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Molecular weight controlled sulfonated Poly(Arylene Ether)s and sulfonated Poly(Ether Ether ketone) polymer blends for fuel cell applications

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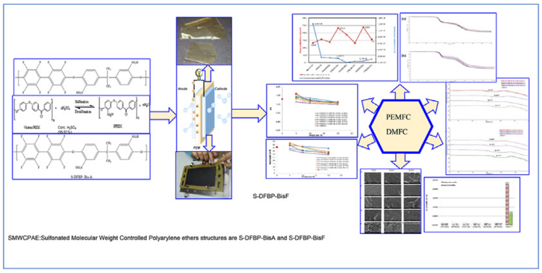
HIGHLIGHTS

- Molecular weights controlled Poly (arylene ether)s has been synthesized and sulfonated.
- The blend membranes we prepared are miscible and mechanically compatible.
- The proton conductivity value up to 238.9 mS/cm has been obtained.
- BMs properties are comparable with, or better than, that of Nafion.
- The membranes are suitable for PEMFC and DMFC applications.

GRAPHICAL ABSTRACT



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ABSTRACT

We synthesized molecular weight-controlled and fluorine-containing PAEs (MWCPAEs) using decafluorobiphenyl (DFBP), 2-bis (4-hydroxyphenyl) propane (Bis A), and 2,2-Bis (4-hydroxyphenyl) hexafluoropropane (Bis AF). Later, commercially available PEEK and the MWCPAEs were sulfonated (SPEEK and SMWCPAE) and blended to fabricate blend membranes (BMs). All BMs have been prepared by solution casting method in 5 wt%-20 wt% concentrations using N,N-dimethylacetamide. The effects of chemical structures, sulfonation levels, MW and compositions on the membrane properties are discussed. We obtained miscible and mechanically compatible BMs. The highest proton conductivity (238.9 mS/cm) was determined for SPEEK70/S-DFBP-Bis-A based blend membrane (M_w: 48.355, 5wt. %). All chemical, mechanical, thermal, and hydrolytic properties of the BMs are comparable with, or better than, that of Nafion. We suggest that designing polymeric

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[1] This paper is dedicated to the memory of Prof. Dr. Atilla Güngör, who passed away while this paper was being peer-reviewed.

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DMFC
PEMFC

structures with desired MWs and sulfonation levels may enable enhanced properties and can help to design materials with on demand properties.

Introduction

PEMFCs are a clean energy source for various applications such as electric vehicles and portable electronic devices. Nafion® membranes are promoted as the benchmark of PEMs. However, high cost, poor proton conductivity above 100 °C, and high methanol permeation are some of the disadvantages of Nafion® membranes limiting the practical application of PEMFCs. Sulfonated poly (arylene ether ketone)s (SPAEKs) and sulfonated poly (arylene ether sulfone)s (SPAESs) are encouraging polymers for developing low-cost and high-performance PEMs to be a possible alternative to Nafion® membranes; owing to their thermal, hydrolytic, mechanical and chemical stability, low cost, and commercial availability [1–21]. SPEEK or poly (ether ketone ketone) (SPEKK) [4,7–9,14,15,22,23,56], sulfonated poly (ether sulfone) (SPES) [1,3,7,12,17,24,25], alkyl sulfonated polybenzimidazole (PBI), sulfonated naphthalenic polyimides (sNPI) [26–28], sulfonated poly (phenylene sulfide) [29,30], sulfonated poly (phenylene arylene)s (SPAs) [31] can be given as potential candidates among higher performing polymers. Sulfonation of polymers can be realized by polycondensation from sulfonic acid-containing monomers [32].

Nafion attracted significant attention as a solid electrolyte for PEMFC due to its unique mechanical and thermal properties. It is a perfluorosulfonic acid (PFSA) membrane and needs water to be proton conductive [33]. Nafion is a polymer with a polytetrafluoroethylene main chain and a sulfonic acid, $-SO_3H$ ending group. The sulfonic acid groups enable an increase in the proton conductivity [34].

On the other hand, acid-base polymer blends have been extensively studied for fuel cell membrane applications and the results have shown good proton conductivities, superb thermal stabilities, and good performances. Examples of these blends include SPEEK Victrex, polyether sulfone (PES), and sulfonated polysulfone (sPSU) Udel [35].

We previously focused on PAE-based type of proton exchange membranes of PEEK [6,36,37], PEES, and their blends with PVDF [13,14]. We noted that the chemical stability, methanol, and gas permeabilities of the membranes were improved by blending with PVDF [13,14]. However, one undesirable result was that by the addition of PVDF, the conductivity of the SPEEK/PVDF blend membranes decreased [36,37].

The recent efforts have been focused on developing LTFC, DMFC, and maybe ITFC (70–110 °C, 150–350 °C, and 200 °C) membranes, respectively, with stable, methanol-resistant, high-performance and low-cost PEMs as an alternative to Nafion® membranes. To meet these goals, we focused on the commercially available blend membrane approach to decrease methanol permeability and cost and increase the conductivity and performance properties. Increasing sulfonic acid groups per repeating unit also increased the WU of SPEEK membranes. Kim et al. [38] fabricated SPEEK/QNPAES membranes and reported 900 h of durability when the membranes were exposed to 60 °C and 20% relative humidity.

The high density of $-SO_3H$ groups may lead to ionic clustering for better water absorption in highly sulfonated PEEK [4,39–41]. Wiles et al. [25] synthesized disulfonated partially fluorinated poly (arylene ether sulfone) copolymer materials to ensure better compatibility with Nafion® 1100 electrode materials; demonstrating higher overall performance.

In this study, we synthesized molecular weight-controlled and fluorine-containing PAEs (MWCPAEs) using Bis AF, Bis A, and DFBP. Later, the MWCPAEs and commercially available PEEK were sulfonated and blended to fabricate membranes for PEMFC. All membranes have been prepared by following the solution casting method in 5 wt%, 10 wt%, and 20 wt% concentrations using N,N-dimethylacetamide (DMAc). We prepared membranes by aiming to obtain partially sulfonated high ion conducting parts offering a phase-segregated structure where the fluorinated and ether part of the PAE structure can increase the blend compatibility while the membrane may also work at low humidity operation. Hence, the hypothesis and objective of this study is that synthesizing SMWCPAEs copolymer structure with a significant ionomer component may enable high proton conductivity in desired sulfonation levels while flourinated ether sections are used as compatibilizers in SMWCPAEs-SPEEK70 blend membranes (BMs). The structure of fluorinated polymers, MW of the PAEs, and SPEEK contents are important parameters. Optimizations of these parameters may help to obtain membranes which can perform better at lower humidity conditions. This may help reduce hydration. The effects of all mentioned parameters on the membrane performance are discussed.

Experimental

Materials

We distilled N, N-dimethylacetamide (DMAc, Fisher Scientific UK) solvent with phosphorus pentoxide over molecular sieves under a vacuum. Potassium carbonate (Aldrich, Darmstadt, Germany) was overnight dried before polymerization. Polyetheretherketone (PEEK) Victrex 450 PF powder (Lancashire FY5 4QD, UK, 25 μm particle size) was obtained from Victrex and was dried overnight at 100 °C under under vacuum atmosphere. We obtained sulfuric acid (95–97 %wt.) and hydrogen peroxide (H_2O_2, Merck KGaA, Darmstadt, Germany) and fumic sulfuric acid (%20 SO_3 H_2SO_4, Merck KGaA, Darmstadt, Germany) from Aldrich and they were all used as

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received. DFBP, Bis AF and Bis A (Sigma-Aldrich Chemie GmbH, Germany) were purchased from Aldrich and were purified by sublimation.

Instrumentation and methods

^{1}H and ^{19}F NMR spectra were collected using Bruker NMR Spectrometer (500 MHz) in DMSO-d6 at room temperature. Agilent (Model 1100) Gel permeation chromatography (GPC) instrument, equipped with three Zorbax columns (PSM60-S, PSM-300-S, PSM 1000-S), was used for molecular weight determinations. The eluent and internal standard were used as THF with a flow rate of 0.4 mL/min at 30 °C and toluene respectively. The polymers molecular weight were determined based on linear polystyrene standards (Polymer Laboratories). FTIR analyses were conducted by using PerkinElmer Spectrum One FTIR Spectrometer. Differential scanning calorimetry (DSC) analyses were conducted using PerkinElmer Jade DSC under nitrogen atmosphere at a 10 °C/min heating rate. We reported the DSC results of the 2nd heating run after cooling of the first run. The proton conductivity of the SMWCPAEs/SPEEK70 blend membranes was determined using BT-512 BekkTech system at 100% RH and 80 °C. JEOL 6335F SEM operated at 15 kV accelerating voltage was used to investigate membrane morphologies.

Poly (Arylene Ether)s synthesis

We used the Carothers equation [42] for designing MWCPAEs, and we made calculations accordingly. An important point that should be mentioned is the difference between ⟨Xn⟩, the number average degree of polymerization (DP), and DP. We defined ⟨Xn⟩ as 1 for our A–A/B–B two-component system/monomer, which is twice the number of repeating units (DP). In order to control Mw of the polymer, the molar monomer A/monomer B ratio was systematically changed from NA/NB = 0.973, 0.959 (polymer 1a, 2a), NA/NB = 0.989, 0.979 (polymer 1b, 2b) to NA/NB = 0.994, 0,990 (polymer 1c, 2c) as shown in Table 1.

The synthesis of 1a was realized following the procedure [43] to obtain MWCPAEs. Below, we provide the procedure for the synthesis of polymer 2a (DFBP-Bis AF). A 33.54 mmol (11.2772 g) of the Bis AF, a 34.97 mmol (11.6842 g) of DFBP, 190 mL of DMAc, and 95.23 mmol (13.1617 g) of potassium carbonate were loaded into a 500 mL round flask. The flask was stirred at 80 °C for 23 h under argon atm. Then, the temperature was kept at 90 °C for 2 h and then to 100 °C for another 2 h. By filtering, the unreacted potassium carbonate and potassium fluoride products were removed from the hot mixture. Finally, the filtered solution was cooled to room temperature, and poured into 3000 mL of water to precipitate the polymers. The polymers were filtered, water-washed six times, dried at 50 °C for 24 h, and were analyzed by IR, ^{1}H NMR, ^{19}F NMR, DSC, and GPC for characterization. The ^{1}H NMR and ^{19}F NMR characterizations of the two synthesized polymers confirming the structure are given below.

FT-IR (KBr, cm^{-1}): *Polymer DFBP-Bis A (1a);* 1005 cm^{-1} (Ar-O-Ar benzene aromatic streching band), 1509–1488 cm^{-1} (DFBF related bipheyl peaks). Additionally, 3436 cm^{-1} (6F Bis A related –OH peak), 12 and 1177 cm^{-1} (C–F, vibration peaks).

FT-IR (KBr, cm^{-1}): *Polymer DFBP-Bis AF* (2a): 900-1000 cm^{-1} (C–F streching of 6F monomer). (Ar-O-Ar benzene aromatic streching band), 929 cm^{-1} (aliphatic flour peaks-(-CF3)), 1509–1488 cm^{-1} (DFBF related bipheyl peaks). Additionally, 1550 cm^{-1} (asymmetric stretching arylene rings attached to the hexafluoroisopropylidene moiety). The 1008 cm^{-1} (diphenyl ether absorption (Ar–O–Ar).

Polymer DFBP-Bis AF (2a): ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.31–7.35 (d, 4H, Ar–H), 7.51–7.63 (d, 4H, Ar–H), ^{19}F NMR (600 MHz, CDCl$_3$, δ): −62.25 (s, 6F), −136.68 (s, 4F), 151,73 (s, 4F), yield: 72%

Polymer DFBP-Bis A (1a): ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 1.71 (s, 6H), 6.98 (s, 4H), 7.24 (s, 4H), ^{19}F NMR (600 MHz, CDCl$_3$, δ): 138.52 (s, 4F), −153.23 (s, 4F), yield: 86%.

