Preparation of a Novel Proton Exchange Membrane Using Radiation Grafted ETFE Film for Fuel Cell

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ABSTRACT

For many different applications, functional polymeric materials are extremely important in electrochemical reactions. The development of polymer electrolytes, such as those used in fuel cells, depends heavily on these functional materials. One of the most significant sources of power for applications in numerous industries is provided by fuel cells. In this study, a proton exchange membrane (PEM) was developed using ethylene tetrafluoroethylene (ETFE) film with binary blends of acrylic acid (AA) and sodium styrene sulfonate (SSS), while NaCl served as an additive. As the monomer concentration increased, the degree of grafting (DG) increased. Gravimetric analyses, Fourier Transform Infrared (FTIR) spectroscopy, mechanical characteristics, and surface morphology (SEM) have all supported the radiation grafting. The physical and chemical durability of 60% DG of ETFE-g-AA-SSS film made it an ideal PEM for this study since it is more durable than other grafted samples of ETFE-g-AA-SSS film. The 60% DG of PEM's ion-exchange capacity (IEC) was determined to be 0.26 mmol g^{-1}. They demonstrated excellent thermal, mechanical, and acid stability characteristics. In H_2O_2 solutions, they are highly stable, and they display significant water uptake. It is therefore applicable to acidic fuel cells.

Keywords: Degree of grafting, ethylene tetrafluoroethylene, FTIR, polymer electrolytes, proton exchange membrane

1.0 INTRODUCTION

For their numerous uses in the sectors of transportation and portable energy, polymer electrolyte fuel cells (PEFC) have already undergone a number of attempts to be prepared using a variety of polymer materials. One essential element of the PEFCs is the proton exchange membrane (PEM). In a PEFC, the electrolyte is a membrane made of a polymer matrix that possesses particular characteristics, including high-energy efficiency at the fuel cell operation temperature, low permeability to the fuel (hydrogen) and oxygen, sufficient hydration to ensure proper operation, and good chemical and mechanical stability for long-term operations. The most common and extensively researched Proton Exchange Membranes (PEMs) are perfluorosulfonated membranes like Nafion [1]. But recently scientists are attracted by other different types of membranes such as polytetrafluoroethylene (ETFE) films, polyethyleneterephthalate (PET), poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) etc. rather than Nafion [2-3].

Although it has outstanding mechanical properties, the fluorine-based ethylene tetrafluoroethylene (ETFE) polymer is chemically inert and has a high hydrophobicity. Therefore, applying scientifically feasible procedures is required to raise the hydrophilicity and proton conductivity of the fabric. To enhance the quality of the ETFE film, monomers are added. In the past few decades, numerous types of grafting polymerization processes have been developed, including polymer oxidation, ionization radiation, photo-induced (UV or chemical initiator), and plasma-induced grafting polymerizations to initiate new groups to the polymer backbone [4-5].

An appealing method for the synthesis of PEM is radiation-induced graft polymerization, which enables the grafting of a monomer with a desired functional group or the grafting of the chains of a precursor-monomer followed by polymer-analogous transformations. Benefits of the radiation-induced graft polymerization method include its low cost, ability to penetrate deeply into the primary polymer matrix, less need for chemical initiators or catalysts, simple control over the degree of grafting and ion exchange capacity, and ease of fabrication from an existing base film [6-7]. In this investigation, sodium styrene sulfonate (SSS) and acrylic acid (AA) were employed as monomers, with NaCl acting as an additive to ETFE, followed by a pre-irradiation technique with gamma ray. The same monomers were utilized by Zu *et al*. [8] without the addition of any additives, whereas ETFE was exposed to electron accelerator radiation and the grafted ETFE film was then used as a cation exchange membrane. The monomer concentrations with respect to the degree of grafting were measured.

Physicochemical properties of the ETFE-g-AA-SS membranes such as water uptake, ion exchange capacity, proton conductivity, and mechanical property were investigated in correlation with the degree of grafting. Moreover, the thermal as well as chemical stability of the membranes was also evaluated. The characterizations of the membranes such as SEM and FTIR spectroscopy were also studied.

2.0 EXPERIMENTAL

Materials and Reagents

The backbone polymer used in this investigation was ethylene tetrafluoroethylene (ETFE) film with thickness 0.025 mm, size 300 × 300 mm and transparent color. It was from Sigma Aldrich, USA. AA and SSS were also purchased from Sigma Aldrich, USA, which were used as monomers. NaOH, NaCl, HCl, H_2O_2, and phenolphthalein indicator obtained from Merck, Germany. Before using, all glassware were cleaned properly at room temperature and dried in an oven at 60°C. Distilled deionized (DDI) water was utilized for every step where necessary. Some physico-chemical properties of the DDI water used in this experiment such as pH, EC and TDS are 6.6, 0.01 µS and 0.1 mgL^{-1} respectively.

