

Effect of Synthesis Parameters on Phosphoric Acid Doped Polybenzimidazole Membranes: A Parametric Evaluation from Microstructural Level to Fuel Cell Performance

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ABSTRACT

In the present study, polybenzimidazole (PBI) polymer which has a great importance in polymer electrolyte membrane (PEM) research was synthesized via the solution polycondensation method, under various synthesis conditions to put forward the effect of the synthesis parameters on the properties of the synthesized polymer and consequently to the quality of the prepared polymer electrolyte membrane. The synthesized polymers were characterized in terms of their chemical structure, thermal degradation behaviour, and molecular weight by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (¹H NMR), thermogravimetric analysis (TGA). The Mechanical properties, acid-doping level capacity, proton conductivity, and fuel cell performances of the produced phosphoric acid doped PBI were investigated. The Thermogravimetric analyses showed that the synthesized polymers have an excellent thermal stability up to 580°C. Mechanical analyses revealed that the mechanical strength of the PBI membranes increases with increasing molecular weight of the polymer and reaches the maximum value of 17.65 MPa. The maximum power density was observed to be 48.6 mW/cm² of the fuel cell test at 120°C.

KEYWORDS: *Phosphoric acid doped polybenzimidazole membrane, Polymer electrolyte membrane, Polymer electrolyte membrane fuel cell, Protonexchange membrane fuel cell.*

1. INTRODUCTION

Fuel cells are recognized as the most promising electrochemical devices to convert

the chemical energy of a fuel, such as H₂, NH₃ or CH₃OH into electricity with high energy conversion efficiencies and low pollutant

J. Polym. Mater. Vol. **36**, No. 4, 2019, 337-349

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DOI : <https://doi.org/10.32381/JPM.2019.36.04.4>

emissions.^[1-3] Polymer electrolyte membrane fuel cells (PEMFCs), among types of fuel cells, have remarkable predominance as power generators for portable and transportation applications.^[4,5] The polymer electrolyte membrane, a key component of PEMFCs, mainly works as a solid polymer electrolyte, both to separate fuel from the oxidant and to transport protons.^[6,7] The most-widely used polymer membrane is a perfluorosulfonic acid based ionomer known as Nafion and produced by Du Pont.^[8,9]

However, a serious limitation of Nafion-type membranes is dehydration at temperatures above 80°C. They conduct protons in the presence of water molecules which evaporate quickly at temperatures above 80°C, leading to a remarkable decrease in their proton conductivity and mechanical stability.^[9,10]

In recent years, research on PEMFCs has focused on developing a PEM in which the proton transport is conducted under dry conditions at high temperatures. Other advantages of working at higher temperatures are faster electrode kinetics, high tolerance to CO in fuel and the elimination of cathode flooding.^[2,11]

There has been much research on the synthesis of new polymers, which can be modified to proton conducting membranes, such as PBI,^[12-15] polyimides, polyether ether ketones,^[16-19] polyphenyloxides,^[20-22] polyvinylidene fluoride,^[23-25] or polyphosphazenes^[26-29] to be found in the literature. Furthermore, there is still much work to be done to improve the chemical and physical properties of PBI.^[3,5] The phosphoric acid doped PBI membrane may be considered as the most promising candidate

in the search for a high temperature PEM to overcome operational difficulties caused by the dehydration of commercially used Nafion membranes over 80°C. This challenge has motivated extensive research activities on PBI synthesis and membrane preparation for PEMFCs in recent years.

The quality of the polymer electrolyte membranes, which have a key role in the fuel cell research, depends on the quality of the polymer from which they are produced. In the present research, a parametric study was carried out with varying synthesis parameters that affects the polymer properties, in order to predict a high quality membrane production. PBI was synthesized from isophthalic acid (IPA) and 3,3'-diaminobenzidine (DAB) by solution polycondensation in polyphosphoric acid (PPA) via a series of polycondensation reactions with different reaction conditions. A pre-polymerization process was identified for PBI polymerization to ensure an efficient and standardized reaction medium. In contrast to the earlier studies, temperature, reaction time and stirring rate were all considered together as reaction parameters and their influence on the properties of the synthesized polymers, especially on the molecular weight, were investigated. The effects of polymer properties on the critical quality features of prepared phosphoric acid doped PBI membranes, such as mechanical strength, acid-doping level capacity, proton conductivity, and fuel cell performances were investigated. Thus, the relation between the microstructure properties of the synthesized polymer and the performance of polymer electrolyte membrane, as the final product, has been examined.