Sulfonation of MWCPAEs (SMWCPAE)

The homopolymers 1a to 1c and 2a to 2c were synthesized via nucleophilic displacement polycondensation reaction. The polymers 1a-1c and 2a-2c were prepared using concentrated and fuming sulfuric acid, respectively. The sulfonation of 2a to 2c polymers was performed using fuming sulfuric acid. The sulfonation process can be optimized by changing the content of SO$_3$ in the sulfonating reagent or by changing the sulfonation time. In this study we varied the sulfonation time. A typical sulfonation procedure is given below for the 2a (S-DFBP-Bis AF) sample.

The prepared DFBP-Bis AF was dried at 105 °C under a vacuum oven for 24 h. Two grams of the DFBP-Bis AF and 40 mL fuming sulfuric acid (20% SO$_3$) were charged into mechanical stirrer-equipped flask operating at 300 rpm, at 30 °C for 8 h under nitrogen atmosphere. The S- DFBP-Bis AFs polymers were precipitated in deionized water with 1% glacial acetic acid. The polymers were filtered and washed with deionized water, to remove unreacted sulfuric acid of the S-DFBP-Bis AFs, until the pH reached a value of 7. The sulfuric

Table 1 – Polymerization conditions and results for the preparation of PAEs.

Parameter				Characterization			
Polymer	Monomer A (DFBP, mmol)	Monomer B1 (Bis A, mmol)	Monomer B2 (Bis AF, mmol)	N_A/N_B	$M_{n,GPC}$ (g/mol)	M_w/M_n	Tg (°C)
1a	34.47	33.54	–	0.973	18.227	1.79	140
1b	33.91	33.54	–	0.989	48.355	2.19	153
1c	33.74	33.54	–	0.994	91.471	1.93	161
2a	34.97	–	33.54	0.959	14.000	2.35	180
2b	34.26	–	33.54	0.979	30.000	1.98	184
2c	33.88	–	33.54	0.990	62.282	2.03	198

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acid-free polymers were dried at 100 °C for 24 h under vacuum. The DFBP-Bis A Sulfonation was achieved similarly to that described for DFBP-Bis AF while sulfonation chemical, time and temperature was different than DFBP-Bis AF.

The DFBP-Bis A sulfonation is given as follows: 2 g of dried DFBP-Bis A and 40 mL of concentrated H_2SO_4 (95–97%) were mixed in a flask equipped; stirred at 300 rpm at 60 °C for 4 h under a nitrogen atmosphere. Schemes 1 and 2 depict the chemical structures of S- DFBP-Bis AFs and S- DFBP-Bis As, respectively. S- DFBP-Bis AFs and S- DFBP-Bis As polymers were identified by FTIR, ^{1}H NMR and ^{19}F NMR.

FT-IR (KBr, cm^{-1}): *Polymer SDFBP-Bis A (1a);* 3434 cm^{-1} (O–H stretching of $-SO_3H$ and absorbed moisture), 1080 cm^{-1} at 1255 cm^{-1} and 1075 cm^{-1}, and 1020 cm^{-1}, (The new absorption bands of sulfur-oxygen (O=S=O), S=O, and S–O which are correlated to the asymmetric and symmetric stretching of sulfone in SO_3H groups). 598 cm^{-1} (C–S band).

FT-IR (KBr, cm^{-1}): *Polymer SDFBP-Bis AF* (2a): 3434 cm^{-1} (O–H stretching of $-SO_3H$ and absorbed moisture), 1080 cm^{-1} at 1255 cm^{-1} and 1075 cm^{-1}, and 1020 cm^{-1}, (The new absorption bands of sulfur-oxygen (O=S=O), S=O, and S–O which are correlated to the asymmetric and symmetric stretching of sulfone in SO_3H groups). 598 cm^{-1} (C–S band).

^{1}H NMR and ^{19}F NMR characterizations of the two synthesized polymers confirming the structure are given below.

Polymer S- DFBP-Bis AF (14.000 g/mol, 2a): ^{1}H NMR (500 MHz, DMSO-*d6*) δ (ppm): 7,96 (d, 1H), 7.28 (d, 1H), 7.22 (d, 1H), ^{19}F NMR (600 MHz, DMSO-*d6*, δ): −58.67 (s, 3F), −133.91 (s, 2F), 150.23 (s, 2F), yield: 80%.

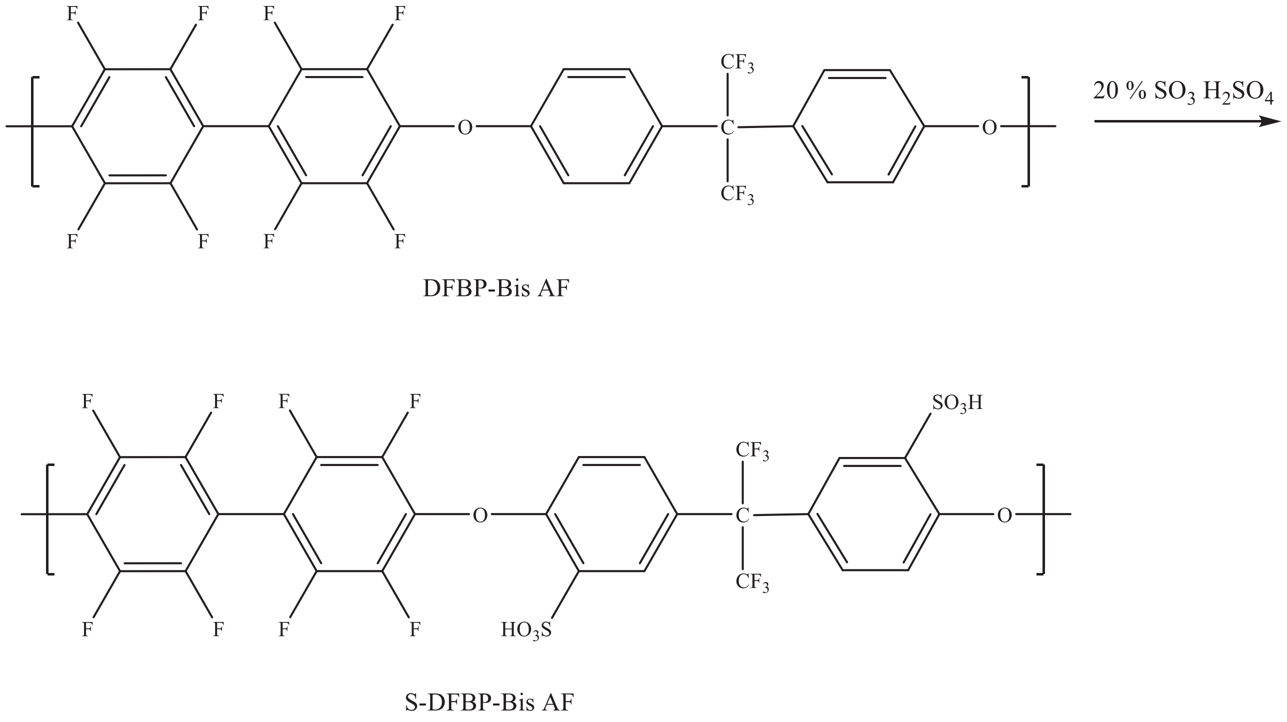
Polymer S-DFBP-Bis A (18 227 g/mol, 1a): ^{1}H NMR (500 MHz, DMSO-*d6*) δ (ppm): 7.68 (s, 1H), 7.18–7.10 (s, 2H), 1.63 (s, 3H), ^{19}F NMR (600 MHz, DMSO, δ): 138.52 (s, 4F), −153.23 (s, 4F), yield: 88%.

PEEK sulfonation (SPEEK70)

Concentrated H_2SO_4 was used to sulfonate commercially available PEEK [36]. The sulfonation of commercial PEEK procedure is given as follows: 5 g dried of PEEK and 100 mL of concentrated H_2SO_4 (95–97%) were mixed in a flask; stirred at 500 rpm under a nitrogen atmosphere at 60 °C for 4 h. The sulfonated PEEK (SPEEK) was precipitated by ceasing the reaction by pouring the flask content into ice cubes containing water mixture. The precipitated SPEEK was filtered, then washed with deionized water to remove unreacted H_2SO_4, until the pH value reached approximately 6–7. The SPEEK was dried stepwise, first in a vacuum oven at room temperature for 12 h followed by drying at 60 °C for 12 h. The SD (%) was determined as 70; IEC 2.02 meq g^{-1} [36].

Preparation of blend membranes (BMs)

Solution casting method [36] was followed in preparation of SMWCPAEs/SPEEK70 membranes. The designated amount of sulfonated polymer (S-DFBP-Bis AF, S-DFBP-Bis A) and SPEEK70 were dissolved in 10 mL of DMAc. The sulfonated polymer concentration in the blend ranged from 0 to 20 wt%. The membranes dried step-wise until the solvent was completely removed. Membranes were removed from the glass plate by immersing the plates in deionized water. The thicknesses of the dry blend membranes were measured by digital micrometer; giving values between 70 and 110 μm.



Scheme 1 – Schematic representation of DFBP-Bis AF sulfonation reaction.

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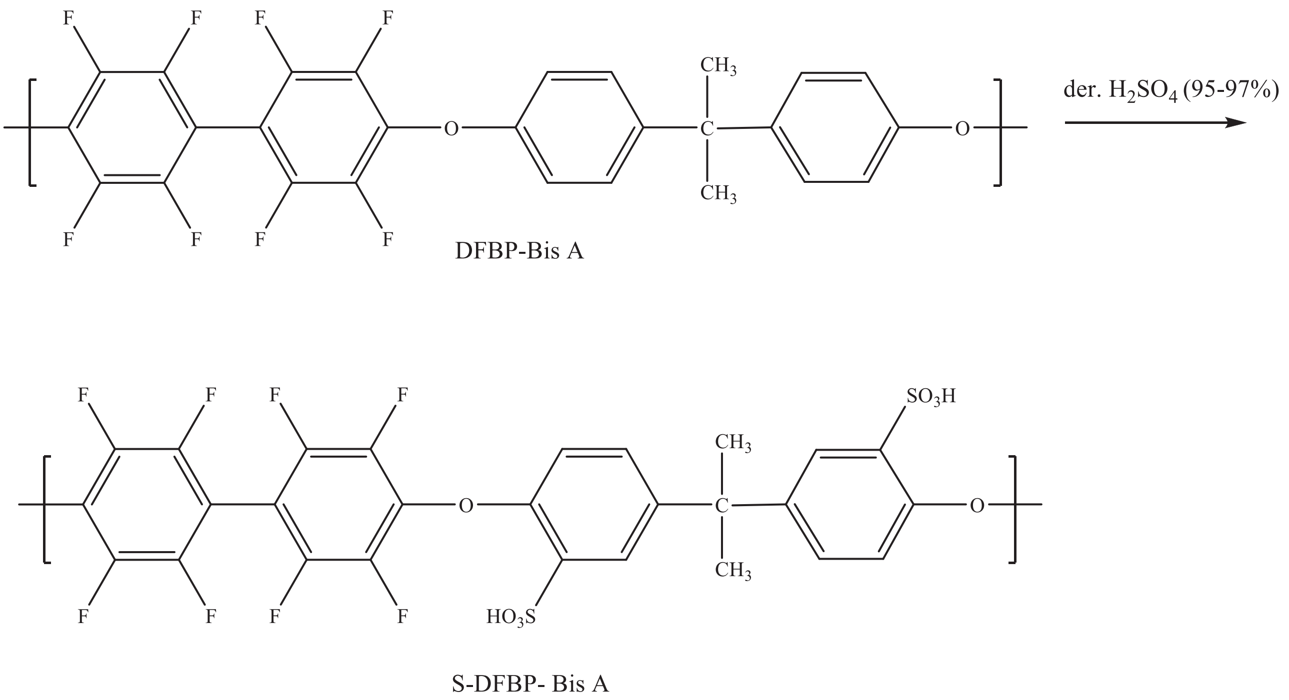

DFBP-Bis A

S-DFBP- Bis A

Scheme 2 – Schematic representation of DFBP-Bis A sulfonation reaction.