Instruments and Apparatus

The Co (60) gamma-irradiator was employed to control the dose rate on the graft copolymer synthesis from Institute of Food and Radiation Biology, Atomic Energy Research Establishment, Savar, Dhaka, Bangladesh. The gamma source was a Panoramic Irradiator of 90 kCi Batch Type provided by BRIT, India. IR

Prestige-21 was used to analyze FTIR spectrum in the wavenumber range of 700-4000 cm^{-1} delivered by Shimadzu Corporation, Japan. The change in surface morphology following grafting was measured by SEM using the model number of VEGA3 TESCAN. With the help of a universal testing machine (Testometric, model M 500-100CT, UK), the mechanical properties of ETFE films were determined. Throughout the experiment, the crosshead speed and gauge length were 2 mm/min and 20 mm, respectively, with a load range of 250 N. The resistance of the membrane was measured by impedance analyzer (Wayne Kerr, London, UK).
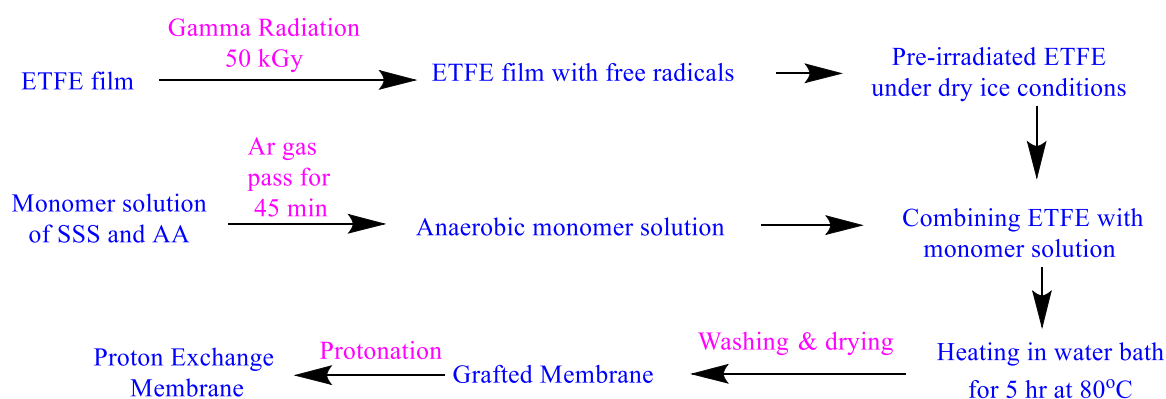
Preparation of Sulphonated ETFE for PEM

Figure 1 depicts the procedure for creating the new polymer electrolyte membrane. A well-known technique for altering the physicochemical characteristics of materials, radiation-induced graft polymerization is particularly interesting for producing specifically desired qualities as well as superior mechanical properties [9–10]. The ETFE films were preirradiated in the first step with a radiation dose of 50 kGy at room temperature. Monomer solution was prepared in the meantime by combining SS and AA with NaCl as an additive. The monomer solution was then passed for 45 minutes through an argon gas medium. Finally, monomer solution and pre-irradiated ETFE film were placed into a vial and left in a water bath at 80°C for 5 hours. The produced membrane was vacuum-dried at 50°C for 24 hours after washing. The sample was removed and held for an hour on fresh silica gel beneath a desiccator before being weighed. The degree of grafting (DG) was calculated as follows:

$$DG = \frac{W_1 - W_0}{W_0} \times 100 \qquad (1)$$

The protonated membranes were prepared by treating the grafted polymer samples with 50 mL of 1M HCl solution for 3 hours with stirring. After that, the PEM was washed with DDI water properly and weighed.

ETFE film →(Gamma Radiation 50 kGy)→ ETFE film with free radicals → Pre-irradiated ETFE under dry ice conditions

Monomer solution of SSS and AA →(Ar gas pass for 45 min)→ Anaerobic monomer solution → Combining ETFE with monomer solution

Proton Exchange Membrane ←(Protonation)← Grafted Membrane ←(Washing & drying)← Heating in water bath for 5 hr at 80°C

Figure 1 Flow chart diagram of the preparation of ETFE-g-AA-SSS film

Ion-exchange Capacity (IEC)

Titrimetric analysis was used to determine the PEM's ion-exchange capacity (IEC). The acidic membrane was soaked for 24 hours at room temperature (25°C) in 40 mL of a 0.1 M NaCl solution. A standardized 0.05M NaOH solution was used to titrate the proton emitted in the

solution. The final point of titration was observed using phenolphthalein indicator (1%). The following equation was used to get the membrane's ion-exchange capacity (IEC):

$$IEC=(C_{NaOH}×V_{NaOH})/ W_{dry} \qquad (2)$$

Where C_{NaOH} (mol L^{-1}) and V_{NaOH} (mL) are the concentration and volume of NaOH solution required for neutralization of the residual solution, and W_{dry} is the weight of the dry sulfonated membrane in protonic form. After IEC measurement the membranes could be regenerated by being treated with 3M HCl.