2. EXPERIMENTAL

2.1 Materials

PPA (115% H_3PO_4 basis), N,N-dimethyl acetamide (DMAc), lithium chloride (LiCl) and phosphoric acid solution (85 wt. % in H_2O) were purchased from Sigma-Aldrich. Sodium hydrogen carbonate ($NaHCO_3$), 3,3'-diaminobenzidine (DAB) and isophthalic acid (IPA) were purchased from Merck. DAB and IPA monomers were dried at 105°C for 24 hours in an oven before polymerization reactions.

2.2 Pre-polymerization process

PBI was synthesized by polycondensation of DAB and IPA monomers in PPA under nitrogen N_2 (99.99%) atmosphere in a four necked jacketed glass vessel (500 mL) (Radley Co.) equipped with a mechanical stirrer. Uniform heating was achieved by circulating a heat transfer fluid through the jacket of the vessel using a heating circulator (Julabo HE). 300 g PPA was added to the reactor as solvent and heated to 150°C. The temperature was kept constant at 150°C for 2 hours to dehydrate the solvent and the PPA was deoxygenated. Equimolar DAB and IPA were then added to the vessel with continuous stirring. The reaction media was flushed by N_2 three times to ensure an inert atmosphere in the reactor. The mixture was stirred at 150°C for 2 hours under N_2 flow to disperse monomers in PPA homogeneously. The operations mentioned above, are identified as a pre-polymerization process and were repeated for each polymerization processes with different synthesis parameters such as reaction time, temperature, and stirring rate.

2.3 Synthesis of PBI

After the pre-polymerization process, the temperature was increased to the reaction temperature. When the temperature was reached to this temperature, the reaction time was started, and the stirring rate was adjusted to the desired value. The polymerization parameters of the PBI syntheses are given in Table 1.

At the termination stage of polymerization, the obtained dark brown, viscous reaction solution was poured into deionized water. The synthesized polymer was washed with deionized water several times and then filtered. After filtration the synthesized polymer was

left in 5% (w/w) $NaHCO_3$ solution for neutralization for 24 hours. The neutralized polymer was washed with deionized water several times and dried in an oven for 24 hours. The synthesized PBI polymers were amber, fibrous and very similar in appearance.

2.4 Membrane Preparation and Acid Doping

The PBI membranes were prepared using the solution casting method. Dried polymers were then grounded into powder. Polymer solutions were prepared dissolving this powder PBI (2.5%, w/v) and LiCl (1.5%, w/v) in DMAc in a double necked flask equipped with a mechanical stirrer which was then immersed in an ultrasonic water bath at 80°C for 5 hours. The obtained polymer solutions were cast on a Petri dishes. It was then dried at 100°C for 24 hours in a ventilated oven. The dried PBI membranes were immersed in boiling water for 5 hours to remove LiCl and were then dried at 100°C for 24 hours. The transparent membranes in amber color were obtained. The DMAc-cast membranes were doped with acid to ensure proton conductivity. PBI is known to be reactive with various acids such as H_2SO_4 , H_3PO_4 , $HClO_4$, HNO_3 , HBr, and HCl. In the present study, phosphoric acid was chosen for acid doping due to its unique proton conductivity, even under anhydrous conditions, as well as its high thermal stability and very low vapor pressure at elevated temperatures. The membranes were doped by immersing them in 85 wt. % phosphoric acid for 1 week at room temperature.

3. CHARACTERIZATION

3.1 Structural and thermal analyses of synthesized polymers

FTIR analysis was conducted using a Perkin Elmer Frontier spectrometer. All the samples were dried at 110°C for 24 hours before analysis. The 1H NMR spectra of the polymers were recorded on a 500MHz Bruker AVANCE II NMR spectrometer. Ground polymers were dissolved in deuterated dimethylsulfoxide (d_6 -DMSO) and chemical shifts were measured against tetramethylsilane (TMS) as an internal standard. Thermogravimetric analysis (TGA) was carried out at a scanning rate of 10°C/min under nitrogen atmosphere in a temperature range of 35–1000°C using a Netzsch STA 449 F3 thermogravimetric analyzer.