BM characterizations

The BMs' chemical and thermal characterizations were conducted using FTIR, 1H NMR, DSC, and TGA. Then, the fuel cell performances of the BMs were determined in terms of proton conductivity, IEC, WU, WVP, mechanical stability, methanol permeability, gas permeability, chemical stability, thermal stability, hydrolytic stability. The details of the fuel cell performance characterizations are provided below.

IEC of BMs

Membranes' IEC values were determined following a titration method [44]. Dried membrane sample (0.1–0.2 g) was treated with 50 mL saturated NaCl solution at 50 °C for 48 h to form sulfonic acid sodium salt of the membrane. The H^+ ion released from the membrane was titrated using 0.1 N NaOH solution and bromothymol blue indicator.

Water uptake (WU) of BMs

ASTM D 570–98 [45] was followed to determine WU values of the SMWCPAEs/SPEEK70 membranes. The BMs were kept in an oven at 105 °C for 1 h; followed by 50 °C for 24 h. BMs were cooled to room temperature in a desiccator, then weighed immediately (Wdry). For water uptake the BMs were treated with deionized water at room temperature for 24 h. Water-absorbed membranes were released from water, wiped off free water using tissue paper, and finally weighed immediately (Wwet) again. The WU wt.% value was calculated as follows. WU (wt.%) = 100x $(W_{wet}\text{-}W_{dry})/W_{dry}$.

BMs oxidative stability

As previously proposed [46,47], we used Fenton's reagent (3% H_2O_2 aqueous solution with 4 ppm of Fe^{++}) at 68 °C to test the oxidative stability of the BMs. The BMs were all soaked in this reagent and the BMs oxidative stability was determined.

Methanol permeability

A jacketed diffusion glass cell as described in Ref. [36] was used to measure the methanol permeabilities of the BMs.

The following equation was used to calculate methanol diffusion coefficient:

$$-\ln((2C_A / C_{A0}) - 1) = (2A_M D_{AB}) \times t / (V_0 \times \Delta X)$$

where A_M is the effective area (4.15 cm^2), Δx is the thickness of membrane, V_o is the volume of permeated compartment, C_{A0} is the ethanol concentration in methanol chamber, C_A is the water chamber and D_{AB} is the methanol diffusion coefficient [47].

Gas permeability

The BMs gas permeabilities were assessed according to ASTM D1434-82 [48] and H_2 flow rate was calculated using the following equation:

$$\text{Gas permeability } (cm^3_{STP}{*}cm / cm^2{*}s{*}cm\ Hg) = VxL / (A{*}t\ {*}\Delta P)$$

where V is the permeated gas volume, A is the membrane cross-sectional area, t is time, ΔP ithe s partial pressure difference of gas between the feed side and the permeating side of a membrane. L is the membrane thickness.

Water vapor permeability (WVP)

The ASTM E 96-/E–96M – 13 method was followed for performing this test [49]. WVP of the membranes was determined based on water vapor transmission rate (WVTR). Membrane specimens of approximately of 11 mm diameter were placed

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in the glass containers containing anhydrous calcium chloride as a desiccant and the membrane.

Proton conductivity

We used a Four-point probe method to determine proton conductivities of the sulfonated BMs utilizing in-plane membrane conductivity test system (BT-512 Model, BekkTech LLC, Loveland, CO) (6, 13, 14, 36, 37). Approximately (5 × 30 mm) sample membrane was placed in connection with four probes. The Keithley 2400 Sourcemeter was used to measure the voltage–current values set. Conductivity were measured under different RH conditions varying between 30 and 100% at 80 °C. The desired relative humidities set by passing nitrogen gas through the conductivity cell. Four electrode conductivity (s) was calculated from measured membrane resistance (R) using following equation:

$$\sigma = L/R{*}W{*}T$$

where L is the distance (cm) between two reference electrodes, W is the width and T is the thickness (cm) of the dried sample membrane [36].

Mechanical properties

Mechanical properties of the BMs were conducted according to the ASTMD 882-12 standard method [36,50] in 50–60% relative humidity condition and under ambient temperature by using Material Testing Machine Z010/TN2S with crosshead speed of 5 mm/min to determine tensile strength, Young modules, and elongation at break values.of the membranes. Nafion 112 membrane was also tested at the same conditions [36,37].

PEMFC single cell test

Single cell PEMFC performance tests have been carried out following the setup and conditions listed in Table 2.

Results and discussion

The overall schematic representation of the synthesis and fabrication of SMWCPAEs-SPEEK70 blended membranes (BMs) summarized in Fig. 1.

Sulfonation of PEEK and PAEs (SPEEK70 and SMWCPAEs)

The PAEs sulfonation of aromatic polymers is similar to an electrophilic substitution reaction, where an activated site aromatic proton is replaced by an $-SO_3H$ group. The electrophilic substitution site in a particular polymer highly affected by the groups attached to the ring. The methyl group of the DFBP-Bis A is more electron-donating than the trifluoromethyl group of the DFBP-Bis AF; therefore, the sulfonation reaction for the DFBP-Bis A sample was achieved easily compared to that for the DFBP-Bis AF sample. As a result, fuming sulfuric acid (20% SO_3) was used as the sulfonating agent for the DFBP-Bis AFs. We used concentrated sulfuric acid (95–97%) as the sulfonating agent for the DFBP-Bis A, PEEK. SPEEK sulfonation degree (SD) were determined as 70% with an IEC of 2.02 at 60 °C in 4 h. FTIR characterization of PEEK sulfonation shows (Fig. 2.) that the intensity of the absorption band at 3434 cm^{-1} increased due to the O–H stretching of $-SO_3H$ and absorbed moisture. The new absorption bands of sulfur-oxygen (O=S=O), S=O, and S–O which are correlated to the asymmetric and symmetric stretching of sulfone in SO_3H groups were observed at 1080 cm^{-1} at 1255 cm^{-1} and 1075 cm^{-1}, and 1020 cm^{-1}, respectively an they are characteristic of the sulfonate groups of aryl sulfonate and the absorption band at 598 cm^{-1} confirms the C–S band. However, these peaks are invisible in the PEEK sample as also mentioned by Kim et al. [51].

The IEC and sulfonation degree values of PAEs are given below in Table 3.

BMs characterization

MWCPAEs/SPEEK BMs were prepared by using SPEEK70 and S-DFBP-Bis A, S-DFBP-Bis AF based polymers with different molecular weights (S-DFBP-Bis A: Mw = 18.227, 48.355, 91.471, S-DFBP-Bis AF: Mw = 14.000, 30.000, 62.282) in 5, 10 and 20 wt% concentrations.

Membrane morphology by SEM

We utilized Scanning Electron Miscroscopy (SEM) for study of the morphology of SMWCPAEs/SPEEK. Fig. 3 depicts cross-sectional SEM images of SPEEK70 and different molecular weight S-DFBP-Bis A and S-DFBP-Bis AF based polymers with different concentrations of SMWCPAEs. Pristine SPEEK70, S-DFBP-Bis AF based polymer (14.000 g/mol)-(e) and S-DFBP-Bis A based polymer (18.227 g/mol) membranes without copolymer reflected no obvious macroscopically phase separation. Increase in the contents of S-DFBP-Bis A and S-DFBP-Bis AF polymers in SPEEK70 gave similar morphologies that can be associated to more chain entanglements at higher molecular weights. It is meaningful to argue that high MW may be important in pinhole formation prevention, and fatigue resistance improvement and thus long-term stability due to the good miscibility probability of the BMs. Membranes exhibited homogeneously distributed domains by blending SPEEK70 with S-DFBP-Bis AF polymers (Fig. 3 a,b) and S-DFBP-Bis A polymers (Fig. 3 c,d) in all ratios (5–20 % wt/v). But for (c) SPEEK70/S-DFBP-Bis A (18.227 g/mol) blend membranes showed finger-like cavities that might be due to the trapped air during the membrane preparation process. No apparent pinhole defects were observed on the surfaces of the as-prepared membranes designating the uniformity of the samples, with well-film transparencies.

Table 2 – PEMFC Single Cell performance test conditions.

Anode	0.7 mg Pt–C/cm^2
Cathode	0.7 mg Pt–C/cm^2
Catalyst	*% 40 Pt–C Vulcan XC 72, ETEKL1400*
OCV *(Open circuit voltage)*	1,0141
H_2 flow rate	500 mL/min.
O_2 flow rate	500 mL/min.
Cell Temperature	65 °C
Humidification Temp.	65 °C
Line temperature	75 °C
Active membrane area	25cm^2

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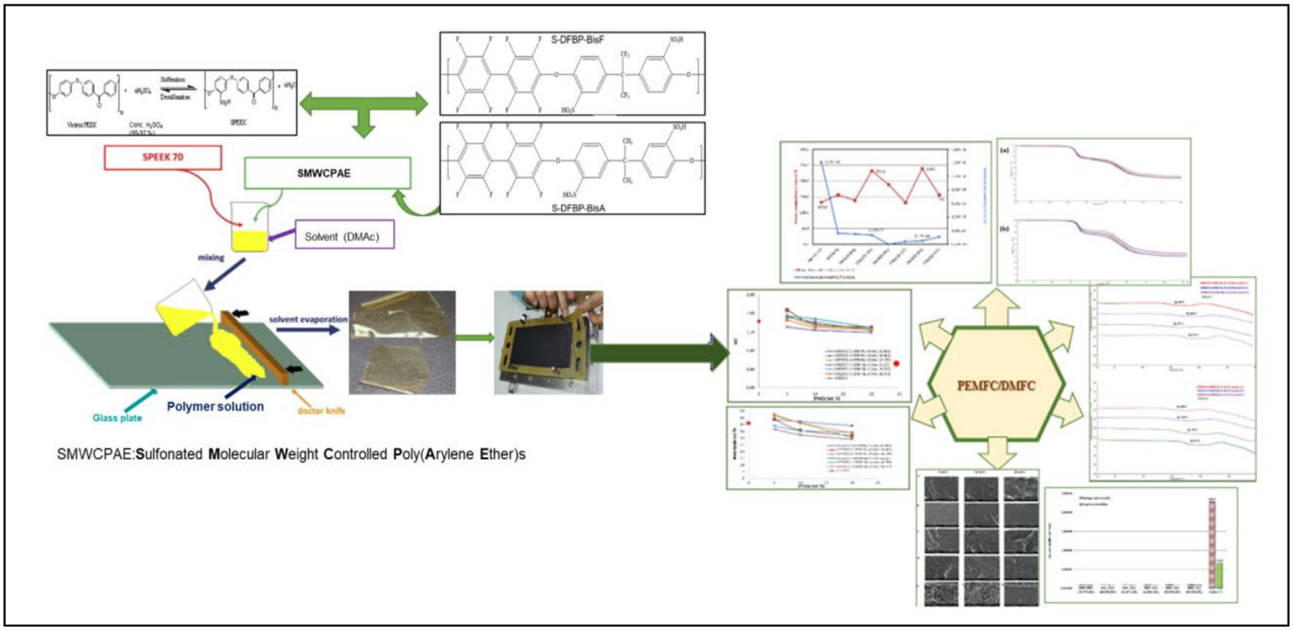

Fig. 1 – The overall schematic representation of the synthesis and fabrication of SMWCPAEs-SPEEK70 BMs.

