

UV RADIATION INDUCED GRAFT COPOLYMERIZATION OF ALLYL ACETATE ONTO POLY(ETHYLENE TEREPHTHALATE) (PET) FILMS FOR FUEL CELL MEMBRANES

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Abstract Ultraviolet (UV)-induced graft copolymerization of allyl acetate (AA) monomer onto poly(ethylene terephthalate) (PET) films and the subsequent sulfonation on the monomer units in the grafting chain using chlorosulfonic acid (ClSO₃H) were carried out to prepare proton exchange membranes (PEMs) for fuel cells. A maximum grafting value of 12.8% was found for 35 vol% allyl acetate after 3 h radiation time. Optimum concentration of ClSO₃H was selected for the sulfonation reaction to be 0.05 mol/L based on the degree of sulfonation and the tensile strength studies of the membrane. The degree of sulfonation increased as the sulfonation reaction temperature and sulfonation time were increasing. The radiation grafting and the sulfonation have been confirmed by titrimetric and gravimetric analyses as well as FTIR spectroscopy. The maximum ion exchange capacity (IEC) of 0.04125 mmol g⁻¹ was found at 12.1% degree of sulfonation and the maximum proton conductivity was found to be 0.035 S cm⁻¹ at 30°C and a relative humidity of 60%. The various physical and chemical properties of the PEMs such as water uptake, mechanical strength, thermal durability and oxidative stability were also studied. To investigate the suitability of the prepared membrane for fuel cell applications, its properties were compared with those of Nafion 117.

Keywords: Polymer electrolyte membrane; Allyl acetate; Fuel cell; UV radiation; Grafting; Sulfonation.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs), one of the main technologies for the generation of power in the future, can generate energy from renewable sources instead of fossil fuels and have made much interest as a convenient and viable alternative source of power with promising potential to reduce the excess consumption of fossil fuel and emission of carbon dioxide^[1]. The promising alternative energy device is capable to produce high current densities with high energy conversion efficiency, which makes the system suitable for a wide range of portable, stationary and automotive applications^[2]. In spite of these advantages, the actual use of fuel cells for production of energy is still quite limited due to the economic considerations^[1].

The proton exchange membrane (PEM) is a key device in fuel cells, which acts as proton transferring electrolyte as well as provides a barrier to the passage of electrons between the electrodes^[2]. At the present time, perfluorinated membranes, Nafion are the most commonly used PEM around the world, due to their superior chemical and electrochemical stability, as well as high proton conductivity under fuel cell operating conditions^[3]. However, their critical drawbacks of high cost, low gas-barrier property and low stability at high

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Received March 25, 2011; Revised April 23, 2011; Accepted April 28, 2011

doi: 10.1007/s10118-012-1116-4

temperatures limit their further wide applications. In view of this, there have been considerable efforts focusing on the development of alternative non-fluorinated, graft-type PEMs which are very inexpensive and are highly stable at high temperatures^[2, 4].

The radiation-induced grafting method can advantage extensive penetration of monomers in the polymer matrix as well as rapid and uniform radical formation for initiating grafting in many polymer materials^[5]. This technique allows to introduce ion conducting regions at inner polymer chains of films for the desired physical and chemical properties^[6]. Various kinds of grafting polymerization techniques including ion-radiation induced, photo-induced (UV and chemical initiator) and plasma-induced grafting polymerization have been developed in the last few decades^[7–10]. However grafting on PET films using UV-radiation, that is more available and less expensive than other techniques^[11] demands more extensive study.

In a previous communication, we briefly reported the preparation of PET-based PEM by UV-radiation-induced graft copolymerization of styrene monomer onto PET films, followed by sulfonation using chlorosulfonic acid^[12]. The development of PEM with new non-styrene monomer grafts greatly expands the new possibility of the graft-type PEM for fuel cells^[4]. In view of this, PET-based PEM was successfully prepared by the same grafting technique^[12] using allyl acetate (AA) monomer in the current study. Optimizations of AA monomer and chlorosulfonic acid concentration were carried out to obtain maximum grafted and maximum sulfonated PEM with satisfactory tensile strength. The characterizations of the membranes including different chemical and physical parameters such as water uptake, tensile strength, ion exchange capacity, proton conductivity, thermal durability and FTIR spectroscopy were also studied.