3.2 Determination of Molecular weight

PBI based polymers are completely insoluble in a large number of solvents. Consequently, the average molecular weight of the PBI based polymers cannot be determined by standard gel permeation chromatography. So it is commonly calculated by means of inherent viscosity. Viscosity measurement was conducted using an Ubbelohde viscometer (Cannon Ins. Co.) using polymer solutions in concentrated sulfuric acid. The molecular weight is determined using Mark-Houwink-Sakurada equation as η_i is related to the weight-averaged molecular weight (M_w):

$$\eta_i = KM_w^\alpha \quad (1)$$

where, the empirical constants K and α are 1.94×10^{-4} and 0.79, respectively. [30,31]

3.3 Determination of Water uptake and acid doping

The membranes were dried at 105°C overnight prior to water uptake measurements. After measuring the weights of the dry membranes, the sample films were soaked in deionized water for 3 days at room temperature. After this, the membranes were taken out and the water on the membrane surfaces was wiped

off. The weights of the hydrated membranes were then taken. Water uptake, which can be expressed as the mass of water absorbed per gram of dry polymer, was calculated by the following formula:

$$\text{Water uptake (\%)} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100$$

Where, W_{dry} and W_{wet} refer to the weights of the dry and wet membranes, respectively.

The acid doping level of the membrane was calculated from the mass gain of the membrane samples during both water and acid doping. In order to separate the contributions by acid and water, the doped membranes were dried at 105°C under vacuum until an unchanged weight was reached. Weight loss during drying was due to water evaporation. Therefore, the water content in the doped polymer membranes and the acid doping level could be obtained. Next, the acid-doped membranes were washed with methanol to remove free acid and were dried at 80°C under vacuum. The weight of the remaining bonded acid inside the membrane was determined. The acid doping level which represents the number equal to the number of absorbed phosphoric acid molecules per repeat unit of PBI is calculated using the following equation:

$$\text{Acid doping level} = \frac{\text{Weight increase}}{\text{Initial weight}} \times \frac{M_w \text{ of PBI repeated unit}}{M_w \text{ of H}_3\text{PO}_4} \quad (2)$$

3.4 Tensile measurements

Tensile measurements were conducted by following the procedures outlined in ASTM D882-10 at a crosshead speed of 10 mm min⁻¹ with an Instron instrument (INSTRON 5944) at room temperature. For each membrane, three samples were used for the measurements. The tensile strength and the percentage elongation at break (EB%) were calculated from the averaged values of the three samples.

3.5 Proton conductivity measurements

Acid doped membrane samples were prepared as ribbons and placed in a Teflon conductivity cell (Bekktech 112) connected to four Pt electrodes. The

distance between the two inner electrodes was used to measure the potential difference through the sample by delivering dry air (relative humidity (RH)=0%) into the system at 80°C. There have been studies concerning the effect of relative humidity on proton conductivity and it is known that the conductivity of PBI is improved with increasing humidity. Nevertheless, the dependence was much smaller than that for Nafion membranes. In this study, proton conductivity tests were conducted under zero humidity. Because of the hopping-like proton conduction mechanism and almost zero electro-osmotic drag number of PBI membranes compared to the drag number of 0.6-2.0 for Nafion membranes, they do not need water for proton

transport, unlike the Nafion membranes. This unique feature of the acid doped PBI membrane allows the fuel cell to be operated at low gas humidification without membrane dehydration, which starts at 80°C for Nafion membranes.^[32,33]

A Solartron 1287 Frequency Response Analyzer was used for proton conductivity measurements. The resistance (R , Ω) of a membrane was calculated from the slope of the voltage vs. current graphs taking an average of 30 cycles of experimental impedance data for each membrane. Proton conductivities of the membrane samples were calculated using the following formula:

$$\sigma = \frac{1}{R} \times \frac{L}{W \times T} \quad (4)$$

Where, L , T and W refer to the distance between the voltage sense electrodes (two inner electrodes) (0.425 cm), membrane thickness and sample width (1.1 cm), respectively.

3.6 Single cell performance test

A standard fuel cell test station was used as described in our previous work.^[34] Acid doped PBI membranes were sandwiched in between the catalyst coated electrodes to obtain the membrane electrode assembly (MEA). The Pt loadings of the cathode and anode were 0.5 mg cm⁻². SGL-25BC was used as a catalyst support. The current densities and power densities of the fuel cell were recorded by potentiostatic measurements. PEMFC single cell performances of the MEAs were tested at 80, 100 and 120°C. Hydrogen and oxygen were both fed to the fuel cell at a rate of 80 sccm without external humidification at ambient pressure. The MEAs were activated by operating the unit cell at a constant voltage until a stable performance was obtained before the polarization scans. Polarization curves were obtained by measuring the current density with a stepwise increment and decrement of voltage between 0.2 to 0.9 V with an interval of 0.1 V. These stepwise increment-decrement sequences were repeated three times for each membrane and the mean value of the obtained current density data was used in the calculations.