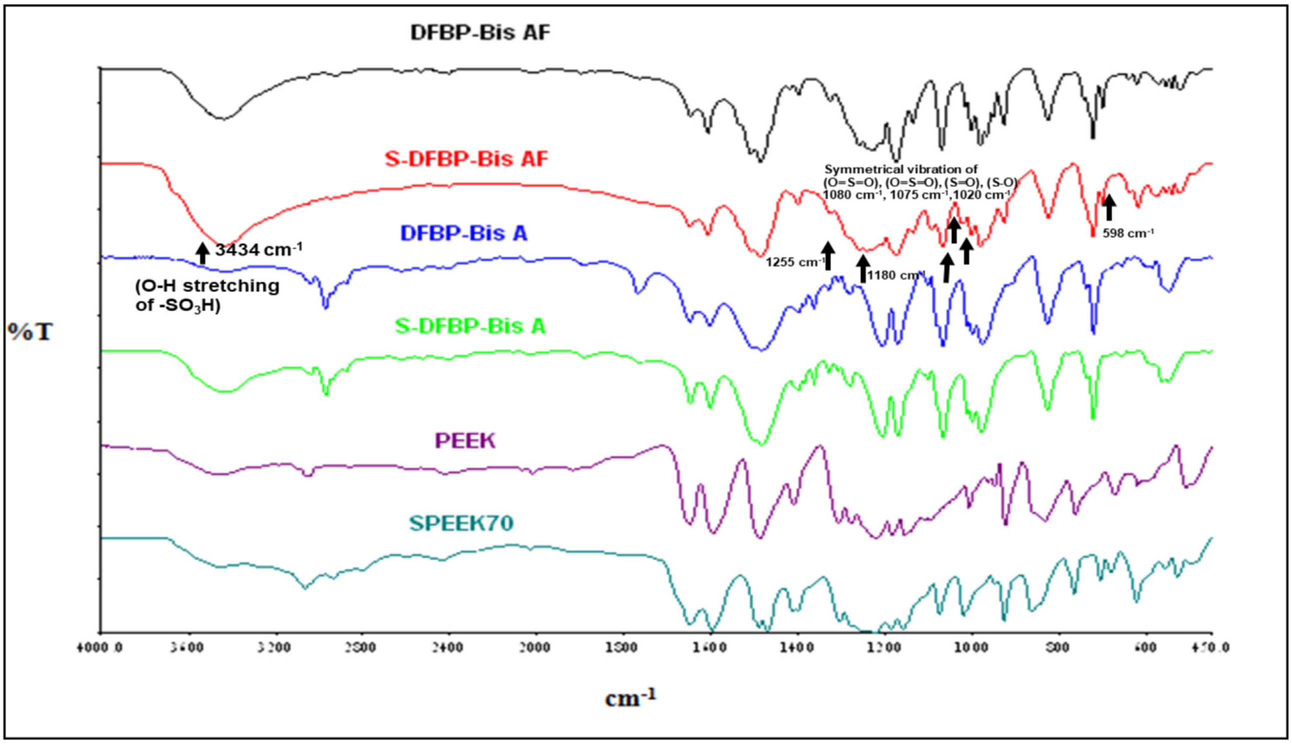

Fig. 2 – FTIR spectra of the (PAE)s, S-(PAE)s, PEEK and SPEEK70.

Thermal characterization of BMs by TGA and DSC

For harsh condition applications, glass transition temperature (Tg) and thermal stability are important parameters for LTFC, ITFC, and DMFC (70–110 °C, 150–350 °C and 200 °C) applications. Thermal characterizations of BMs are based on TGA and DSC analysis results. Fig. 4 illustrates the TGA of the BMs of various compositions. They all show similar thermal gravimetric behaviors. Three-step weight loss (WL) is observed from 300 to 400 °C, from 500 to 600 °C, and above 600 °C. The first WL is due to the cleavage of the sulfonic acid groups. The

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Table 3 – Ion-exchange capacity and sulfonation degree values of S-(PAE)s.

Polymer	IEC_p^a (meq g^{-1})	SD %	MWs
S-DFBP-Bis A (N_A/N_B: 0.973)	0.590	31.1	18.227
S-DFBP-Bis A (N_A/N_B:0.989)	0.611	34.0	48.355
S-DFBP-Bis A (N_A/N_B:0.994)	0.598	33.2	91.471
S-DFBP-Bis AF (N_A/N_B: 0.959)	0.684	46.3	14.000
S-DFBP-Bis AF (N_A/N_B: 0.979)	0.691	46.8	30.000
S-DFBP-Bis AF (N_A/N_B:0.990)	0.698	47,4	62.282

IEC_p ^{a}: ion exchange capacity.

second WL is due to decomposition of the sulfonated polymers (S-DFBP-Bis A and S-DFBP-Bis AF) and the third WL is interpreted to be due to decomposition of the SMWCPAEs main chain. These results reveal that the BMs have proper thermal stabilities and meet the rquirements of both (LTFC, DMFC) sytems as a PEM.

The DSC results of the SPEEK70/S-DFBP-Bis A (Mw = 18.227, 48.355, 91.471 g/mol) (5%) blends are displayed in Fig. 5. The glass transition temperature (Tg) for SPEEK70 was determined as 173 °C and a single Tg value was observed for all blend membranes; with increased Tg values after sulfonation. This can be explained by the sulfonyl groups attached to the polymers resulting an increase in Tg values due to the constraints on the segmental movements in the polymer blocks. Addition of 5 wt % S-DFBP-Bis AF and S-DFBP-Bis A polymers to the SPEEK70 membranes also gave one glass transition temperature confirming the homogeneity of the membranes. The Tg values of the blend membranes decreased with respect to pristine SPEEK70 (Tg_{SPEEK} = 173 °C), but the increase in molecular weight and the sulfonation degree seem to have positive effect on Tg values (e.g., the values are increased from 157 to 164 °C and from 160 to 167 °C for SCMWPAE-S-DFBP-Bis AF and SCMWPAE-S-DFBP-Bis A, respectively). The thermal stability of the BMs, as shown from TGA analyses, is very similar. Therefore, glass transition temperature results suggest a strong preference for polymers of intermediate Mws.

All the blends are miscible in the case of existence of one glass transition temperatures. The depression of glass transition temperature indicates the interaction between the polymer segments are maximum shifting toward low temperature as the SMWCPAEs added acting as a polymeric diluent of the blend [52].

BMs' IEC, proton conductivity (PC) and WU

The proton conductivity (PC) of MWCPAEs depended on the WU and IEC values of the membranes as reported earlier [53–55]. The IEC, PC (T = 80 °C and RH = 100%), WU values for BMs are listed in Table 4 andFig. 6. The PC is extremely affected by the degree of hydration and the temperature of the surrounding. Hence, we immersed all membranes in water at room temperature for hydration before proton conductivity measurements. The conductivity of pristine SPEEK70 was measured as 156.1 mS/cm with our test system.

We have taken Nafion membrane as a standard material in our study and found as 133 mS/cm at the same conditions. Blending 5 wt% S-DFBP-Bis AF with SPEEK70 for different molecular weights (M_w:14.000 5%; M_w:30.000 5%; M_w: 62.282 5%) showed conductivity (138.9, 232.2, 188,4 mS/cm), water uptake (43.7, 43.9, 46.4 wt %) and IEC values (1.52, 1.67, 1.56 meq g^{-1}) respectively. The mid-MW and low concentration values resulted in the best conductivity (138.9–83.7 mS/cm; 232.2–100.0 mS/cm and 188.4–92.2 mS/cm) and IEC values (1.52–1.23; 1.67–1.30 and 1.56–1.28 mS/cm), respectively. Increasing contents from 5 to 10 and 20 wt% did not lead to any further improvement on the properties.

SPEEK70/S-DFBP-Bis A based blends with different molecular weight combinations (Mw:18.227; Mw:48.355 and Mw: 91.471) and with 5% concentration, the proton conductivity (132.3; 238.9 and 156 mS/cm) and IEC (1.31 meq g^{-1}; 1.54 meq g^{-1} and 1.46 meq g^{-1}) values determined has the same behaviour as S-DFBP-BisAF-SPEEK70 blend membranes. The best values also determined for low (5 wt%)concentration and intermediate molecular weight (48.355) combination for S-DFBP-BisA-SPEEK70 blend membrane. The highest proton conductivity value was determined as 238.9 mS/cm for SPEEK70/S-DFBP-Bis A blend membrane (5% concentration and Mw:48.355). Although the effect of MW seems not to be conclusive, the data as shown in Table 3 suggest that use of medium MW of the polymer leads to a better performing membrane.

Fig. 6 clearly shows that the highest proton conductivity, IEC and water uptake values were recorded for membranes with minimum concentration (5 wt%) and intermediate molecular weights (Mw:30.000 and Mw: 48.355) for SPEEK70/S-DFBP-Bis AF and SPEEK70/S-DFBP-Bis A membranes, respectively.

Increasing SMWCPAEs contents (or decreasing SPEEK content) from 5 wt% to 20 wt% resulted decrease in WU and PC values for all MWs and for two different chemical structures. The WU values decreased gradually by increasing the MWs and it is not easy to say that the MW has clear influence on proton conductivity under fully hydrated conditions.

The SD (sulfonation degree) values of the PAEs seem to be more effective on WU and PC values than MW itself for two different structures and the highest values mainly obtained for the highest SD/IEC values. The SD % values changed almost same for all MWs and was around 46–47% for S-DFBP-Bis AF- PAE structure while the values changed between 31 and 34% for S-DFBP-Bis A -PAE structure due to the effect of sulfonation reagents used (fuming sulfuric acid (20% SO_3) for DFBP-Bis AFs; concentrated sulfuric acid (95–97%) for the DFBP-Bis A). The highest PC values has also been observed for the highest SD and IEC values for both structures at medium MWs. Increasing MW caused SD decrease for the DFBP-Bis A structure which can also be used as an indication of MW effect of PAE structures on the end BMs.

Oxidative stability of BMs

The time elapsed in Fenton's reagent at 68 °C just before the membrane breaks is very indicative for oxidative stability to peroxide radical attack [46]. The chemical stabilities of SMWCPAEs-SPEEK70 blend membranes were enhanced with the addition of different molecular weights of SMWCPAEs. The degradations of BMs under the Fenton test ranged between 2.5 and 4 h (Table 4.)while the degradation time of pristine SPEEK70 was 2 h at the same conditions [36].