Proton Conductivity

The protonated membrane was immersed in water at room temperature for 24 hours prior to measuring the resistance. The following equation was used to determine the proton conductivity using the resistance value of PEM:

$$Proton\ conductivity, σ=l/R×S \qquad (3)$$

Where R is the resistance (ohm) of the membranes, l is the thickness (cm) of the membranes and S stands for contact surface area (cm ^{2}) of the electrode.

Water Uptake

The DDI water was poured over the dry membrane samples in acidic form with a size of 2 cm×2 cm until swelling equilibrium was reached. Three different temperatures (60°C, 80°C, and 100°C) of DDI water were used to determine the durability of the prepared membranes. The membrane samples were rapidly removed from the water, blotted using absorbent paper to remove any remaining water that had adhered to the surface, and

then weighed. The following equation was used to determine the membrane's water uptake:

$$Water\ uptake\ (\%) =100×(W_{wet}−W_{dry})/W_{dry} \qquad (4)$$

Where W_{wet} is the weight of PEM after immersing the dry membrane in DDI water at different temperatures for different times and W_{dry} is the weight of dried PEM.

Chemical Stability

By weighing the membrane, it was possible to measure the chemical stability of the polymer electrolyte membranes in an H_2O_2 aqueous solution [11]. A 2 cm x 2 cm membrane was submerged in an H_2O_2 aqueous solution at 80 °C. In this experiment, three different concentrations of H_2O_2 were used including 0.01 M, 0.02 M, and 0.05 M. After soaking period (1 to 9 days) the membrane was removed from the solution, dried, and the weight gains were estimated using the formula below:

$$H_2O_2\ tolerance\ (\%) =100×(W_{wet}−W_{dry})/W_{dry} \qquad (5)$$

Where W_{wet} is the weight of PEM after immersing the dry membrane in H_2O_2 at different concentrations for different times and W_{dry} is the weight of the dried PEM.

Mechanical Properties

Due to the existence of mechanical and swelling strains, as well as the close connection of the H_2 and oxygen gas flows, strong fuel cell membranes are necessary. Regarding the manufacturing, handling, and longevity of membranes, mechanical integrity is one of the most crucial prerequisites

for polymer electrolyte fuel cell membranes. Tensile strengths were determined to measure mechanical properties of the PEMs. The membrane samples were cut into 12 cm x 2.5 cm pieces and submerged in water for 9 days to assess their tensile strengths.

3.0 RESULTS AND DISCUSSION

Preparation of Protonated Membranes

The manufacturing process for the freshly developed polymeric adsorbent is depicted in Figure 1. The ETFE strips were divided into 2 cm by 4 cm pieces and washed in DDI water and acetone before being dried in a vacuum oven at 50°C and then weighed (W_0). The monomer solutions were made by combining SSS and AA in a 1:2 ratio in water. Monomer concentration were varied from 9%, 13.5%, 15%, 18%, 24%, and 30%, with adding 4% NaCl solution in DDI water. Polymer strips were exposed to a 50 kGy dose of gamma radiation using the Cobalt-60

(^{60}Co) irradiator. Then, the irradiated films were swiftly maintained under dry ice conditions.

In the meanwhile, argon gas was bubbled for 40 minutes at room temperature in gas passing bottle holding monomer solution. The two irradiation films were then each put into a 25 mL sealed vial with a bubbling monomer mixture as soon as possible to stop the air from oxidizing. The grafting process was then allowed to finish for 5 hours in a water bath set at 80°C. The fact that no inhibitor was added during the grafting simplified the procedure. The homopolymers and unreacted monomers were removed from the grafted polymers by repeatedly washing them in DDI water. Additionally, the amount of DG can be controlled by appropriately changing the irradiation and reaction settings. In contrast, the ETFE films soaked in the monomer solution remained unaltered without pre-irradiation even after several weeks and at a high temperature. In Scheme 1, the chemical reactions in these steps are depicted.
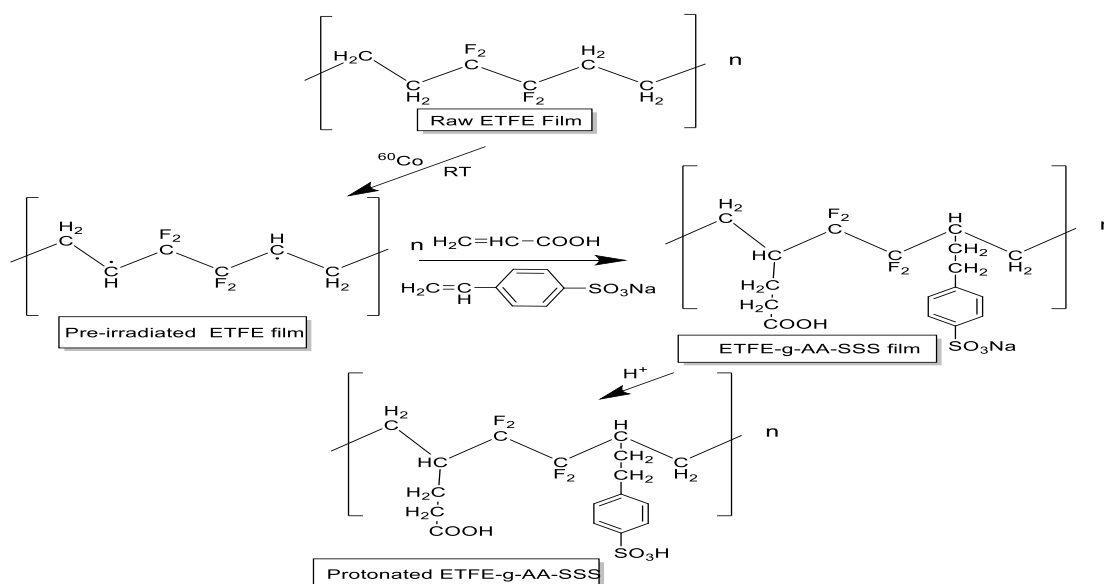