4. RESULTS AND DISCUSSION

Structural Analyses

Structural analyses of synthesized polymers were conducted by ¹H-NMR and FTIR analyses (Figs. 1 and 2). The peaks at 3412-3422 cm⁻¹ in the FTIR spectrum of synthesized PBI polymers correspond to non-hydrogen bonded free N-H groups in an imidazole ring. The bands at 1529-1533 cm⁻¹ are attributed to in-plane ring vibration of 2-substituted benzimidazole. The peaks at ~1627 cm⁻¹ characterize C=C and C=N stretching vibrations. The peak at 1278 cm⁻¹ was ascribed to the imidazole-ring. Although shifting occurred at negligible levels, the spectrum of the synthesized polymers is almost identical. The FTIR peak assignments are in good agreement with the anticipated chemical structure and reported studies.^[2,11,35,36]

Although FTIR provides good evidence that polymer syntheses were performed successfully, the proton NMR study is more useful for looking into the polymer structure. The NMR spectra for all the synthesized polymers are the same. A ¹H-NMR spectrum representing all the polymers is shown in Fig. 2. Five resonances, in the range 7.5–9.2 ppm, are attributed to aromatic protons denoted as H_b, H_c, H_d, H_e and H_f. A peak indicating a characteristic imidazole proton (N-H), denoted as H_a was observed at 13.4 ppm. The spectra of the synthesized polymers confirm each other and previous studies.^[11,35] Thus all synthesized polymers from PBI1 to PBI6 have the same chemical structure.

Molecular Weights

The properties that distinguish the synthesized polymers obtained by the different synthesis

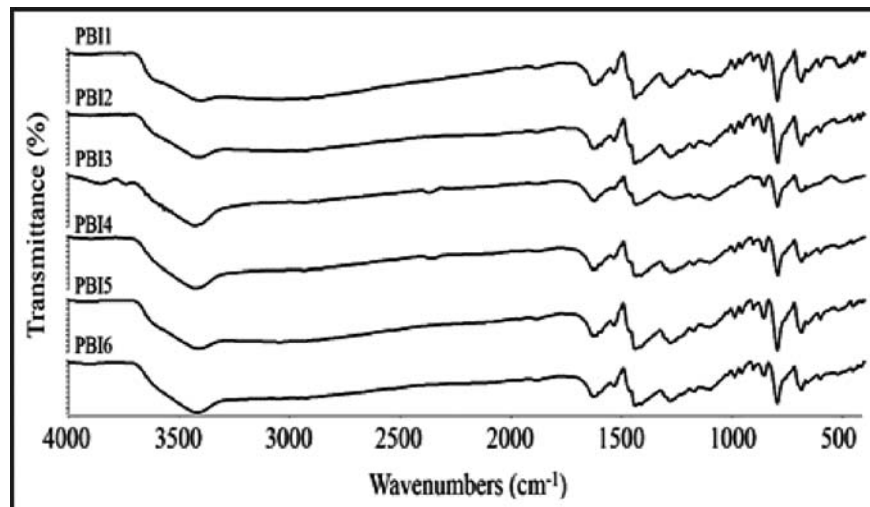


Fig. 1. FTIR spectra of synthesized PBI polymers.

parameters are summarized in Table 1. The variations in the synthesis parameters resulted in extreme changes in the molecular weight of the polymers. It was concluded that the molecular weight of the synthesized polymer increased with increasing reaction temperature between 190°C and 220°C. These temperature limits were determined by preliminary studies.

When reaction time and stirring rate are maintained the same at 22 hours and 300 rpm, respectively, and reaction temperature is increased from 190°C to 210°C, molecular weight was increased from 57.010 kDa to 76.632 kDa for PBI2 and PBI1, respectively. The increment of molecular weight with increasing temperature can be explained by an improvement in reaction kinetics and polymer chain lengths as a result of decrease in viscosity of the reaction medium at higher temperatures. When comparing PBI3 and PBI4, the molecular weight doubles from 90 kDa to 182 kDa where stirring rate was increased from 150 rpm to 300

rpm and reaction time and temperature are kept at 21 hours and 220°C, respectively. An easier removal of water formed in the reaction and a faster monomer transport may explain the increment of molecular weight with increased stirring rate. Keeping temperature and stirring rate constant at 200°C and 300 rpm, respectively, the decreasing reaction time from 20 hours to 18 hours resulted in a negligible molecular weight increment (73 kDa and 73 kDa for PBI5 and PBI6, respectively). This result indicates that 18-19 hours of polymerization is sufficient to complete the polymerization.