The Fenton test has been reported as an accelerated hydrolytic stability test for simulating the lifetime and durability of the membranes real-time environment [46,47]. The test

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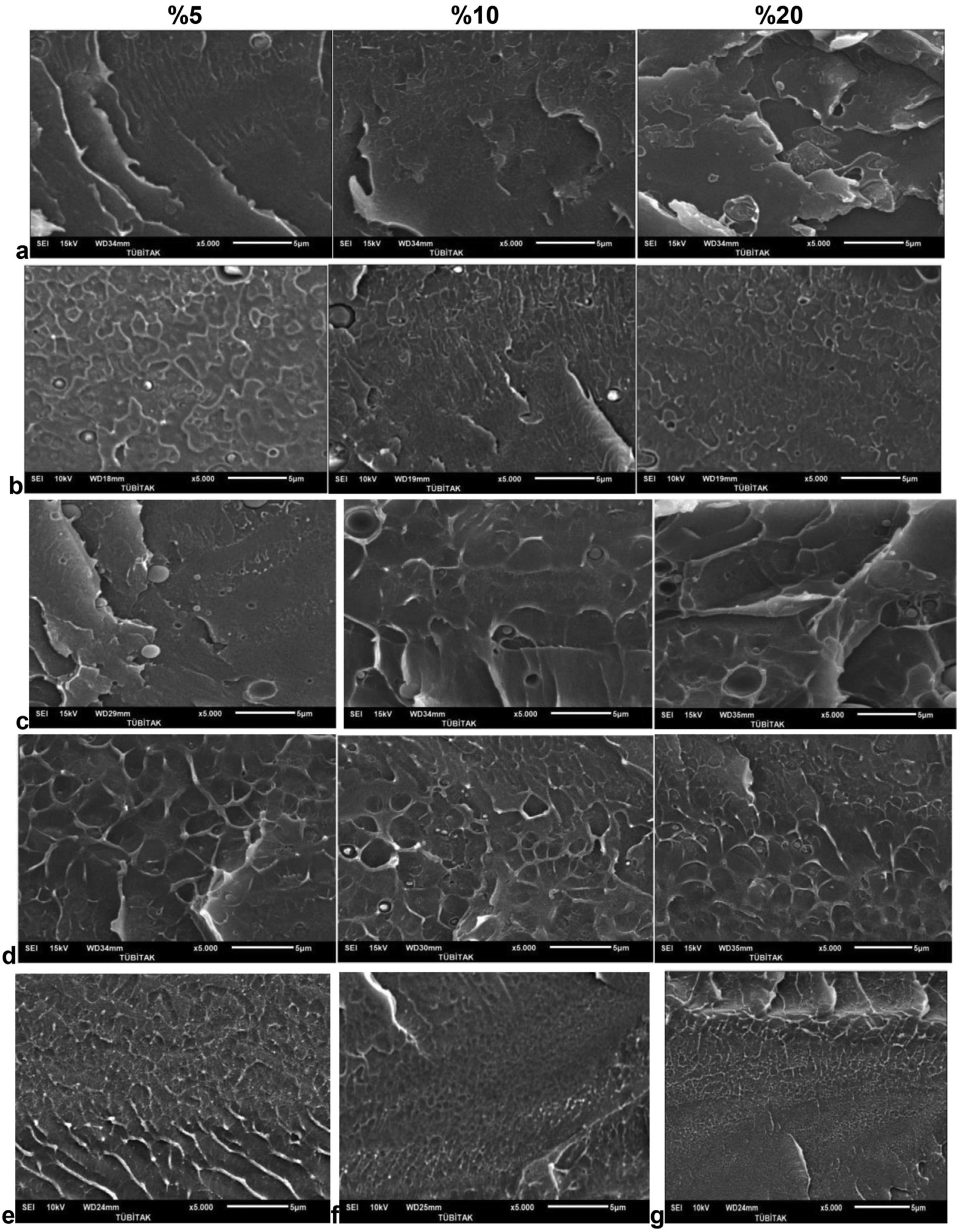

Fig. 3 – SEM results of the SPEEK70/MWCPAE BMs (CSX5000; CS: cross-section): (a) SPEEK70/S-DFBP-Bis AF (14.000 g/mol), (b) SPEEK70/S-DFBP-Bis AF (62.282 g/mol), (c) SPEEK70/S-DFBP-Bis A (18.227 g/mol), (d) SPEEK70/S-DFBP-Bis A (91.471 g/mol), (e) S-DFBP-Bis AF polymer (14.000 g/mol), (f) S-DFBP-Bis A polymer (18.227 g/mol), (g) SPEEK70 polymer.

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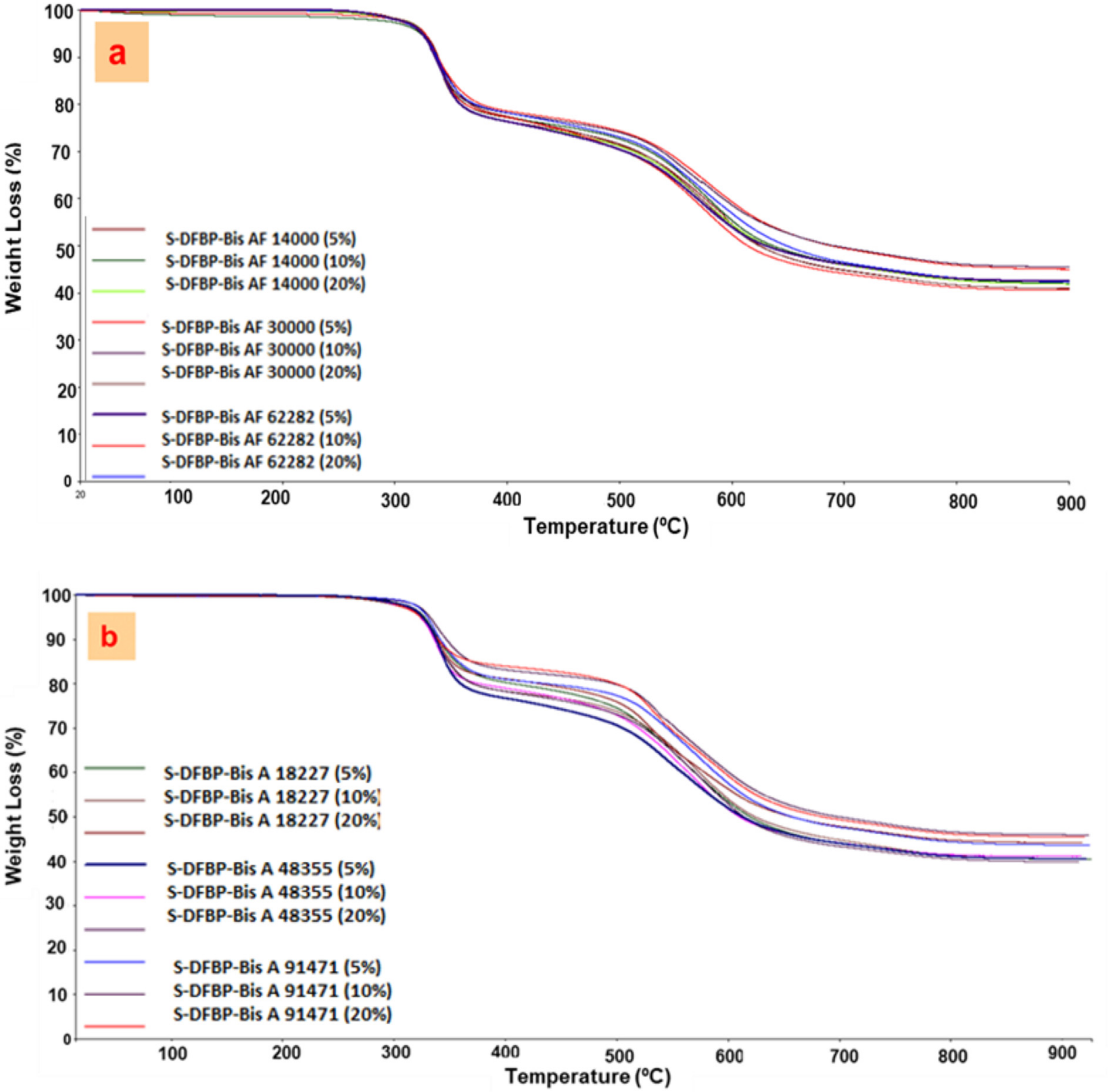

Fig. 4 – TGA results of the BMs (5, 10 and 20%). (a) Molecular weight effect of S-DFBP-Bis AF polymers (Mw = 14.000, 30.000, 62.282 g/mol) (b) Molecular weight effect of S-DFBP-Bis A polymers (Mw = 18.227, 48.355, 91.471 g/mol).

conditions are very harsh and expose the membrane to an unrealistically high level of radicals. The polybenzimidazoles (PBI) membranes' long-term durability test was determined over 5000 h in real time fuel cell system whereas the average decomposition time of these membranes was only 30 min [46,47]. The durability of the SPEEK70 membrane (2hr) with the addition of SMWCPAEs, blend membranes test results improved (2.5–4 h) compared to the values reported in the literature [40–53] and best values were obtained for the intermediate Mw and low concentrations blend membrane concentrations (Mw = 48.355; Mw = 30.000, 5 wt%). However, prior to any application, we recommend a long-term durability and chemical stability test for membranes in fuel cell systems.

Methanol permeability of BMs

The methanol permeability value of pure SPEEK70 was determined as 1.63 × 10^{-7} cm^2 s^{-1} and increasing molecular weight of S-DFBP-Bis AF (5%) in the SMWCPAE/SPEEK70 BMs decreased the methanol permeability (Fig. 7.). The methanol permeability values for SPEEK70/S-DFBP-Bis AF (Mw:14.000; Mw:30.000; Mw:62.282, 5 wt%) and SPEEK70/S-DFBP-Bis A (Mw:18.227; 48.355; 91.471, 5 wt%), were determined as 1,53 × 10^{-7} cm^2/s; 1,34 × 10^{-7} cm^2/s; 6,72 × 10^{-10} cm^2/s,

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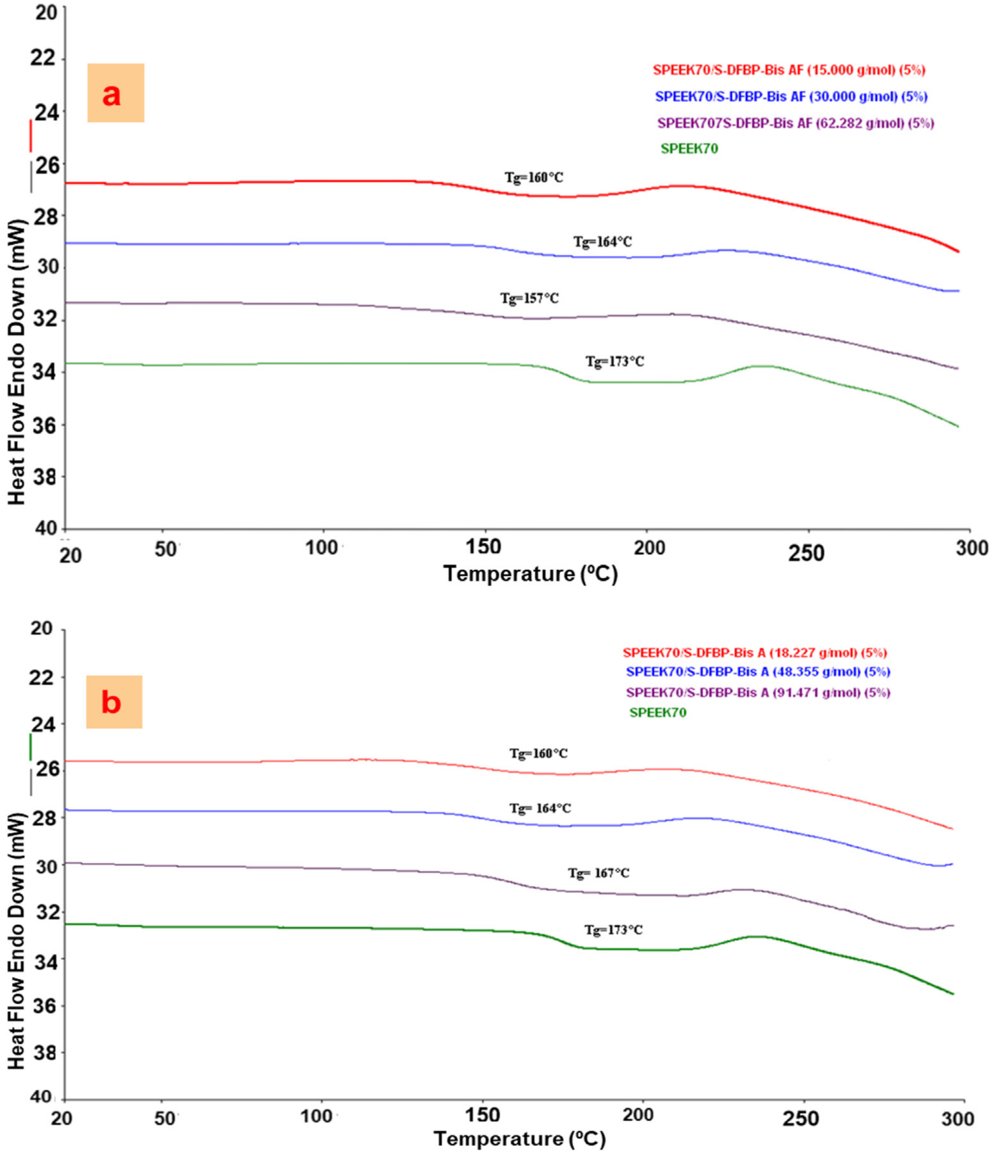

Fig. 5 — DSC results of the BMs (5%). (a) Molecular weight effect of S-DFBP-Bis AF polymers (Mw = 14.000, 30.000, 62.282 g/mol) (b) Molecular weight effect of S-DFBP-Bis A polymers (Mw = 18.227, 48.355, 91.471 g/mol).