Scheme 1 Schematic representation of preparation of PEM obtained by the mixture of AA and SSS onto ETFE film

SEM Studies

Figure 2 displays SEM images of bare ETFE, ETFE-g-AA-SSS, and protonated ETFE-g-AA-SSS film. After grafting, the surface characteristics of the ETFE sample remained nearly the same. The structure of ETFE-g-AA-SSS revealed a surface with some grafted areas of varying sizes where they were absent in bare ETFE film. The surface of the raw ETFE film was thick, continuous, uniform, and smooth, just like the surface of most semi-crystalline polymers, such as LDPE, PP, etc. have [12]. The surface of the ETFE changed a little after the grafting reaction, and just a few regions of various-sized grafted pieces were visible, which may have been caused by the ETFE's softness [13]. With protonation, the dispersion of spots of various sizes grows uniformly. As the distribution and concentration of the protonation on the surface were similar, this suggests that the grafting of SSS and AA onto ETFE was homogeneous.
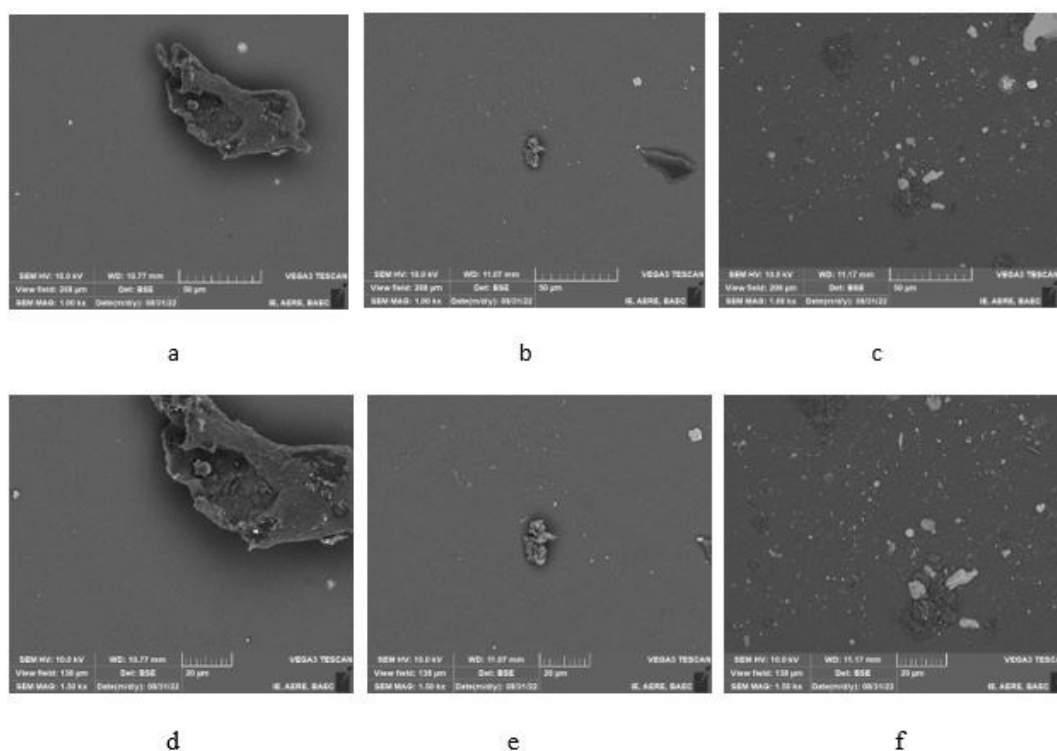
Figure 2 SEM micrographs of a) Bare ETFE b) ETFE-g-AA-SSS and c) protonated ETFE-g-AA-SSS film (magnification: 1000×) and d) Bare ETFE e) ETFE-g-AA-SSS and f) protonated ETFE-g-AA-SSS film (magnification: 1500×)
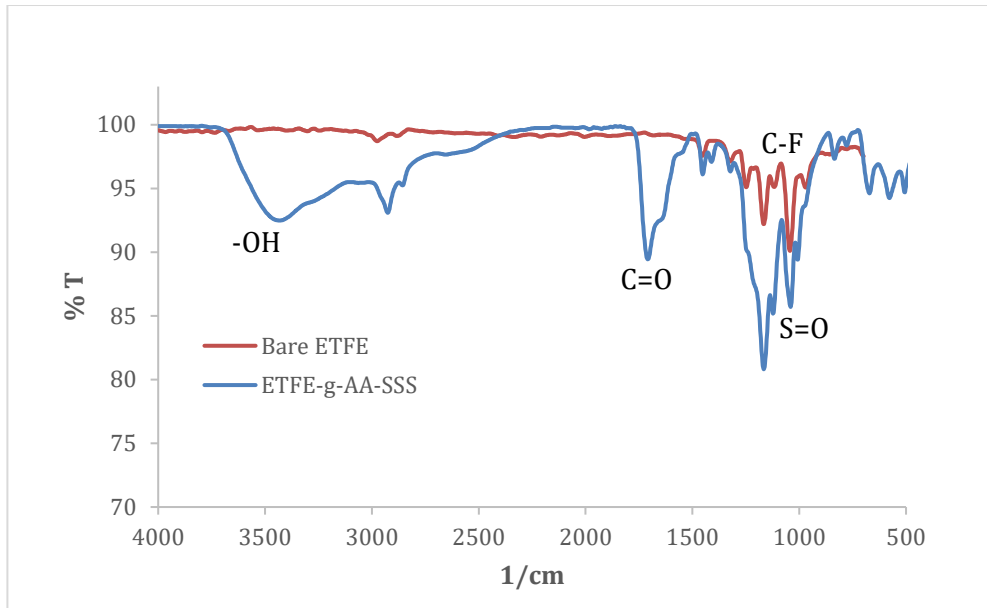
FTIR Spectroscopy