Thermal Properties

The TGA curves and thermal degradation behavior data for six PBI polymer samples are presented in Fig. 4 and Table 1, respectively. Two weight loss patterns are observed in all the polymers; the first weight loss at around 100-200°C is assigned to the

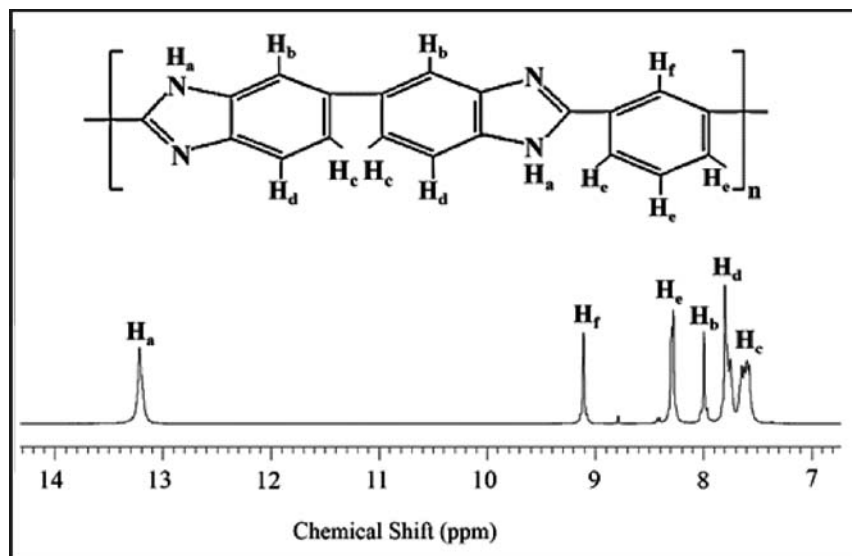


Fig. 2. ¹H-NMR spectrum of the synthesized PBI polymer

loss of adsorbed water molecules from the membranes. All the samples were dried at 110°C for 24 hours before studying the TGA and FTIR. Despite this drying process, a loss of loosely-bound absorbed water molecules was observed in the TGA curves (Fig. 3) and O-H stretching for water molecules in the FTIR spectrum (Fig. 1). These results show that PBI absorbs moisture very easily from the atmosphere, even during the sample handling time. The degradation of the polymer backbone, responsible for the second weight loss, was observed at around 580-600 °C.

All the PBI polymers which were heated up to 600°C resulted in less than 4.5% weight loss, revealing the excellent thermal stability of the synthesized PBI polymers. When Table 1 is examined, it can be seen that PBI2, the polymer with the lowest molecular weight has the highest thermal stability with 2.64% mass loss between 200-600°C. PBI4 which has the

highest molecular weight shows the weakest thermal stability with 4.10% mass loss between 200-600°C.

Table 2 summarizes the acid doping level, water uptake, average thickness, tensile strength, EB% and proton conductivity data of the prepared membranes. It is well known that PBI has a high tendency to absorb moisture because of its hydrophilic structure. As shown in Table 2, water uptake of PPA doped PBI membrane is between 10.6-17.8 wt%. The highest acid doping level and water uptake, 20.4 and 17.8 respectively, coincide with the highest molecular weight PBI membrane. The water uptake results are in good agreement with those in the literature, in which PBI is reported to be able to absorb 15-19 wt% of water from a moist atmosphere.^[37] As can be seen from Table 2, PBI membranes with higher molecular weight show a higher affinity for water uptake and

acid doping. This is believed to be due to an intensifying of the intermolecular hydrogen bonding between water and N and N–H groups in the PBI when molecular weight is increased. At higher acid doping levels, water uptake is increased indicating that acid doping level and water uptake corroborate each other.

In support of this, the water uptake and acid doping level values are almost same, with a negligible increment of molecular weight from 73.507 kDa to 73.819 kDa.