4,29 × 10^{-8} cm^2/s; 5,17 × 10^{-8} cm^2/s; 1,13 × 10^{-7} cm^2/s, respectively. The methanol permeability value (6,72 × 10^{-10} cm^2/s) of SPEEK70/S-DFBP-Bis AF (Mw:62.282 5%) was nearly four- and three-order of magnitudes lower than that of Nafion 117 (1,21 × 10^{-6} cm^2/s) and pristine SPEEK70 (1,63 × 10^{-7} cm^2/s) membrane, respectively. These results indicate that BMs are resistant to methanol permeability and as a result they are suitable for DMFC applications.

Table 5 lists proton conductivity and methanol properties of some PAE based FC membranes from the literature and from this study. As shown, the best values determined so far are those from this study.

Gas permeability

The PEMFCs and DMFCs require low gas permeability since gas permeability could enormously affect the performance and the durability of the systems since the gas sealing property helps isolating fuels and oxidants. Hydrogen permeability (HP) of the SMWCPAE/SPEEK70 the BMs and Nafion 112 membrane were measured at 25 °C (Fig. 8.). The gas permeability of all BMs with 5% composition showed much lower hydrogen and oxygen permeability values than Nafion® membrane (hydrogen permeability (HP); 2.29 10^{-3} cm^3/s, oxygen permeability (OP); 6.64 10^{-4} cm^3/s). SPEEK70/S-DFBP-Bis AF (Mw:62.282 5%) blend membrane showed the lowest value proving that they could be a very good candidate to be used for PEMFC and DMFC applications.

Mechanical properties of the BMs

Two or more polymers have been mixed to create blends as a new material with different physical properties. Compatible

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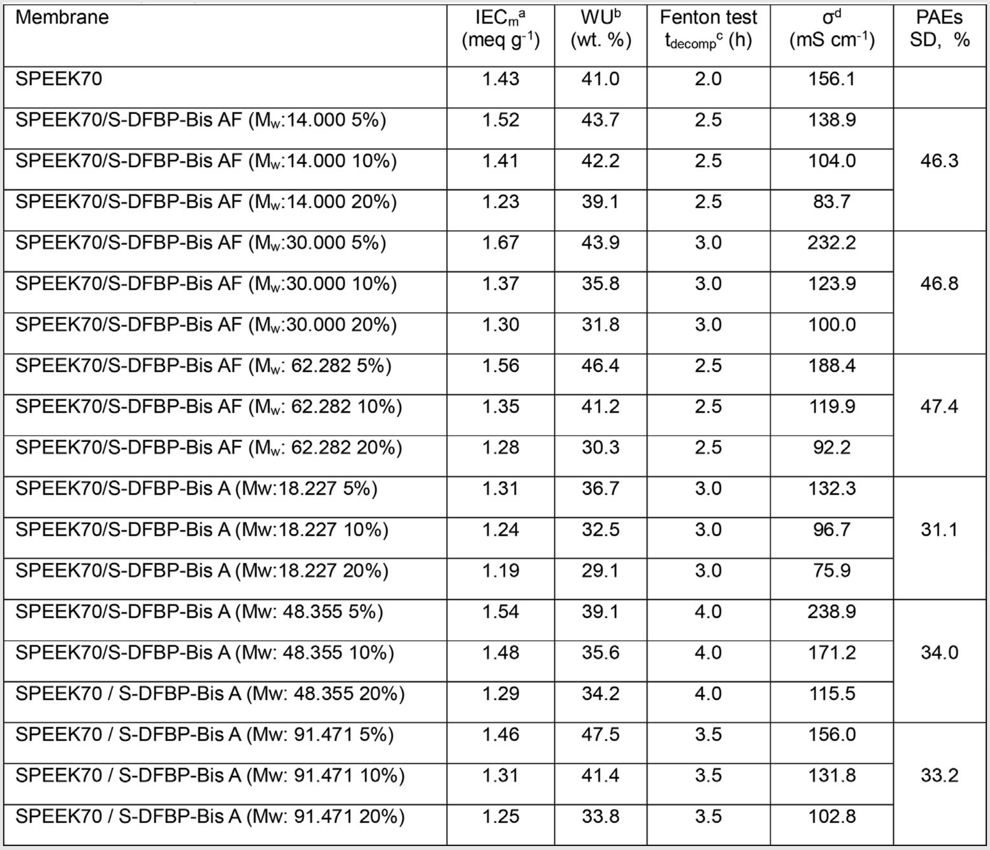
Table 4 – IEC, WU, Fenton test and σ^d characterization of BMs.



Membrane	IEC_m^a (meq g^{-1})	WU^b (wt. %)	Fenton test t_{decomp}^c (h)	σ^d (mS cm^{-1})	PAEs SD, %
SPEEK70	1.43	41.0	2.0	156.1	
SPEEK70/S-DFBP-Bis AF (M_w:14.000 5%)	1.52	43.7	2.5	138.9	46.3
SPEEK70/S-DFBP-Bis AF (M_w:14.000 10%)	1.41	42.2	2.5	104.0	
SPEEK70/S-DFBP-Bis AF (M_w:14.000 20%)	1.23	39.1	2.5	83.7	
SPEEK70/S-DFBP-Bis AF (M_w:30.000 5%)	1.67	43.9	3.0	232.2	46.8
SPEEK70/S-DFBP-Bis AF (M_w:30.000 10%)	1.37	35.8	3.0	123.9	
SPEEK70/S-DFBP-Bis AF (M_w:30.000 20%)	1.30	31.8	3.0	100.0	
SPEEK70/S-DFBP-Bis AF (M_w: 62.282 5%)	1.56	46.4	2.5	188.4	47.4
SPEEK70/S-DFBP-Bis AF (M_w: 62.282 10%)	1.35	41.2	2.5	119.9	
SPEEK70/S-DFBP-Bis AF (M_w: 62.282 20%)	1.28	30.3	2.5	92.2	
SPEEK70/S-DFBP-Bis A (Mw:18.227 5%)	1.31	36.7	3.0	132.3	31.1
SPEEK70/S-DFBP-Bis A (Mw:18.227 10%)	1.24	32.5	3.0	96.7	
SPEEK70/S-DFBP-Bis A (Mw:18.227 20%)	1.19	29.1	3.0	75.9	
SPEEK70/S-DFBP-Bis A (Mw: 48.355 5%)	1.54	39.1	4.0	238.9	34.0
SPEEK70/S-DFBP-Bis A (Mw: 48.355 10%)	1.48	35.6	4.0	171.2	
SPEEK70 / S-DFBP-Bis A (Mw: 48.355 20%)	1.29	34.2	4.0	115.5	
SPEEK70 / S-DFBP-Bis A (Mw: 91.471 5%)	1.46	47.5	3.5	156.0	33.2
SPEEK70 / S-DFBP-Bis A (Mw: 91.471 10%)	1.31	41.4	3.5	131.8	
SPEEK70 / S-DFBP-Bis A (Mw: 91.471 20%)	1.25	33.8	3.5	102.8	

polymer blends enhances the mechanical properties while incompatible polymer blends lead to mechanical properties lower than their starting values [57]. Table 6 shows the mechanical properties of different BMs. Increasing contents of SMWCPAEs in the SMWCPAEs/SPEEK70 composition led to increase in Young modulus values for S-DFBP-Bis AF from 581 to 849 MPa and for S-DFBP-Bis A based membranes from 570 to 934 MPa. The tensile strength values also increased from 28.63 to 49.21 MPa for S-DFBP-Bis AF membranes and 24–44 MPa for S-DFBP-Bis A membranes. The miscibility can be improved by mixing with low-molecular-weight analogues. The analogues that exhibit negative heat of mixing are miscible, while the analogues exhibiting positive heat of mixing are immiscible [57]. In fact that we obtained a single Tg value for all blend membranes suggests the miscibility of the mebranes. The SEM results supported that increasing the content of copolymer of 1a, 1b in BMs compositions has resulted higher density and more compact membranes with stronger and homogeneous structures. The elongation at break of SMWCPAE-SPEEK70 BMs varied between 9 and 19 MPa with much lower elongation values than that of Nafion (249 ± 0.5%). The Fenton test results also support the results obtained from mechanical testing. The addition S-DFBP-Bis A, S-DFBP-Bis AF into the SPEEK70 polymer definetly increased the decomposition values of the resulted membranes from 2 to 4 h. The membranes presented excellent mechanical properties; strong enough for FC applications. Increase of MW of BMs improved mechanical properties.

As expected, both Young modulus and tensile strength values have been inceased with the increasing SMWCPAE contents in all BMs (Table 6). The blends are miscible and mechanically compatible. The results confirm the old idea that like dissolves like [52].

Water vapor permeability of BMs

WVP is indicative of water transportation through the membrane and Water vapor transmission (WVT) via PEMs is important for fuel cell operation. A high WVP represents higher diffusion of the water via the membrane during FC operation, which could projectile a more uniform water distribution during fuel cell operation [37].

WVTR and WVP values of SPEEK70, Nafion and SPEEK70/S-DFBP- Bis A, S-DFBP-Bis AF blend membranes with 10% concentrations of SCMWPAEs are given presented in Table 7 Nafion117 has the highest WVTR (17.9 g/m^2 h) and WVP (5.6×10^{-10} g/m s Pa) values. The lowest WVTR and WVP values were obtained for intermediate molecular weight of SPEEK70/S-DFBP- Bis A (48.355 10%) polymer as 10.9 g/m^2 h and 8.71×10^{-11} g/m s Pa, respectively. Table 7 shows that SMWCPAEs-SPEEK70 BMs may also work at lower humidity values by controlling molecular weights of the PAEs, their sulfonation degree and SPEEK content in the BM compositions.

