

# FT-IR, TGA, DSC and PCM Characterization of Synthesised 1-Vinyl-1,2,4-Triazole Proton Exchange Membranes (PEMS) for Use in Polymer Electrolyte Membrane Fuel Cells (PEMFCS)

Shamsu Ahmad<sup>1</sup> and Iliyasu Aliyu Bashir<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, Federal University Duste, Jigawa, Nigeria.

<sup>2</sup>Department of Chemistry, Kano University of Science and Technology, Wudil, Kano, Nigeria.

## Authors' contributions

The synthesis and the statistical analysis were designed and carried out by author SA while. Author IAB carried out spectral interpretation and wrote the first draft of the manuscript. Authors SA and IAB studied the results and the final analysis. Both authors read and approved the final manuscript.

## Article Information

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## ABSTRACT

**Aim:** To synthesize a polymer electrolyte membranes with semi interpenetrating polymer network (semi-IPN) structures consisting of poly (vinylidene fluoride) (PVDF) and poly(1-vinyl-1,2,4-triazole-co-divinyl benzene) (P(VTri-co-DVB)) and to characterized by FT-IR spectroscopic analysis, thermo gravimetric Analysis (TGA), proton conductivity measurement and Differential scanning calorimetry (DSC).

**Study Design:** Synthesizing anhydrous electrolyte membranes, cheaper than DuPont's Nafion, and with high proton conductivities at elevated temperatures.

**Place and Duration of Study:** Department of Chemistry Fatih University, Istanbul, Turkey. Between September 2013 to January 2014.

**Methodology:** The methodology employed is the in situ synthesis, whereby all reactants are mixed before the triggering the polymerization or cross-linking reaction.

**Results:** The synthesized membranes, PVDF/P(VTri-co-DVB)/TA, were characterized by FTIR

\*Corresponding author: E-mail: [iliyayye@hotmail.com](mailto:iliyayye@hotmail.com);

spectroscopy. Thermal stability of the samples was investigated using TGA. The TGA plots of PVDF/P(VTri-co-DVB)/TA membranes with two different PVDF contents showed a satisfactory thermal stability up to 320°C and 340°C. As PVDF content was doubled, thermal stability slightly increased as expected.

**Conclusion:** Polymer electrolyte membranes with semi interpenetrating polymer network (semi-IPN) structures consisting of poly (vinylidene fluoride) (PVDF), poly (1-vinyl-1,2,4-triazole-co-divinyl benzene) (P(VTri-co-DVB)), and triflic acid (TA) were successfully fabricated in one pot and in a single step.

*Keywords: PVDF; PEMFC; semi-IPN; vinyl triazole; TGA; DSC.*

## 1. INTRODUCTION

Quite recently, polymer electrolyte membrane fuel cells (PEMFCs) have attracted a great deal of interest due to their high energy density, high energy conversion efficiency and wide range of application areas. Perfluorosulfonic acid membranes, the best known example of which is DuPont's Nafion, are most widely used in fuel cell research because of its high proton conductivity, high chemical stability and excellent mechanical properties. In these systems, the proton conduction is mainly supplied by water content and therefore, their usage is restricted to below 100°C. For that reason, there has been a great deal of research in the development of anhydrous electrolyte membranes with high proton conductivities at higher temperatures which should be cheaper than Nafion.

Proton exchange membrane fuel cells (PEMFCs) are nowadays widely studied because of their applications in the transportation, mobile and stationary fields. The electrolyte is generally anion- conducting polymer membrane ensuring the proton migration between the anode and cathode. This membrane, acting as gases separator, should exhibit high proton conductivity as well as good chemical and mechanical stability. Nafions (marketed by DuPont), a perfluorosulfonic acid copolymer, is the reference membrane for PEMFC because of its high proton conductivity and good chemical stability. However, Nafions, in addition to its high cost, displays a loss of gas barrier properties and a strong drop in its mechanical stability with increasing temperature (especially above 80°C) [1]. Therefore, a large part of the current research on new polyelectrolyte materials focuses on non-perfluorinate sulfonated polymers such as sulfonated poly (ether ether ketone) (SPEEK) [2], polyimide (SPI) [3] or poly sulfone (SPSU) [4]. They show lower gas permeability and more stable thermo-mechanical properties than Nafion and generally exhibit

satisfactory proton conductivity at high ion exchange capacity values (IEC) [5]. Such a high IEC generally leads to excessive water swelling and a low stability in oxidative media [6]. To limit these draw backs, these linear polymers can be cross-linked [7], as carried out for SPEEK [8] or SPI [9].