Based on Table 2, we can see that the mechanical strength of the PBI membranes

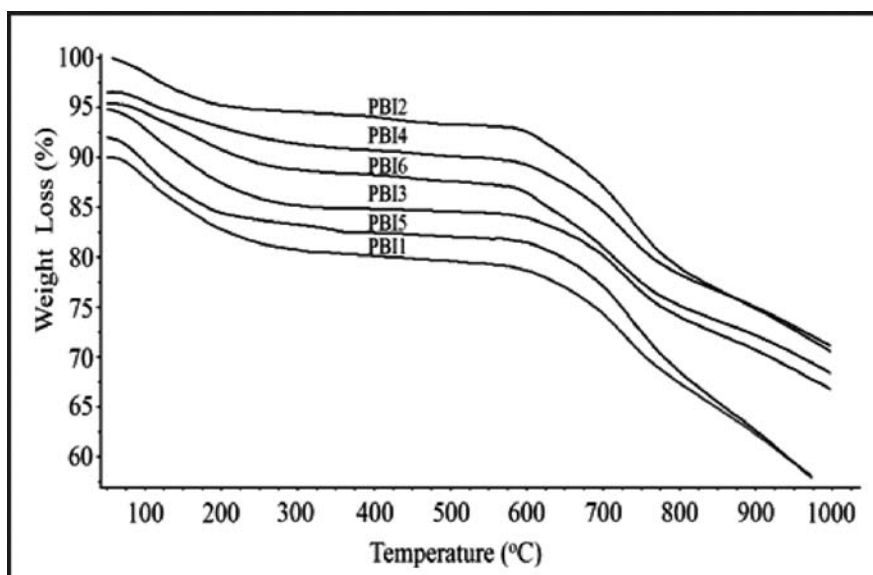


Fig. 3. TGA thermograms of synthesized PBI polymers

TABLE 1. Polymerization parameters and properties of synthesized PBI polymers

Synthesized PBI	Reaction time (hour)	Temperature (°C)	Stirring rate (rpm)	Intrinsic viscosity (dL.g ⁻¹)	Molecular weight (kDa)	Mass loss (wt%) between 50-200°C	Mass loss (wt%) between 200-600°C
PBI1	22	210	300	1.417	76.632	4.91	4.10
PBI2	22	190	300	1.121	57.010	7.42	2.64
PBI3	21	220	150	1.623	90.999	3.53	3.73
PBI4	21	220	300	2.811	182.190	4.62	4.28
PBI5	20	210	300	1.376	73.819	7.23	4.10
PBI6	18	210	300	1.371	73.507	7.58	2.95

increases with increasing molecular weight. The mechanical strength of pure PBI membranes is provided by hydrogen bonding between the –N and –NH– groups, which is the dominant force. When doped with phosphoric acid, the molecular cohesion of PBI is decreased. However, stronger hydrogen bonds between the –N and phosphoric acid molecules are formed than those between the –N and –NH– groups as a result of the acidity of the phosphoric acid. Significant improvement of the membrane tensile strength (σ_t) and EB% were observed for the polymer with higher molecular weights. With an acid doping level of 17.8, the tensile strength and EB% were found to be about 17.65 MPa and 42.73%, respectively, for the membrane with a molecular weight of 182.190 kDa. However, corresponding values were found to be 3.86 MPa and 12.01%, respectively, for the membrane with a molecular weight of 57.01 kDa.

As can be seen in Fig. 4, tensile strength and EB% show an increasing trend as molecular weight increases. This observation indicates that, as the molecular weight increases, induction interactions and London forces become increasingly significant. On the other hand, the slope of the tensile strength and EB%- Mw graph decreases as the molecular weight is increased. This observation is thought to be due to the fact that excess acid loading weakens the mechanical strength of the membrane. When Fig. 4 and Table 2 are examined together, the acid loading level of about 14 seems to be the limit at which mechanical resistance begins to deteriorate. Acid doping causes an increased separation for PBI backbones, due to the volume swelling of the PBI membranes. As a result of volume swelling, intermolecular forces weaken and consequently the mechanical properties of the

TABLE 2. Acid doping level, water uptake, average thickness, tensile strength, EB% and proton conductivity data of the prepared phosphoric acid doped PBI membranes

Synthesized PBI	Acid doping level	Water uptake (wt%)	Average membrane thickness (μm)	Tensile thickness (MPa)	EB%	Proton conductivity (S/cm)
PBI1	12.2	13.3	269.4	9.66	26.44	0.0021
PBI2	6.3	10.6	269.2	3.86	12.01	0.0006
PBI3	14.3	14.6	271.2	12.71	32.78	0.0025
PBI4	20.4	17.8	270.6	17.65	42.73	0.0039
PBI5	8.5	12.4	269.8	7.97	21.92	0.0007
PBI6	8.3	12.2	270.2	6.77	21.53	0.0007

membranes weaken. The influence of membrane thickness on the mechanical properties was not taken into account since they are very close.