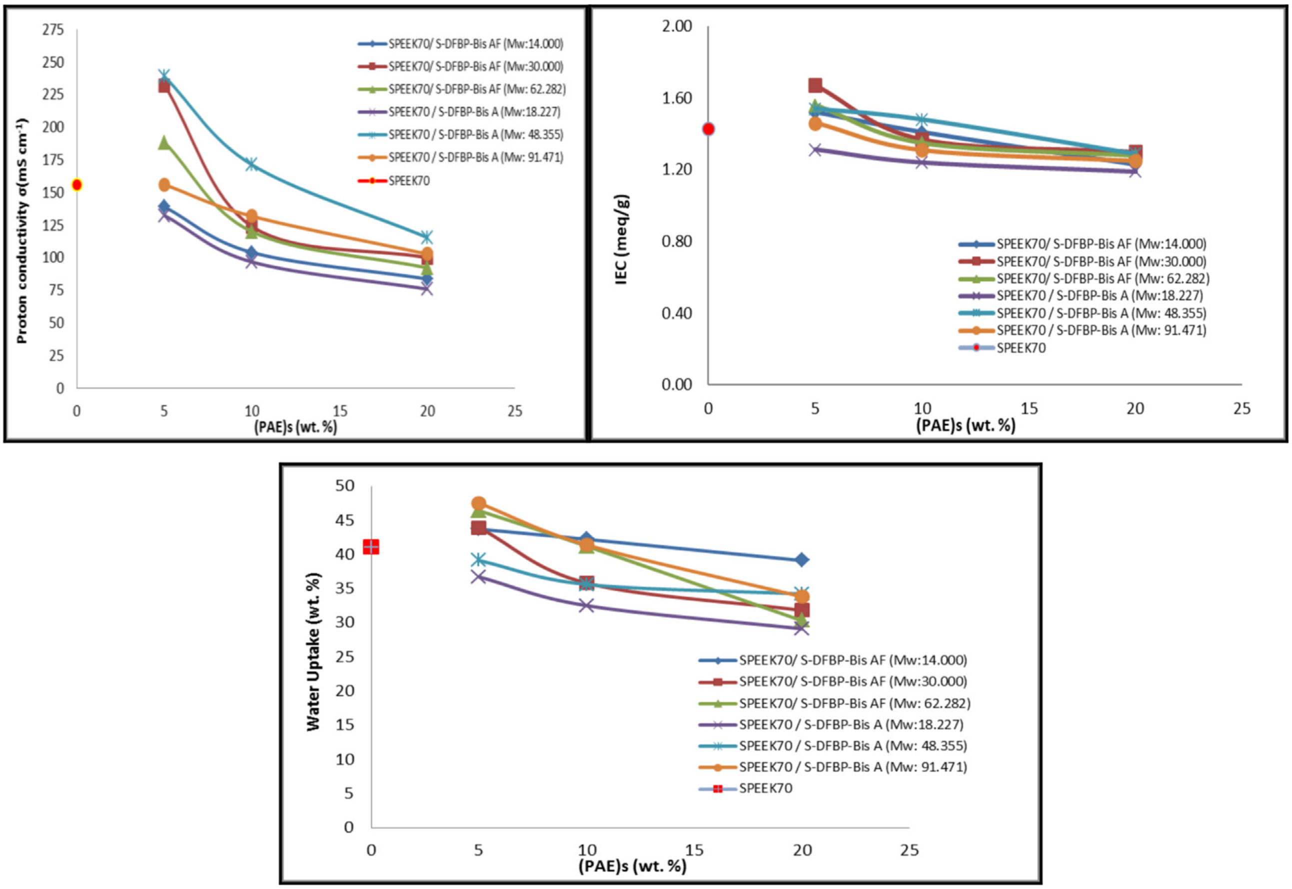


Fig. 6 – PC (atT = 80 °C, RH = 100%), IEC and WU of SPEEK70/MWCPAE based blend membranes of different concentrations.

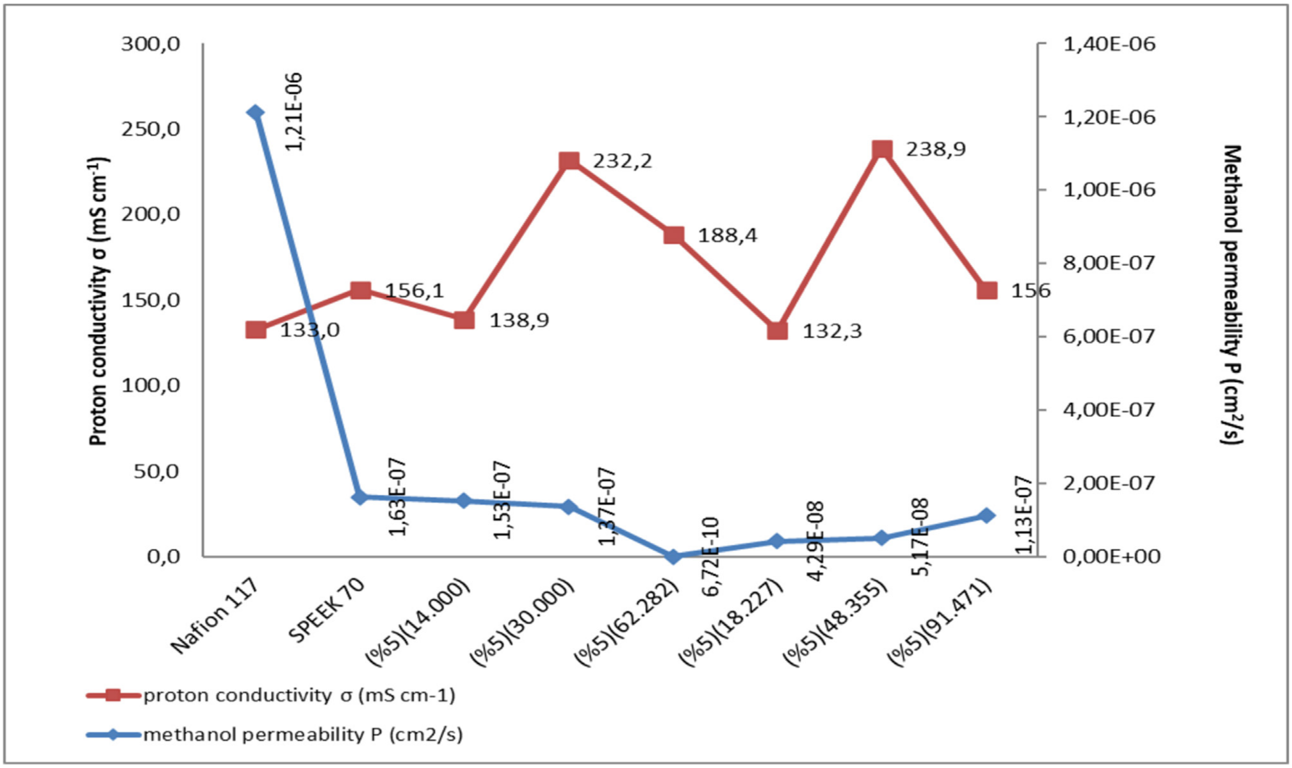


Fig. 7 – Proton conductivity and methanol permeability of the BMs.

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Table 5 – PAE based FC membrane's some of properties from the literature.

PEMs	Additive Type	IEC (meq g^{-1})	Proton Conductivity (mS/cm)	Methanol Permeability (cm^2/s)	Reference
SPEEK/PVDF	Polymer-PFSA		3.6–8.2 @30 °C	5.2×10^{-7} @30 °C	[1]
SPAES/PBI	Polymer-PBI		77@30 °C 201@80 °C	2.15×10^{-7} @30 °C	[1]
SPEEK/PANI	Polymer-PANI		<2@25 °C	2.08×10^{-7} @25 °C	[1]
SPEEK/CS	Polymer-CS		39-44@25 °C	2.81×10^{-7}	[1]
SPAES/PAN	Polymer-PAN		164@80 °C 62@25 °C		[1]
SPAEKS/PVA	Polymer-PVA		41@80	2.95X10-7@25 °C	[1]
SPEEK–SPI Blend-40	SPEEK–SPI	1.73	120 at 100 °C		[47]
SPEEK–BP (copolymers)	Polymer–BP		1×10^{-2} @50 °C		[47]
SPEEK/QNPAES (6 wt%)	Polymer–QNPAES		136@90 °C		[38]
SPEEK70/PVDF (Mw = 275.000)	Polymer-PVDF		123@80 °C	3.13E^{-07}	[36]
SFBC-50	Polymer-SFBC	1.50	43@90 °C 24@30 °C		[51]
SFBC-50/SPEEK-20	Polymer-SFBC		91@90 °C		
SPEES72/PVDF180 (10 wt%)	Polymer-PVDF		144@80 °C	2.4×10^{-6}	[14]
SPAEK-6Fmembranes	Polymer-SPAEK-6F		80@80 °C		[51]
SPEEK60/Cs-TPA	Inorganic-Cs-TPA		13@80 °C	4.7×10^{-7}	[20]
SPEEK70/SMWCPAE (M_w:48.355, 5 wt)	Polymer-SPAE	1.54	238.9@80 °C	6,72 × 10^{-10}	This study
SPEEK70/S-DFBP-Bis AF (M_w:30.000 5%)	Polymer-SPAE	1.67	232.2@80 °C	1,34 × 10^{-7}	This study
SPEEK 70	Polymer	1.46	156@80 °C	1,63 × 10^{-7}	[36]
SPEES61	Polymer		126@80 °C		[13]
Nafion 115	Polymer		133@80 °C	4.8×10^{-6}	[14]
Nafion 117	Polymer	0.95	51@30 °C 121@90 °C	1,21 × 10^{-6}	[51]

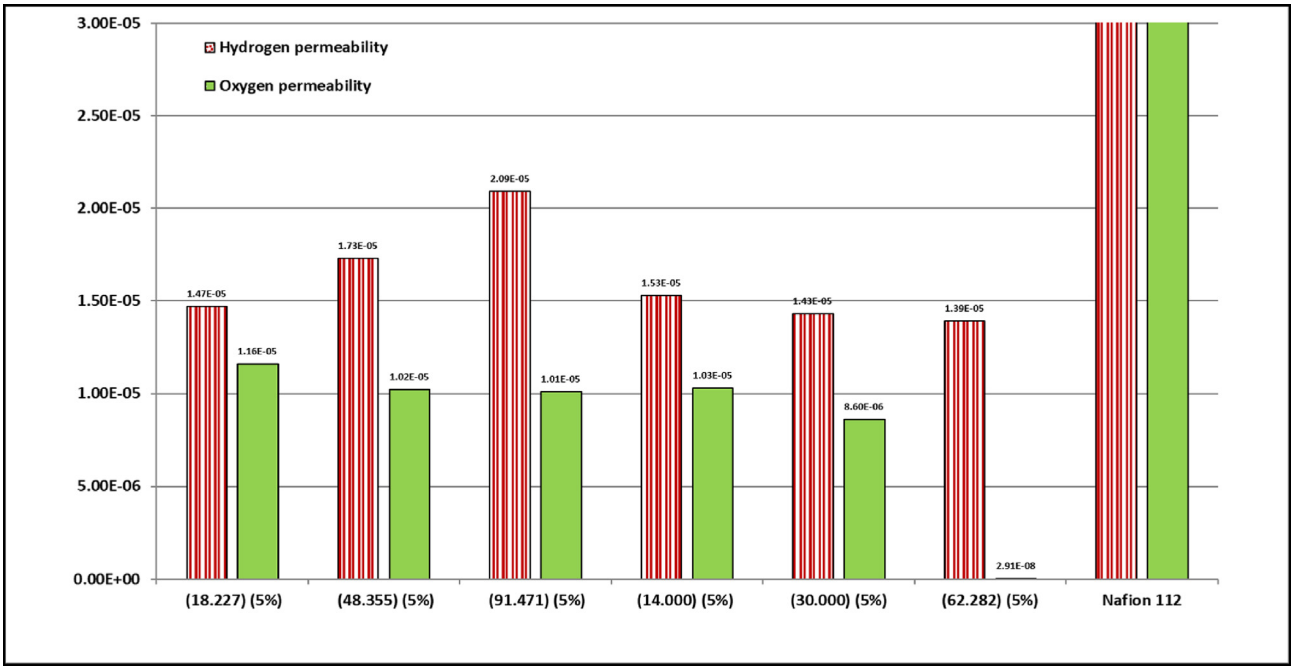

Fig. 8 – Hydrogen and Oxygen permeability of the BMs.

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Table 6 – The mechanical properties of the composite membranes.