The spectra of ETFE film in Figure 3 (a) showed several strong bands in the 1000–1400 cm^{-1} range that reflected the C–F of CF_2 groups, as well as a minor band at 2916 cm^{-1} that represented symmetric stretching vibrations of CH_2 groups. When comparing the spectra (a) and (b), it can be seen that the -OH stretching vibrations of AA exhibited a large absorption peak between 3200 and 3600 cm^{-1}. The C=O groups of AA corresponded to the absorption peak at 1718 cm^{-1}. A symmetrical stretching vibration of S=O was responsible for the peak at 1030 cm^{-1}; for

antisymmetric, it was 1168 cm^{-1} [14-15]. These numerous additional absorption peaks demonstrated the successful grafting of AA and SSS onto the ETFE film.


**Figure 3** FTIR spectroscopy of Bare ETFE and ETFE-g-AA-SSS

Effect of Monomer Concentrations on the DG

Compared to other proton exchange membranes (PEMS) with single monomers, binary monomer PEMS are significantly more effective. As shown visually in Figure 4(a), monomer concentrations exhibited a considerable impact on DG since DG grew dramatically as monomer concentrations increased. For all monomer solutions, the monomer concentrations for SSS:AA in water were maintained at 1:2. The concentrations ranged from 9% (3% SSS and 6% AA in water) to 30% (10% SSS and 20% AA in water), with an addition of 4% NaCl. Initially when the monomer concentration was 9% to 12%, DG increased very little, ranging from 4.5% to 12.5%. But it then grew dramatically to reach its greatest point of 470% at a mixture of 10% SSS and 20% AA in water.
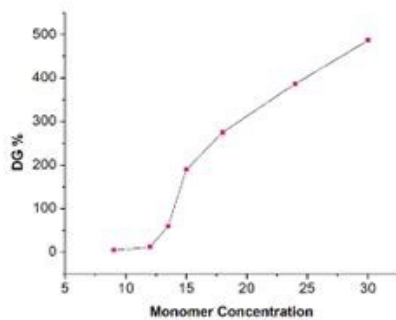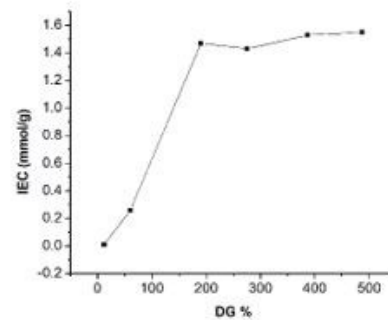
(a)   (b)