An Interpenetrating Network (IPN) is a polymer comprising two or more networks which are at least partially interlaced on a polymer scale but not covalently bonded to each other. The network cannot be separated unless chemical bonds are broken. The two or more networks can be envisioned to be entangled in such a way that they are concatenated and cannot be pulled apart, but not bonded to each other by any chemical bond.

Semi-IPNs differ from IPNs in that they are composed of one linear polymer entrapped within the network of another polymer. The IUPAC definition is: "A polymer comprising one or more networks and one or more linear or branched polymer(s) characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules" [10].

PVDF based proton-conducting membranes are one of the most important components for a polymer electrolyte fuel cell (PEFC), serving as a separator to prevent mixing of the reactant gases and as an electrolyte for transporting protons from the anode to the cathode. PVDF is a partially fluorinated polymer with excellent thermal, mechanical and chemical stability along with lower cost compared to perfluorinated membrane such as the Nafion series from DuPont, which is the most common polymer electrolyte membranes used in fuel cells applications [11]. Thus, there has been a great deal of research activity on the development of novel proton conducting membranes to substitute the perfluorinated ones [12].

## 2. EXPERIMENTAL

### 2.1 Materials

Poly (vinylidene fluoride) (PVDF, avg. Mw~534 000) was purchased from Fluka. Dimethylformamide (DMF≥99.9%), were purchased from Merck. Divinylbenzene (DVB, analytical grade) from Fluka Co. 1-Vinyl-1,2,4-triazole (>97.0%)(Avg. Mw~95.10), supplied from Aldrich Chemical. Trifluoromethanesulfonic acid (triflic acid) and azodiisobutyramidin dihydrochloride (AIDABC) purum were purchased from Aldrich Chemical. They were all reagent grades and used as received.

### 2.2 Synthesis

Five samples of the same polymer membranes were prepared using the following procedure. Poly(vinylidene fluoride) (PVDF), divinylbenzene (DVB), 1-vinyl-1,2,4-triazole, azodiisobutyramidin dihydrochloride (AIDABC), and trifluoromethanesulfonic acid were dissolved in DMF, poured in a teflon petri dish, and kept there at 70°C for 2 hours for polymerization. The solvent was allowed to evaporate for several hours under the hood. After having been dried in

vacuum at 40°C, the polymer was recovered as a flat-sheet membrane from the bottom of the petri dish see Fig. 1.

## 3. RESULTS AND DISCUSSION

### 3.1 FT-IR Analysis

The FT-IR spectra (4000-400  $\text{cm}^{-1}$ ) were recorded with a Bruker Alpha-P in ATR-FTIR. Infrared spectroscopy was employed to provide information about the chemical structures of the membranes. Fig. 3 shows fully modified FTIR spectra of PVDF/P(VTri-co-DVB)/TA samples with different compositions. For heterocyclic compounds containing an N-H group, an N-H stretching band is observed in the range between 3469–3400  $\text{cm}^{-1}$  and aromatic C-N and C=N stretching between 1600 - 1300  $\text{cm}^{-1}$  of the triazole ring [13], the position of which depends upon the degree of hydrogen bonding. These compounds show characteristic band patterns in the 1600–1300  $\text{cm}^{-1}$  ring stretching region. The nature of the substituent affects the pattern. In addition, the patterns of out-of-plane C-H bending bands in the 878–629  $\text{cm}^{-1}$  region are characteristic for PVTri membrane.