EXPERIMENTAL

Materials

PET granules were purchased from MITSUIPET, Thailand. The monomer allyl acetate, photoinitiator (Darocur^(R) 1173-2-hydroxy-2-methyl-1-phenyl-propan-1-one), methanol, toluene and chlorosulfonic acid were procured from Merck, Germany. 1,2-Dichloroethane and H₂O₂ were purchased from BDH limited, Poole, England. Sodium chloride and sodium hydroxide were purchased from Wako pure chemical industries, Ltd., Japan. Nafion 117 was purchased from Ashahi Glass Co. Ltd., Japan.

Preparation of PEM

The PET film was prepared from PET granules using the heat and cold press machine (SHIMADZU Corporation, Japan). The PET film of 0.11 mm thickness was cut into rectangles with size of 1 cm × 5 cm and the rectangles were washed with acetone to remove impurities on film surface. After drying, the washed films were immersed in 20 mL of methanol solution containing different concentrations (25 vol%, 30 vol%, 35 vol%, 40 vol%, and 45 vol%) of AA monomer and 2% photo initiator under UV-radiation for different times (1, 2, 3, 4, 5, and 6 h). UV radiation was carried out with a medium-pressure mercury lamp (254–313 nm and 90 W, IST Technik, Germany). After grafting, the adhered homo-polymers and residual monomers were removed from the film by Soxhlet extraction process with a large amount of toluene.

The grafting degree, G (%) was calculated by the following equation:

$$G (\%) = ((W_g - W_0)/W_0) \times 100 \quad (1)$$

where W_g and W_0 are the film weights after and before graft polymerization, respectively.

The grafted films were immersed in different concentrations (0.2, 0.1, 0.05, 0.03, 0.01 mol/L) of chlorosulfonic acid (ClSO₃H) in 1,2-dichloroethane at different temperatures for different times. The unreacted chlorosulfonic acid adhering on the films was removed by washing them in distilled water. The degree of sulfonation of dried sulfonated films was calculated by the following equation:

$$S (\%) = ((W_s - W_g)/W_g) \times 100 \quad (2)$$

where W_s and W_g are the film weight after and before sulfonation, respectively.

The sulfonated membranes were then hydrolyzed in distilled water for 24 h at 60°C.

The Ion-exchange Capacity (IEC)

The ion-exchange capacity of the PEM was determined by titrimetric analysis. The prepared dried membrane in the protonic form was immersed in a 0.1 mol/L NaCl aqueous solution for 24 h at room temperature. The H^+ ions, substituted by Na^+ ions, were released into the solution. Then the solution was titrated by a 0.05 mol/L NaOH solution. The IEC of the membrane was calculated using titration result with the following equation:

$$IEC = (c_{NaOH} \times V_{NaOH})/W_{dry} \quad (3)$$

where c_{NaOH} (mol/L) and V_{NaOH} (mL) are the concentration and volume of NaOH solution required for neutralization of the residual solution containing released H^+ s, respectively and W_{dry} is the weight of the dry sulfonated membrane in protonic form.

The Water Uptake

The water uptake of the sulfonated membrane was calculated by the following equation:

$$\text{Water uptake (\%)} = 100 \times (W_{wet} - W_{dry})/W_{dry} \quad (4)$$

where W_{wet} is the weight of PEMs after immersing the dry membrane in water at different temperatures for different times and W_{dry} is the weight of the dry PEM. The water uptake of Nafion 117 was also investigated at 100°C for 9 h.

The Proton Conductivity

The proton conductivity, σ of the PEM was calculated by the following equation:

$$\sigma (S \text{ cm}^{-1}) = l/R \times S \quad (5)$$

where R is the resistance (Ω) of the membranes, l is the thickness (cm) of the membranes and S stands for contact surface area (cm^2) of the electrode. Before measuring the resistance, the membrane was soaked in water at 80°C for 24 h and then the hydrated membrane was platinized by Pt/C (act as electrodes) after wiping off excess water on the membrane surface and connected with Cu wire to impedance analyzer (SHIMADZU Corporation, Japan). The resistances of the membranes were read out from the Impedance Analyzer at room temperature (30°C) and at relative humidity of 60%.

Oxidative Stability

The weight loss of the sulfonated membrane in H_2O_2 solution of different concentrations was calculated by the following equation:

$$\text{Weight loss (\%)} = 100 \times (W_{H_2O_2} - W_{dry})/W_{dry} \quad (6)$$

where $W_{H_2O_2}$ is the weight of PEMs after immersing the dry membrane in H_2O_2 at different temperatures for different time and W_{dry} is the weight of the dry PEM. Nafion 117 was also studied in terms of oxidative stability in a 0.05 mol/L H_2O_2 solution at 80°C for 10 days.