Figure 4 Influence of (a) monomer concentration on degree of grafting (DG) and (b) degree of grafting (DG) on IEC

Ion Exchange Capacity (IEC)

The relation between the degree of grafting and the ETFE-g-AA-SSS membranes' IEC is depicted in Figure 4(b). It is clear that IEC is significantly influenced by the grafting level. The IEC of the membranes raised as the level of grafting does. However, the IEC displayed greater values for the membranes which had more than 60% DG. The IEC exhibited 0.26 mmol/gm for ETFE-g-AA-SSS membranes of 60% DG, while between 190% and 487% it displayed 1.47 to 1.55 mmol/gm. This behaviour can be adequately attributed to the fact that as the degree of grafting increases, more acid groups enter into the membrane. Since it is widely known that IEC exerts significant control over membrane characteristics, by adjusting the degree of grafting in present grafting technology offers a real chance to produce proton exchange membranes with suitable characteristics.

Proton Conductivity

It is widely recognized that the membrane's IEC and water uptake are related to the proton conductivity of the membrane. In order to reduce the interfacial energy, the attachment of water (swelling) to the acid functionality in the membrane causes an alteration of the cluster structure that results in spherical water pools. Through the water channel, both water and protons are able to travel over the membrane. The significantly increased IEC and water absorption of the membrane imply a stronger proton conductivity. [8]. The computed proton conductivities of PEM in the current investigation increased with increasing frequency showed in Figure 5. At a frequency of 14000 kHz, the proton conductivity of membrane with 60%

DG was determined to be 0.003 S cm^{-1}. Although the value is lower than other results, such as those from Nasef *et al.* [16], who discovered that the proton conductivity of the styrene onto PFA films was 0.04 S cm^{-1} at room temperature, our prepared membrane can still be a good candidate for using in PEM fuel cells.
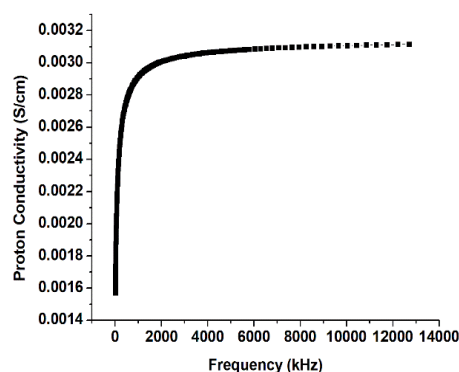
Figure 5 Proton conductivity of membrane with 60% degree of greafting (DG) vs. frequency
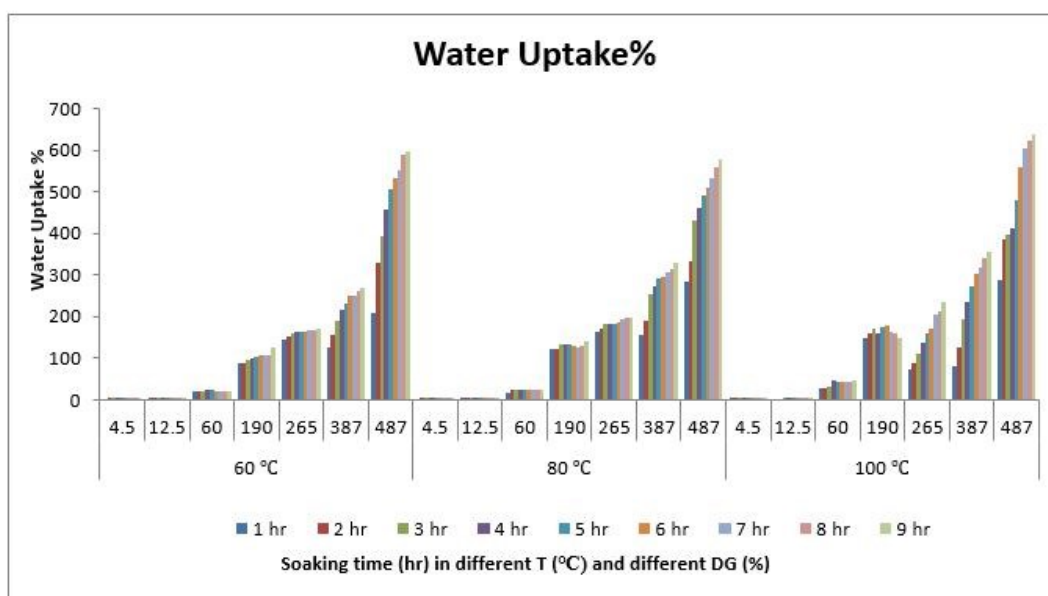
Water Uptake