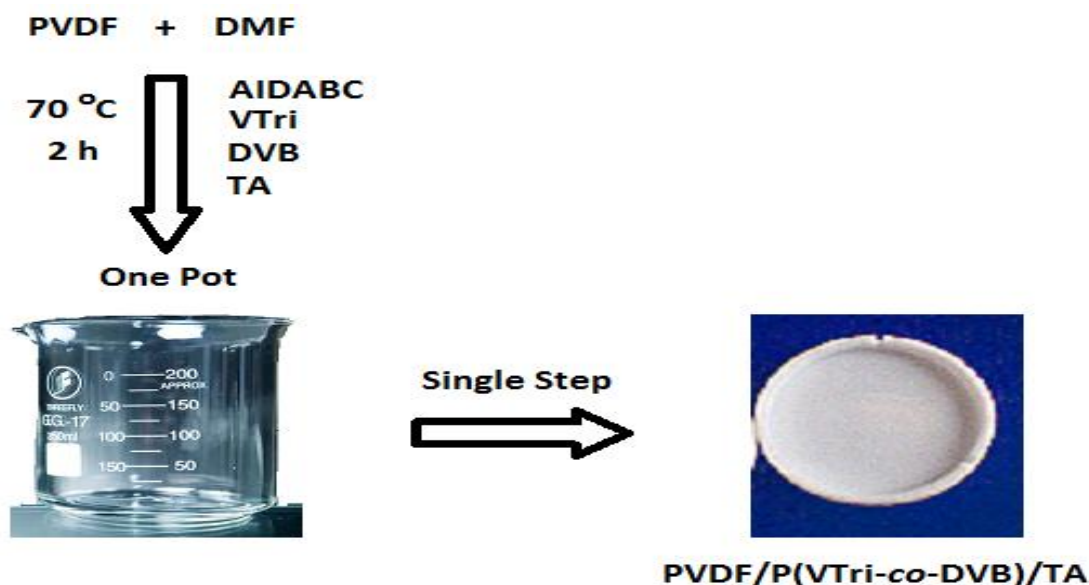
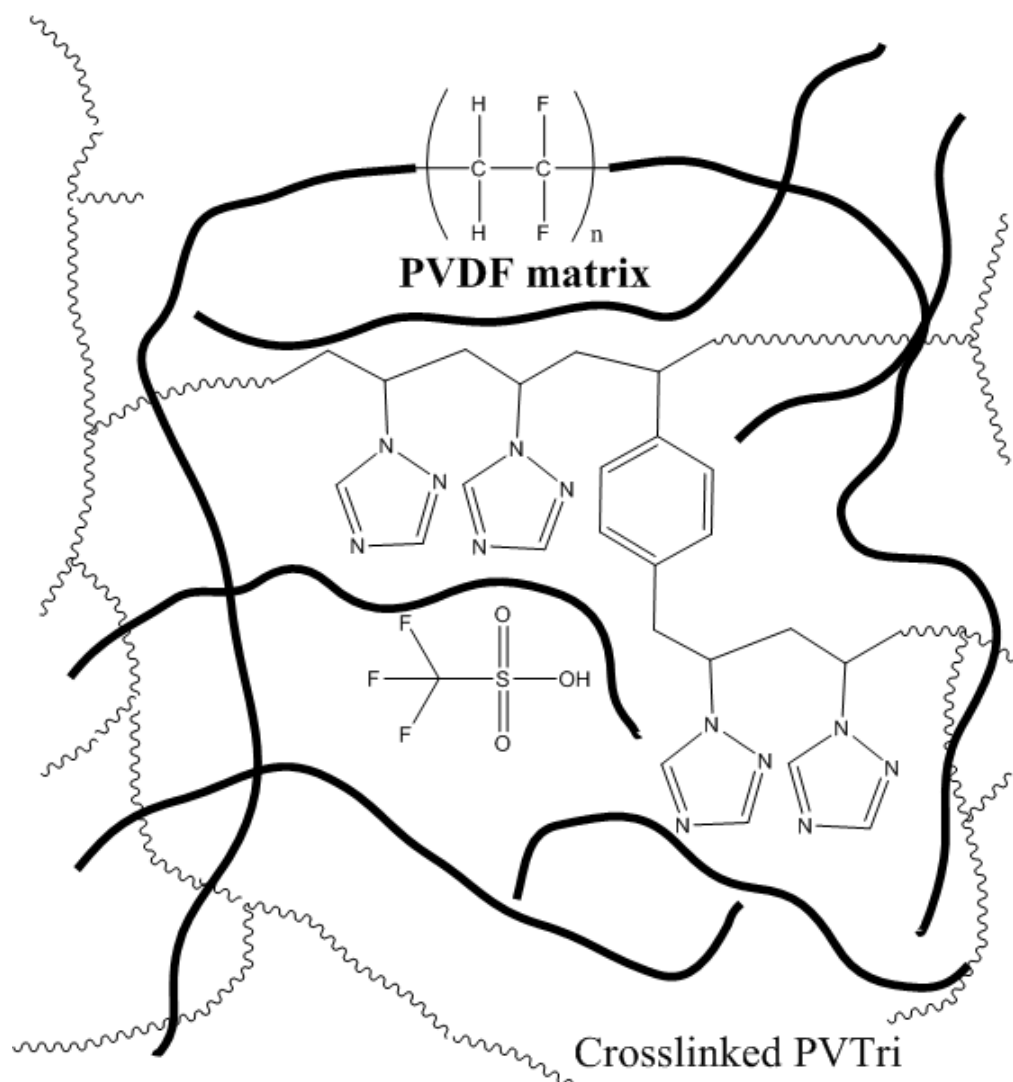