Mechanical Stability

Tensile strength of the PEMs and Nafion 117, after soaking in H_2O at 80°C for 9 days, was determined by a tensile strength testing machine (INSTRON Corporation, UK).

IR Analysis

IR spectra of original, grafted and sulfonated PET films in the range of 400–4000 cm^{-1} were measured by a Fourier transform infrared spectrophotometer (SHIMADZU Corporation, Japan).

RESULTS AND DISCUSSION

Preparation of the Sulfonated Film

Sulfonated PET films were prepared by two steps: the AA-grafted PET films was first prepared by simultaneous UV radiation-induced grafting of allyl acetate (AA) onto PET films; the grafted films was then sulfonated by

ClSO_3H . Many factors such as monomer concentration and radiation exposure time affect grafting of allyl acetate (AA) onto PET films whereas concentration of sulfonating agent, sulfonation reaction time, sulfonation temperature etc affect sulfonation of the grafted PET films^[13]. So these parameters were optimized to get a high performance PEM in this study.

Simultaneous UV radiation-induced grafting of allyl acetate (AA) onto PET films

A simultaneous UV radiation-induced graft copolymerization of AA monomer onto PET films was investigated as a function of monomer concentration at room temperature (30°C) for 2 h (Fig. 1). In our study, G (%) increased with increasing monomer concentration, reached a maximum of 11.2% grafting yield at 35 vol% AA due to the increase of monomer concentration and its diffusion into the PET films which leads to an increment in the grafting yield. After 35 vol% monomer concentration, the grafting yield started to decrease with a further increase in monomer concentration because of increasing homopolymerization rather than grafting which leads an increment of the viscosity of the grafting solution and thus hindering the movement of the monomer toward the substrate and consequently reduces the grafting yield^[5, 13].

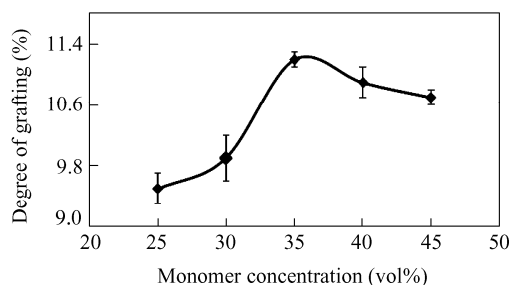


Fig. 1 Degree of grafting, G (%) as a function of monomer concentration at room temperature for 2 h

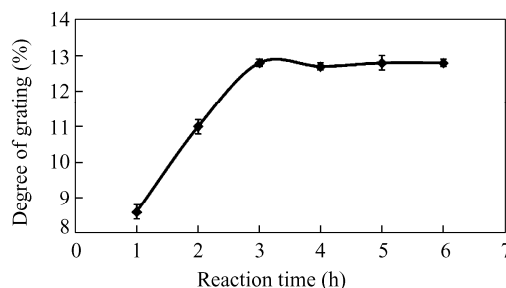


Fig. 2 Degree of grafting, G (%) as a function of UV radiation time at room temperature

Grafting onto the PET film was also carried out at different radiation times, keeping the monomer concentration constant at 35 vol%. As shown in Fig. 2, G (%) first rose with increasing radiation time up to 3 h; it then leveled off, reaching to a saturation grafting value of 12.8%. With increasing radiation time, the number of monomer molecules that diffuse into the PET surface also increases, and thus resulting in a higher degree of grafting. The levelling off of grafting may be attributed to the saturation of active PET back-bone by homopolymers which form a diffusion barrier on the PET surface^[14].