For low-temperature PEMFC (LT-PEMFC), the operating temperature (OT) range varies from 60 to 85°C; however, for high-temperature PEMFC (HT-PEMFC), the OT range varies from 120 to 140°C. A number of studies have selected OT based on 80°C [17-19]. Figure 6 depicts the swelling behavior of our study of ETFE-g-AA-SSS films having various degrees of grafting (4.5% - 487%) as shown by water absorption of the membrane during a period of up to 9 hours at various temperatures of 60°C, 80°C, and 100°C as like LT-PEMFC. With an increase in soaking time and aqueous solution temperature, it was noticed that the membrane's capacity to absorb water increased. The amount of vinyl's side chains increases with longer soaking times and higher temperatures, which causes the

decrease in the PET domain in the whole membrane resulting in the decrease of the hydrophobicity of the membrane. Accordingly, with lengthier soaking times and higher solution temperature, the membrane is predicted to develop an increased hydrophilic element with more scattered water channels. But excessive water absorption causes membrane swelling, mechanical brittleness, and poor dimension stability. In this work, membranes with DG greater than 60% were particularly vulnerable to mechanical fragility and poor dimensional stability at higher temperatures. However, even at 100°C in aqueous solution, ETFE-g-AA-SSS

films with 60% DG retained their dimensional stability. The tensile properties of these membranes of 60% DG were examined after nine days, and the results were encouraging although greater DG membranes' water intake rose dramatically. After 9-hour soaking duration at 100°C, 47.48% water uptake of the 60% DG membrane was seen in this study.; this value is higher than that of the PET-based proton exchange membrane [1]. The prepared membrane could become a suitable membrane for assisting proton transport in the fuel cell since sufficient water content within the membrane is a key need for proper ionic conductivity in fuel cells.

Figure 6 Variation of weight gain (%) with time (hour), different temperatures (°C) and DG (%) during water uptake

Chemical Stability

H$_2$O$_2$, which was produced during fuel cell operation as a result of oxygen penetration through the membrane and insufficient reduction at the fuel cell anode, severely degraded the polymer electrolyte membrane. An essential PEM fuel cell metric is the assessment of oxidative stability because PEM

must endure H$_2$O$_2$ ambient conditions. So, over the course of nine days, H$_2$O$_2$ was used to test the membrane's oxidative stability. The weight gain (%) with time during the immersing of the ETFE-g-AA-SSS membrane samples having various degrees of grafting in H$_2$O$_2$ solution is shown in Figure 7. This experiment employed three distinct concentrations

of H_2O_2 (0.01 M, 0.02 M, and 0.05 M) at 80°C. The primary cause of membrane deterioration is thought to be the generation of OH or OH_2 radicals, which are precursors to H_2O_2. There was no significant change of membrane's tolerance up to 60% DG for 9 days. However, after that there was a massive change for other highly grafted membranes even after treatment with 0.01 M H_2O_2. Membranes with DG greater than 60% gained weight quickly with degradation. The degradation increased with increasing DG and H_2O_2 content such that 945% of weight gain was recorded for 190% DG membrane with

degradation. However, the result shows the excellent oxidative stability for the membrane of 60% DG. A tiny steady weight gain was observed during its three cycles of treatment with three different concentrations of H_2O_2. It showed weight gain of 17.56% even treated with 0.05M H_2O_2 at 80°C for 9 days. Similar chemical stability trend was recently reported for the polypyridobisimidazole and polybenzimidazole membrane with enhanced acid doping where little remaining weight was counted during chemical stability measurement [20-21].
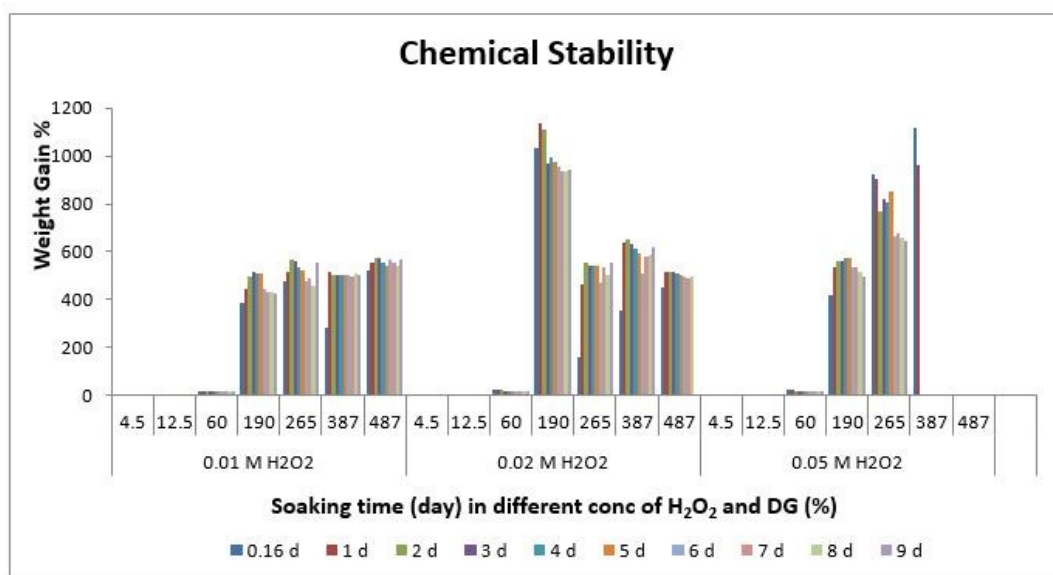
Figure 7 Variation of weight gain (%) with time (day), DG (%), and different concentrations of H_2O_2 (0.01 M, 0.02 M and 0.05 M)