Fig. 1. Sketch for the in situ synthesis of Semi-IPN membranes



**Fig. 2. Tentative structure of PVDF/P(VTri-co-DVB)/TA Semi-IPN membrane**

The characteristic peak was observed between  $1200\text{-}1000$  and  $450\text{ cm}^{-1}$ , which represents fluorocarbon of PVDF absorption (C–F band absorption). The strong peak appeared at  $1380\text{ cm}^{-1}$  corresponds to  $\text{CH}_2$  stretching vibrations of PVDF. The strong bands at  $1230$  and  $1163\text{ cm}^{-1}$  are attributed to  $\text{SO}_2$  and a strong absorption peak at  $1030\text{ cm}^{-1}$  most probably belongs to  $-\text{SO}_3^- (\text{H}^+)$ . The intensity of  $\text{SO}_2$  peak also increases in parallel with the increase in the molar ratio of triflic acid in the blends.

The bands,  $1610$ ,  $879$  and  $750\text{ cm}^{-1}$  are due to the di-substituted benzene ring of DVB cross links which varies in composition within the samples. From this results it can be concluded

that the samples PVDF/P(VTri-co-DVB)/TA using DVB as cross linker modifies the membranes to some extent. Similarly, the intensity of these new peaks related to the degree of cross linker chains increased with the decrease in the degree of cross linker and increase with the monomer. The variation in the intensity of the PVDF/P(VTri-co-DVB)/TA characteristic bands peaks reflects the difference in the degree of the cross linker.

### 3.2 Thermogravimetry Analysis (TGA)

Thermal stabilities of all samples were examined by thermo gravimetric (TG) analysis with a Perkin Elmer STA 6000. The samples ( $\sim 10\text{ mg}$ ) were heated from room temperature to  $800^\circ\text{C}$  under

$N_2$  and  $O_2$  atmosphere at a scanning rate of  $10^\circ C/min$ . The effect of dopant on thermal stability was determined using TG curves.

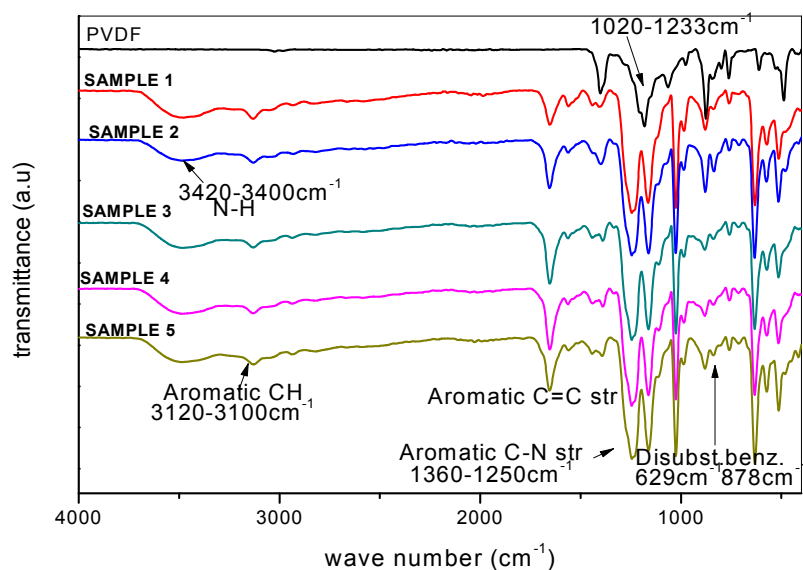
The thermal stabilities of the samples (Sample 1, 2, 3, 4 and 5) were shown in Fig. 4. Pure PVDF shows an enhanced thermal stability up to around  $480^\circ C$ . PVDF/P(VTri-co-DVB)/TA membranes with two different PVDF content show a satisfactory thermal stability up to  $320-340^\circ C$ . It is noteworthy that as PVDF content was doubled (membranes 4 & 5), thermal stabilities slightly increased to  $340^\circ C$  as expected.