Composite membranes	Young Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
SPEEK70	482 ± 6	14 ± 5	19 ± 4
SPEEK70/S-DFBP- Bis AF (14.000, 5%)	581 ± 4	29 ± 3	16± 2
SPEEK70/S-DFBP- Bis AF (14.000, 10%)	617 ± 5	30 ± 1	15 ± 2
SPEEK70/S-DFBP- Bis AF (14.000, 20%)	729 ± 4	38 ± 2	10 ± 1
SPEEK70/S-DFBP- Bis AF (30.000, 5%)	594 ± 4	30± 4	189 ± 48
SPEEK70/S-DFBP- Bis AF (30.000, 10%)	715 ± 3	37 ±3	12 ± 2
SPEEK70/S-DFBP- Bis AF (30.000, 20%)	755 ± 5	42 ± 2	9 ± 4
SPEEK70/S-DFBP- Bis AF (62.282, 5%)	631 ± 6	33 ± 5	16 ± 2
SPEEK70/S-DFBP- Bis AF (62.282, 10%)	774 ± 5	43 ± 2	13 ± 5
SPEEK70/S-DFBP- Bis AF (62.282, 20%)	849 ± 69	49 ± 2	13 ± 5
SPEEK70/S- DFBP- Bis A (18.227, 5%)	570.0 ± 39	24 ± 2	18 ± 1
SPEEK70/S- DFBP- Bis A (18.227, 10%)	6469 ± 69	30 ± 2	5 ± 3
SPEEK70/S- DFBP- Bis A (18.227, 20%)	739 ± 3	32 ± 4	10 ± 2
SPEEK70/S- DFBP- Bis A (48.355, 5%)	647 ± 6	13 ± 1	18 ± 3
SPEEK70/S- DFBP- Bis A (48.355, 10%)	695 ± 4	28 ± 48	13.0 ± 1
SPEEK70/S- DFBP- Bis A (48.355, 20%)	771 ± 7	33 ± 3	9 ± 2
SPEEK70/S- DFBP- Bis A (91.471, 5%)	748 ± 3	24 ± 6	16 ± 1
SPEEK70/S- DFBP- Bis A (91.471, 10%)	871 ± 5	37 ± 1	135 ± 4
SPEEK70/S- DFBP- Bis A (91.471, 20%)	934 ± 5	44 ± 4	11 ± 0.5

Table 7 – Water vapor transmission and permeability of blend membranes.

	WVTR (g/m^2 h)	WVP (g/m.s.Pa)
SPEEK70	12.1	1.56×10^{-10}
SPEEK70/S- DFBP- Bis A (18.227 10%)	11.3	1.96×10^{-10}
SPEEK70/S- DFBP- Bis A (48.355 10%)	10.9	8.71×10^{-11}
SPEEK70/S- DFBP- Bis A (91.471 10%)	11.3	1.21×10^{-10}
SPEEK70/S-DFBP- Bis AF (14.000 10%)	13.9	1.29×10^{-10}
SPEEK70/S-DFBP- Bis AF (30.000 10%)	13.0	2.54×10^{-10}
SPEEK70/S-DFBP- Bis AF (62.282 10%)	12.6	2.12×10^{-10}
Nafion® 117	17.9	5.60×10^{-10}

PEMFC single cell performance test

The PEMFC performance tests of pristine SPEEK membranes with varying sulfonation degrees and Nafion 112 were performed at 65°C and compared as shown in Fig. 9. The maximum power density (PD) of pristine SPEEK70, 65 and 60 membranes has been determined as 291.1 mW cm^{-2}; 134.2 mW cm^{-2}; 262.4 mW cm^{-2}, respectively. The highest PD value was obtained for SPEEK 70 membrane and this supported our reason for selecting SPEEK70 membrane as blend component of the MWCPAEs. SPEEK70/PVDF blend membranes PEMFC single test results are provided in Fig. 10. A comparison of maximum PD values different membranes are presented Fig. 11. The highest power density for SPEEK/PVDF (Mw: 275 000, 10 wt%) membrane combinations has been determined to be 384.2 mW cm^{-2}; which is the closest value of the Nafion 112 membrane.

The performance tests that have been conducted, earlier in-house, on flourinated SPEEK/PVDF blends, as discussed above, suggest that sulfonated membranes with acceptable Fenton test results also perform well in single-cell PEMFC systems. Our previous results supported Zhang et al.'s [46] work that suggested Fenton tests are strongly indicative of the performance of membranes in PEMFC systems. Therefore, the lack of single performance test on the BMs we have discussed

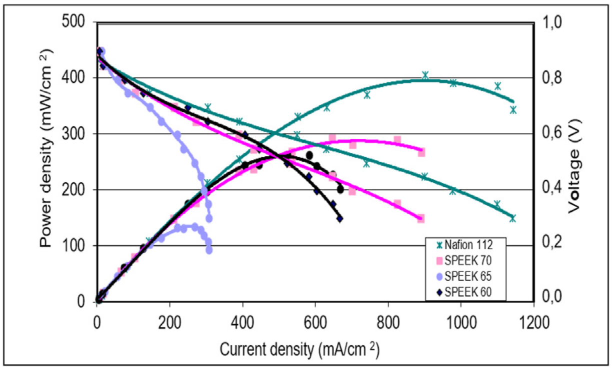

Fig. 9 – PEMFC performance test results for pristine SPEEK60, 65 and 70 membranes. Increasing curves with increasing current density depict power density whereas decreasing curves with increasing current density depict voltage.

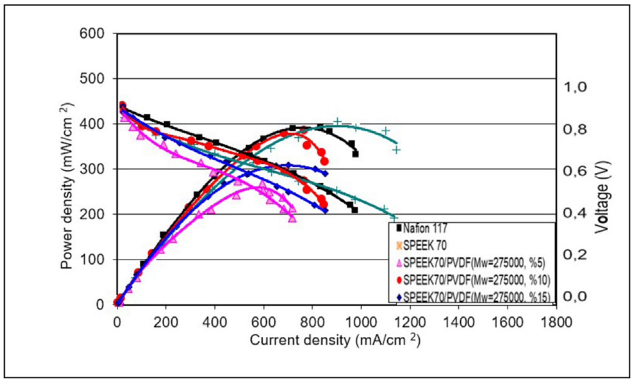

Fig. 10 – PEMFC performance test results for pristine SPEEK70/PVDF BMs. Increasing curves with increasing current density depict power density whereas decreasing curves with increasing current density depict voltage.

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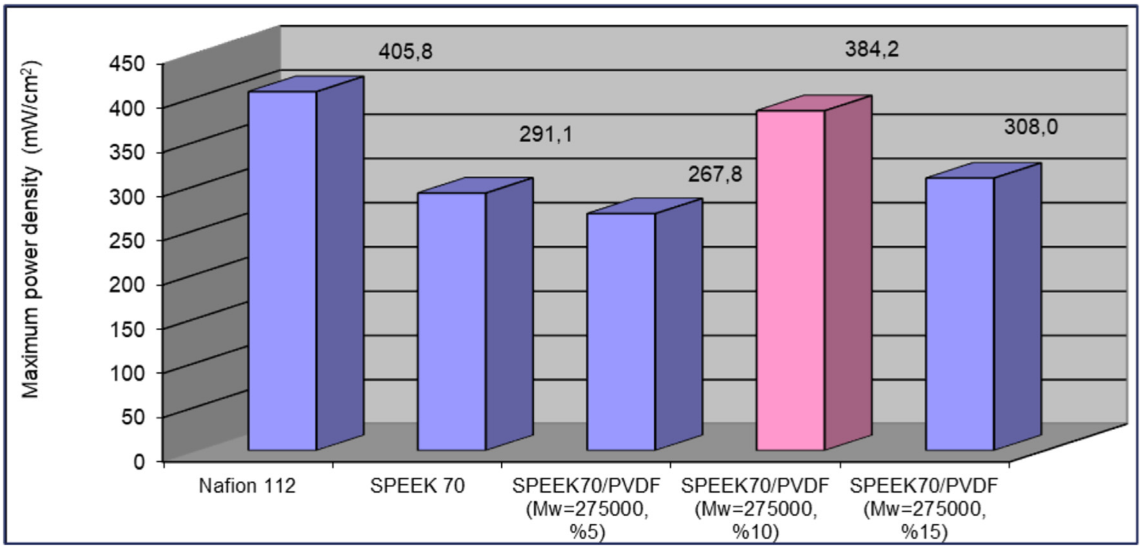

Fig. 11 – PEMFC performance test results for SPEEK70/PVDF BMs.

in this study; namely, MWCPAE BMs, is not a handicap and this is mainly because the material has been exhausted and re-synthesis is quite time-demanding. However, these BMs will be synthesized and single-cell performance tests will be conducted and reported in a future work. For this study, we can safely speculate that SPEEK70/MWCPAEs membranes are expected to have higher PEMFC performance results than that SPEEK70/PVDF membranes.

Conclusions

Molecular weights controlled Poly (arylene ether)s has been synthesized, sulfonated and blended to fabricate fuel cell mebranes. Based on the results, we conclude that all chemical, mechanical, thermal, and hydrolytic properties of the membranes we synthesized are comparable with, or better than, that of Nafion. Membranes with minimum concentration (5 wt%) of SMWCPAEs and intermediate MWs ($Mw_{SPEEK70/S\text{-}DFBP\text{-}Bis\ AF}$ = 30.000, 5 wt%; $Mw_{SPEEK70/S\text{-}DFBP\text{-}Bis\ A}$ = 48.355, 5 wt%) achieved the best conductivity performances. The highest proton conductivity (238.9 mS/cm) was determined for SPEEK70/S-DFBP-Bis-A based blend membrane (M_w:48.355, 5wt. SMWCPAE %). Therefore, we suggest that designing polymeric structures with desired MWs and sulfonation levels may enable enhanced properties and can help produce materials with properties on demand.

Here we summarize the test results and the implications below.

- The highest proton conductivity (238.9 mS/cm) for SPEEK70/S-DFBP-Bis-A based blend membrane (M_w:48.355, 5wt. SMWCPAE %) is the one of superior value in the literature.
- Membranes with minimum concentration (5 wt%) and intermediate MWs ($Mw_{SPEEK70/S\text{-}DFBP\text{-}BisAF}$ = 30.000, 5 wt%; $Mw_{SPEEK70/S\text{-}DFBP\text{-}BisA}$ = 48.355, 5 wt%) of SMWCPAEs achieved the best conductivity performances. The MWCPAE BMs have excellent proton conductivity values.
- Increasing the concentrations of SMWCPAEs in BMs showed similar and homogeneous morphologies that are associated to more chain entanglements at higher molecular weights.
- Tensile strengths and Young modulus values increased by increasing the concentrations (5 wt%, 10 wt%, 20 wt%) of the SMWCPAEs while elongation values decreased. The molecular weight increase for S-DFBP-Bis A, increased the tensile strength values more due to their lower sulfonation, higher molecular weight and lower bond strength of C–H than C–F combinations.
- Chemical stability of the BMs enhanced strength and no decomposition was observed in 2.5–4 h intervals under Fenton test at 68 °C. BMs showed a phase-segregated structure where sulfonated part offers high ionic conductivity, flourinated PAE structure enhanced the compatibility of the blend system by improving the blend homogeneity.
- Only one glass transition temperature was apparent for all combinations of SMWCPAE-SPEEK70 blend membranes in the range of 157–167 °C confirming homogeneous membrane morphologies.
- Methanol permeability values of the BMs were decreased with the addition of SMWCPAEs into SPEEK70 matrix.
- The gas permeability values of the BMs were also much lower than the Nafion membrane confirming the membranes resistance to methanol permeability and suitability to DMFC applications.
- The WVP values for 10% concentrations of membranes were determined to be lower than that of Nafion 117 membrane. The results also showed lower VWP than that of Nafion®117 membrane.
- The BMs are nominees of highly conductive, thermally, mechanically and chemically stable PEMs which are promising for PEMFC or DMFC applications.

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- Optimization of polymeric structures, MWs, and sulfonation levels may enable enhanced properties of membranes
- We can suggest that SPEEK70/MWCPAEs membranes are expected to have high PEMFC performance

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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