Mechanical Properties of ETFE-g-AA-SSS Films

ETFE films have superior mechanical properties to other PEMs. Tensile properties of ETFE-g-AA-SSS films were measured using Universal Testing Machine. Mechanical characteristics typically declined as radiation dose and DG increased. As the ETFE-g-AA-SSS film of 60% DG outperformed the other grafted samples

of ETFE-g-AA-SSS in terms of ion exchange capacity, water uptake, temperature tolerance and chemical stability, it was further investigated for its mechanical strength. It was soaked into water for 9 days and after that tensile strengths were measured for both water soaked and water unsoaked films. Tensile strengths of water soaked and water unsoaked of ETFE-g-AA-SSS films were found to be 50 MPa and 55 MPa respectively which is

much higher than the LDPE-AEM (100 kGy) [22]. Here, Wang at al. also showed a reduced tensile strength and elasticity of ETFE-AEM (30 kGy) compared to the pristine precursor ETFE film which is aligned to our result. In our study, tensile strength of pristine ETFE film was found to be 60MPa. When Wang at al. [22] compared the LDPE-AEM (100 kGy)

film, the ETFE-AEM (30 kGy) film also showed a higher tensile strength. In another investigation, after being grafted with the co-monomer, the ETFE film which has a tensile strength of 37.4 MPa and an elongation of 104%, displayed a reduced tensile strength of 21.6 MPa and an elongation of 57.8% [23] as like our study.

Table 1 Physico-chemical properties of ETFE-g-AA-SSS membrane with compared to other membranes

Membrane	Water Uptake (%)	Tensile Strength (MPa)	IEC mmol/g	Proton Conductivity	Ref. no
PET	14.5	20	0.043	0.015	[24]
ETFE	35	26	2.5	0.076	[25]
PET	31	-	0.9	0.075	[1]
Nafion-CeO$_2$	25.9	-	0.84	1.76	[26]
SPEEK	600	-	1.95	0.01	[27]
BisaF-BPSH	71	-	1.6	1.3	[28]
ETFE	47.48	50	0.26	0.003	Pres. Study

Comparison of ETFE-g-AA-SSS Membrane with Other Membranes

Table 1 compares the physical and chemical properties of the ETFE-g-AA-SSS membrane (60% DG) with those from other studies with comparable characteristics. Under the same experimental conditions, our produced membrane (60 % DG of ETFE-g-AA-SSS) was compared to other membranes including nafion also. Despite having a lower proton conductivity, its physico-chemical characteristics, such as chemical stability, water absorption, and IEC were much higher than those of competitors. However, for practical usage in electrochemical applications,

their proton conductivity needs to be further enhanced.

4.0 CONCLUSION

Radiation-induced graft polymerization of a binary combination of acrylic acid and sodium styrene sulfonate onto ETFE film was effectively used to create ETFE-g-AA-SSS as PEM in fuel cells. The newly developed PEM was characterized by FTIR, tensile strength, and SEM. SSS is a hydrophilic sulfonate group-containing vinyl monomer that is as strongly reactive as AA. By varying the grafting conditions, it was possible to regulate

the DG to the required levels, making it suitable for use in fuel cells. Several monomer concentrations (9%-30% in water) were used to select the optimum DG of membrane. Comparing other membranes with varying DGs, the membrane with 60% DG demonstrated greater physical and chemical endurance. Hence, it was selected for further studies. It had uniform graft distribution, appealing physicochemical characteristics, and strong chemical stability. The proton conductivity of this membrane reached a value of 0.003 cm^{-1} at the frequency of 14000 Hz. The value of water uptake (100∘C), acid durability (0.05 M H_2O_2 at 80∘C), and IEC of this grafted membrane were found to be 47.48%, 17.57% and 0.26 mmol g $^{-1}$ respectively. Even though the ETFE-g-AA-SSS membrane of 60% DG had a poor proton conductivity, its other physico-chemical characteristics were excellent than other grafted membranes with different DG. The overall findings imply that even at high temperatures, the ETFE-g-AA-SSS membrane with 60% DG can be a potential option for use in PEM fuel cells and will encourage further investigation. The findings would be useful for optimizing ETFE-g-AA-SSS membranes, and the following research will concentrate on increasing the conductivities of ETFE-g-AA-SSS membranes and improving their mechanical properties.

ACKNOWLEDGEMENT

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