The initial weight loss is generally attributed to the loss of PVTri (depolymerization). The weight loss taking place in the second step is due to decomposition of PVDF by random chain scissions, reported as characteristic of the PVDF backbone degradation. However, in our case,

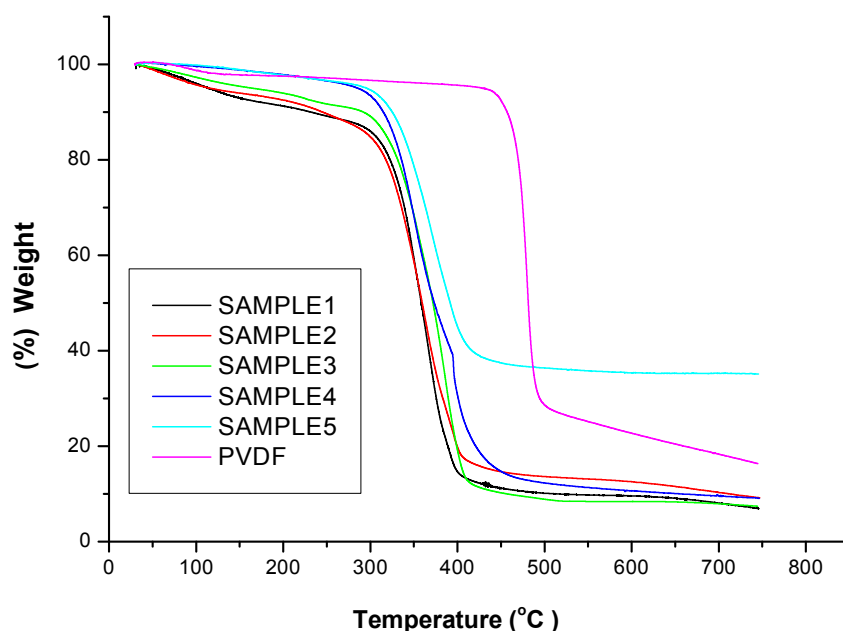
only a slight weight loss was detected above  $100^\circ C$ , which might originate from humidity loss. Table 1 shows the amounts of reagents in feed for the synthesis of PVDF/P(VTri-co-DVB)/TA membranes. The TGA results agree to some extent with the given values. It can be seen that the thermal stability decreased as the amounts of VTri and TA increased. For instance, sample 5 with lower VTri and TA was found to be more thermally stable up to  $340^\circ C$ , above which it started to decompose to about (40 wt. %) while sample 3 was found to be stable up to  $320^\circ C$ . From these results, it can be suggested that the lower the amounts of 1-vinyl-1,2,4-triazole and triflic acid in the samples, the higher it's thermal stability and vice versa. Hence the compositions in moles of mixing PVDF + VTri for maximum thermal stability are as in sample 4 and 5. Sample 5 PVDF:VTri ratio was  $6.25 \times 10^{-3} : 1.91 \times 10^{-3}$  and in sample 4 was  $6.25 \times 10^{-3} : 3.47 \times 10^{-3}$  respectively.

**Table 1. Amounts of reagents in feed (PVDF/P(VTri-co-DVB)/TA)**

Samples	VDF repeat units, mol	DVB, Mol	TFA, Mol	VTri, mol	VTri / DVB, mol / mol
Sample 1	$3.13 \times 10^{-3}$	$7.68 \times 10^{-4}$	$1.04 \times 10^{-2}$	$1.04 \times 10^{-2}$	13.5
Sample 2	$3.13 \times 10^{-3}$	$2.30 \times 10^{-3}$	$7.37 \times 10^{-3}$	$8.09 \times 10^{-3}$	3.51
Sample 3	$3.13 \times 10^{-3}$	0	$1.07 \times 10^{-2}$	$1.16 \times 10^{-2}$	-
Sample 4	$6.25 \times 10^{-3}$	$7.68 \times 10^{-4}$	$3.68 \times 10^{-3}$	$3.47 \times 10^{-3}$	4.52
Sample 5	$6.25 \times 10^{-3}$	$3.07 \times 10^{-4}$	$2.45 \times 10^{-3}$	$1.91 \times 10^{-3}$	6.22



**Fig. 3. IPN membranes of PVDF/P(VTri-co-DVB)/TA with various compositions**



**Fig. 4. TGA graph of PVDF and PVDF/P(VTri-co-DVB)/TA of five samples with different compositions**

### 3.3 DSC Analysis

Differential scanning calorimetric analysis (DSC) data were obtained using Perkin Elmer JADE DSC instrument. The measurements were carried out at a rate of 10°C/min under nitrogen atmosphere.