Proton conductivities of the membranes at 80°C are given in Table 2. The results show that the more phosphoric acid sites are incorporated into the membrane structure, the more proton

conductivity is obtained. PBI1, which has the highest acid doping level with 20.4, shows the highest proton conductivity with 0.0039 S/cm. When comparing PBI1 and PBI2, it can be seen that proton conductivity increases from 0.0006 S/cm to 0.0021 and the acid doping level increases from 6.3 to 12.2. The PBI5 and

PBI6 membranes have very close acid doping levels and the same proton conductivity. As discussed previously, since molecular weight affects the level of acid addition, it indirectly affects the proton conductivity of the prepared membrane.

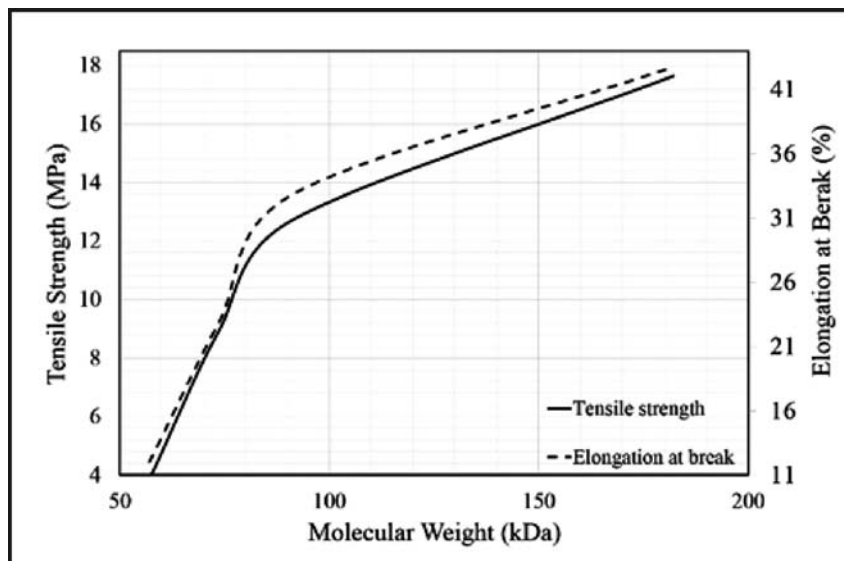


Fig. 4. Tensile strength -Mw and EB% - Mw graphs of phosphoric acid doped PBI membranes

Polarization curves are one of the most effective methods of evaluation of fuel cell performance providing much essential information, including polarization loss of fuel cells. Fig. 5 shows the polarization and power curves for the PEMFCs operated with phosphoric acid doped PBI membranes at 80, 100 and 120°C under ambient pressure with non-humidified H_2/O_2 flowing at a rate of 80 sccm. Advancement of the electrochemical properties of fuel cell by increasing temperature can generally be explained by increased membrane conductivity and enhanced reaction kinetics at elevated

temperatures. According to the polarization graphs of the PEMFCs operated with phosphoric acid, doped PBI4 membrane gives the best results with a maximum power density of 48.6mW/cm² at a current density of 162.2mA/cm² at 120°C.

5. CONCLUSIONS

Based on mechanical tests, a significant improvement of the membrane in tensile strength and EB% were observed for the polymer with higher molecular weights. When the molecular weight was increased from 57

