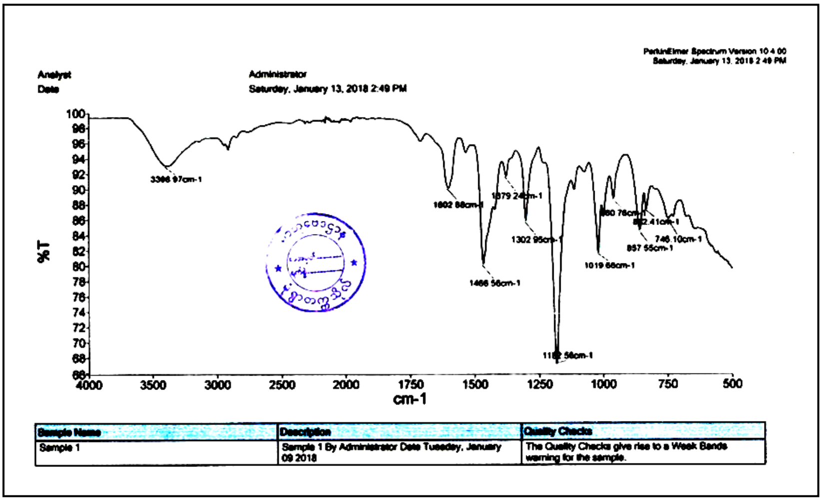


Figure 8: FT-IR spectrum of brominated polyphenylene oxide

Identification of Brominated Polyphenylene Oxide Membrane by Fourier Transform Infrared Spectroscopy

Table 8: FT-IR Assignments of 45 % Brominated Polyphenylene Oxide (BPPO) Membrane

No.	Wave Number	Stretching Frequency
1.	3398.97 cm^{-1}	N-H stretching vibration
2.	3005.10 cm^{-1}	C-H stretching vibration of unsaturated hydrocarbon
3.	2902.50 cm^{-1}, 2842. cm^{-1}	C-H stretching vibration of saturated hydrocarbon
4.	1602.88 cm^{-1}	C=C Stretching Vibration of ring skeleton
5.	1466.56 cm^{-1}, 1379.24 cm^{-1}, 1302. cm^{-1}	C-H bending vibration of methyl group
6.	1182.56 cm^{-1}	C-O stretching vibration of ether
7.	1019.66 cm^{-1}	C-Br stretching vibration
8.	960. cm^{-1}	C-H bending Vibration
9.	857.55 cm^{-1}	C-H out of plane Bending Vibration

Conclusion

In this research work, the three different ratios of brominated polyphenylene oxide (BPPO) membranes were firstly prepared by mixing with DMF solvent and stride using of magnetic stirrer. The characteristic properties of membranes were determined by FT-IR and SEM spectroscopy. In addition, the ion exchange capacity measurement indicates that 45 % BPPO membrane gives 1.48 $mmolg^{-1}$ which is in agreement with the AEM membrane that can be used for fuel cell. The resistance of the membranes was determined by Multimeter at the Department of Physics, Mandalay University where as 45 % brominated (BPPO) membrane shows the suitable conductivity value of 6 MΩ before immersing in 1 M NaOH solution as well as it shows 4.5 MΩ after immersing in 1 M NaOH solution. Furthermore, the swelling ratio of 45 % BPPO membrane indicated unexpected mechanical properties that informs the more ion exchange group corresponds to greater swelling ratio and high solubility.

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