Prior to the analysis, the samples were dried under vacuum at 80°C for 24 h and stored in a glove box. The DSC measurements were carried out under inert atmosphere at a scan rate of 10°C/min and the second heating curves were evaluated. Fig. 5 shows the DSC curves of the samples in a temperature range between 0 - 180°C for the samples and their corresponding  $T_m$  values are designated.

Previously, the  $T_g$  of pure PVTri homo polymer and PVDF film were reported as 165 and -50°C, respectively. The melting point ( $T_m$ ) of PVDF was measured at 158°C. The  $T_g$  of uncross linked PVDF/PVTri/TA membrane (sample 3) was observed around 75°C. However, as the extent of cross linking increased, there was no apparent  $T_g$ , which was just expected since cross linking severely limits the chain movements in the amorphous phase. For instance, sample 1 with VTri/DVB (mol/mol) ratio of 13.5 showed an

evident  $T_g$  whereby, there was none in sample 2 with a much lower VTri/DVB (mol/mol) ratio of 3.51. PVDF/P(VTri-co-DVB)/TA exhibits a melting point ( $T_m$ ) in the range between 153-158°C (Fig. 5). The  $T_m$  was observed due to the presence of crystalline PVDF regions.

**Table 2. Maximum anhydrous proton conductivities of PVDF/P(VTri-co-DVB)/TA polymer membranes at various temperatures**

Samples	Conductivity S/cm
Sample 1	$7.11 \times 10^{-3}$ S/cm at 150°C
Sample 2	$2.26 \times 10^{-3}$ S/cm at 150°C
Sample 3	$9.30 \times 10^{-3}$ S/cm at 140°C
Sample 4	$9.95 \times 10^{-4}$ S/cm at 150°C
Sample 5	$9.32 \times 10^{-4}$ S/cm at 150°C

### 3.4 Proton Conductivity Measurements

The proton conductivity studies of the samples were performed using Novocontrol impedance dielectric spectrometer. The conductivities were measured in the frequency range 3E6 to 1Hz at 10°C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between 20 and 150°C with a precision of 10°C. The hot pressed pellets of