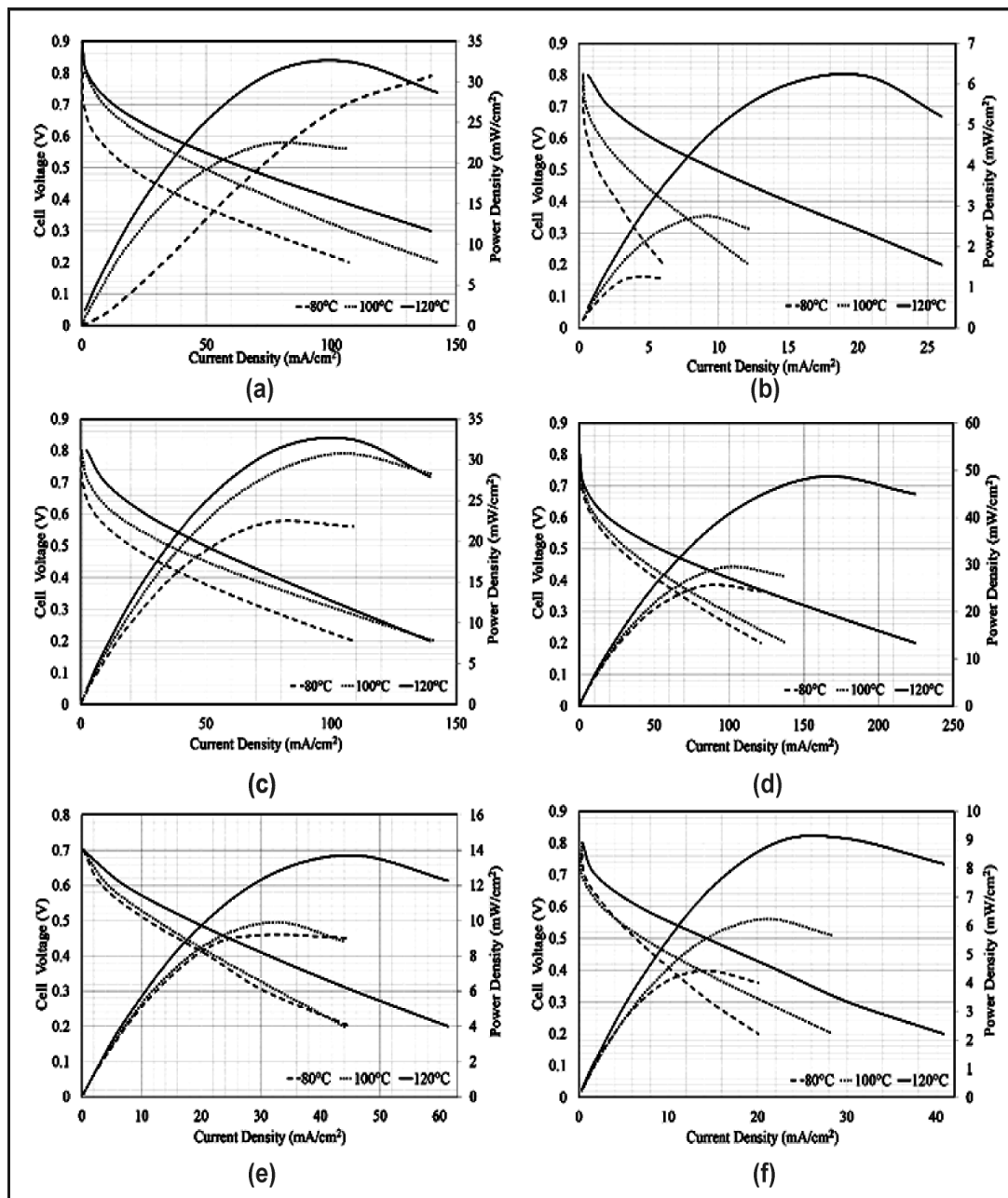


Fig. 5. Polarization and power curves for phosphoric acid doped PBI membranes; (a) PBI1 (b) PBI2 (c) PBI3 (d) PBI4 (e) PBI5 (f) PBI6, tested at 80, 100 and 120°C under ambient pressure with non-humidified H₂/O₂ flowing at a rate of 80 sccm.

kDa to 182 kDa, the tensile strength was increased by 357% from 3.86 to 17.65 MPa and EB% was increased by 256% from 12.01% to 42.73%. The acid doping levels and water uptake of the PBI membranes were also increased with an increase in molecular weight. The results show that the more phosphoric acid sites are incorporated into the membrane structure, the more proton conductivity is obtained. The strong relationship between molecular weight and proton conductivity arises from the influences of molecular weight on the acid doping level. The PBI membrane, produced from the longest chain polymer, which has a molecular weight of 182 kDa gives the best fuel cells performance with a maximum power density of 48.6 mW/cm² at a current density of 162.2 mA/cm² at 120°C.

ACKNOWLEDGEMENTS

This research was funded by the Anadolu University Scientific Research Projects Committee; Project No:1206F102.

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Received: 20-11-2019

Accepted: 27-01-2020