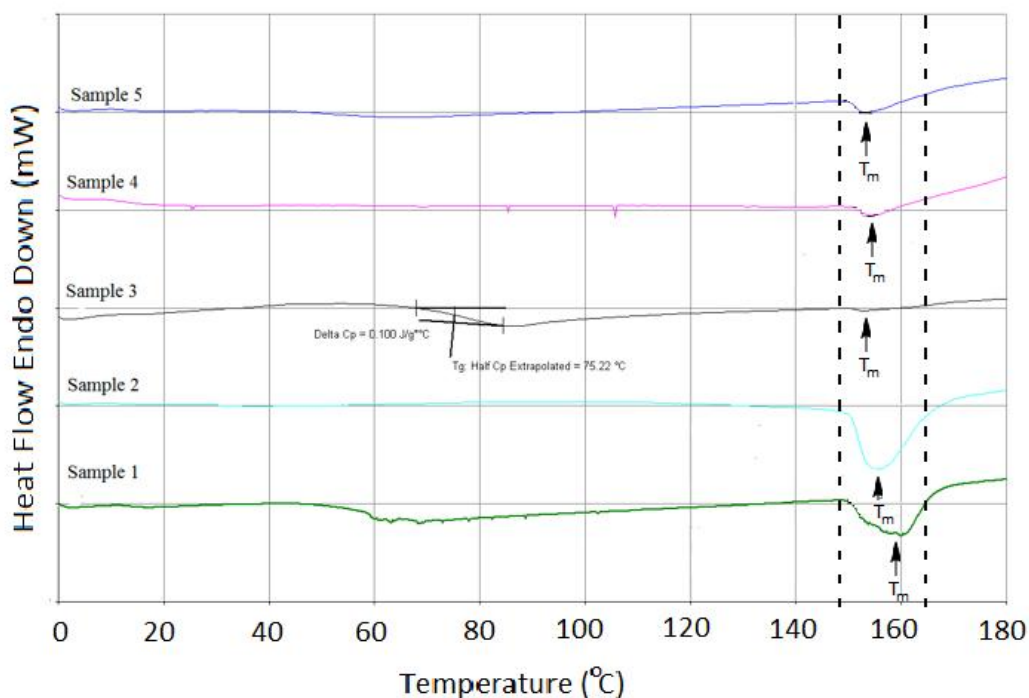


Fig. 5. DSC plots of PVDF/P(VTri-co-DVB)/TA of five samples with different compositions recorded under inert atmosphere at a heating rate of 10°C

Table 3. Relation between proton conductivity and cross linked membrane ratio at various temperatures

Samples	VDF repeat units, mol	DVB, Mol	TFA, Mol	VTri, mol	VTri / DVB, mol / mol	Conductivity S/cm
Sample 1	$3.13 \times 10^{-3}$	$7.68 \times 10^{-4}$	$1.04 \times 10^{-2}$	$1.04 \times 10^{-2}$	13.5	$7.11 \times 10^{-3}$ at 150°C
Sample 2	$3.13 \times 10^{-3}$	$2.30 \times 10^{-3}$	$7.37 \times 10^{-3}$	$8.09 \times 10^{-3}$	3.51	$2.26 \times 10^{-3}$ at 150°C
Sample 3	$3.13 \times 10^{-3}$	0	$1.07 \times 10^{-2}$	$1.16 \times 10^{-2}$	-	$9.30 \times 10^{-3}$ at 140°C
Sample 4	$6.25 \times 10^{-3}$	$7.68 \times 10^{-4}$	$3.68 \times 10^{-3}$	$3.47 \times 10^{-3}$	4.52	$9.95 \times 10^{-4}$ at 150°C
Sample 5	$6.25 \times 10^{-3}$	$3.07 \times 10^{-4}$	$2.45 \times 10^{-3}$	$1.91 \times 10^{-3}$	6.22	$9.32 \times 10^{-4}$ at 150°C

the samples with a diameter of 10 mm and thickness of about 0.2-0.3 mm were sandwiched between two gold-coated electrodes and their conductivities were measured with 10°C intervals under dry-nitrogen atmosphere and the result is tabulated as seen in Table 3 above.

#### 4. CONCLUSION

Polymer electrolyte membranes with semi interpenetrating polymer network (semi-IPN) structures consisting of poly(vinylidene fluoride) (PVDF), poly(1-vinyl-1,2,4-triazole-co-divinyl benzene) (P(VTri-co-DVB)), and triflic acid (TA) were successfully fabricated in one pot and in a single step. The synthesized membranes,

PVDF/P(VTri-co-DVB)/TA, were characterized by FTIR spectroscopy. Thermal stability of the samples were investigated using TGA. The TGA plots of PVDF/P(VTri-co-DVB)/TA membranes with two different PVDF contents showed a satisfactory thermal stability up to 320°C and 340°C. As PVDF content was doubled, thermal stability slightly increased as expected. It was also seen that the thermal stability decreased as the amounts of VTri and TA increased. These observations may suggest that lowering the amounts of 1-vinyl-1,2,4-triazole and triflic acid while increasing PVDF content enhances PEM's thermal stability.

The DSC analysis demonstrated the thermal properties of the PEMs. Tg of uncrosslinked



PVDF/PVTri/TA membrane was available at around 75°C. However, as the extent of crosslinking increased, there was no apparent T<sub>g</sub>, which was just expected since crosslinking severely limits the chain movements in the amorphous phase. PVDF/P(VTri-co-DVB)/TA exhibited a melting point (T<sub>m</sub>) in the range between 153-158°C, which was observed due to the presence of crystalline PVDF regions.

The maximum anhydrous proton conductivity was measured about  $9.3 \times 10^{-3}$  S/cm for uncrosslinked PVDF/PVTri/TA (sample 3) at 140°C. On the other hand, PVDF/P(VTri-co-DVB)/TA semi-IPN (membrane 1) with a maximum conductivity of  $7.11 \times 10^{-3}$  S/cm at 150°C can be suggested to be tested in the fuel cell applications.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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