Sulfonation of the AA-grafted PET using ClSO_3H

The chemical introduction of the sulfonating groups ($-\text{SO}_3\text{H}$) onto the grafted PET films can enhance the solubility of the products so that they could be active as PEMs for using in fuel cell. In this study, the degree of sulfonation, i.e., the molar ratio (%) of sulfonic acid to monomer units of the grafted polymer chain, can vary considerably with the variation of the sulfonation reaction conditions (e.g., reaction time, temperature, chlorosulfonic acid concentration)^[15]. In this study, the degree of sulfonation increased with increasing chlorosulfonic acid concentration (Fig. 3). The grafted PET film with grafting yield of 11.2% exhibited maximum sulfonation yield of 5.6% at 0.2 mol/L ClSO_3H . For fuel cell application, the graft-type PET should have a homogeneous distribution of sulfonic acid in the perpendicular direction to the film surface so as to exhibit high proton conductivity between two electrodes in a fuel cell device^[4]. The homogeneous distribution of sulfonic acid group onto the film surface can make the film rigid^[12]. However, at high ClSO_3H concentrations, the tensile strength of the membrane dramatically decreased with the concentration (Table 1). This can be explained by the fact that the continuous increase in the content of sulfonic acid in the grafted PET film results in the deterioration of mechanical properties of the membranes because of highly hydrophilic property of the film^[2]. Considering the values of tensile strength and degree of sulfonation, optimum concentration of ClSO_3H was selected as 0.05 mol/L.

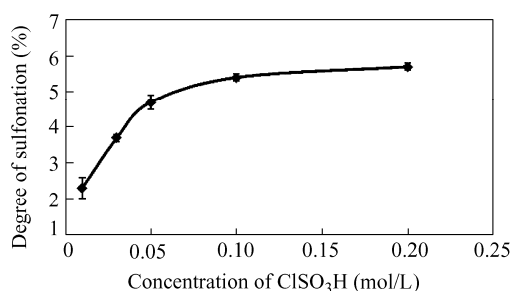


Fig. 3 The degree of sulfonation, S (%) of the AA-grafted PET film with a grafting degree of 12.8% as a function of chlorosulfonic acid (ClSO_3H) concentration in 1,2-dichloroethane at room temperature for 1.5 h

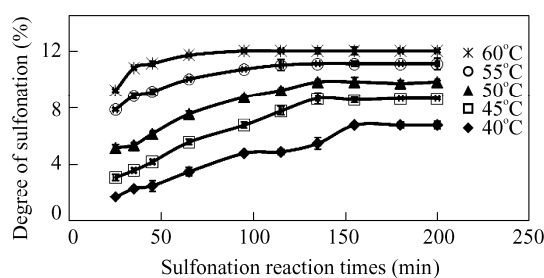


Fig. 4 Degree of sulfonation, S (%) of AA-grafted PET film with a grafting degree of 12.8%, sulfonated with 0.05 mol/L ClSO_3H as a function of reaction time at different temperatures

Table 1. The degree of sulfonation, S (%) of the sulfonated films prepared from different concentrations of ClSO_3H and the corresponding tensile strengths of these films

Concentration of ClSO_3H (mol/L)	Degree of sulfonation, S (%)	Tensile strength (MPa)
0.2	5.6	3
0.1	5.4	7
0.05	4.1	24
0.03	2.7	27
0.01	2.3	31

The degree of sulfonation (S (%)) increased with increasing sulfonation reaction time and temperature (Fig. 4). The elevated reaction temperature shortens the time necessary for full sulfonation of the grafted film. The increment of the sulfonation yield with increasing reaction time and temperature may be attributed to the saturation of grafted PET films by the $-\text{SO}_3\text{H}$ groups.

The Ion Exchange Capacity

The ion exchange capacity (IEC) plays a critical role in determining the proton conductivity of the membrane^[16]. In the current study, IEC increased with increasing S (%) (Fig. 5) due to the incorporation of the increased number of SO_3H groups into the grafted PET film. High value of IEC is desirable to achieve higher proton conductivity in proton exchange membranes. Maximum IEC of the prepared PEM was found to be $0.04125 \text{ mmol g}^{-1}$ at 12.1% degree of sulfonation whereas IEC of Nafion 117 was found to be $0.679 \text{ mmol g}^{-1}$. As the degree of grafting and the degree of sulfonation are lower, it is not surprising to get lower IEC for the membrane.

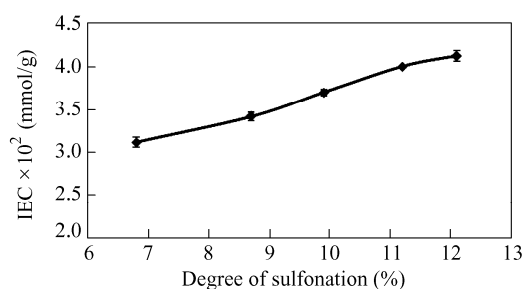


Fig. 5 Ion exchange capacity (IEC) of the membrane as a function of the degree of sulfonation, S (%)

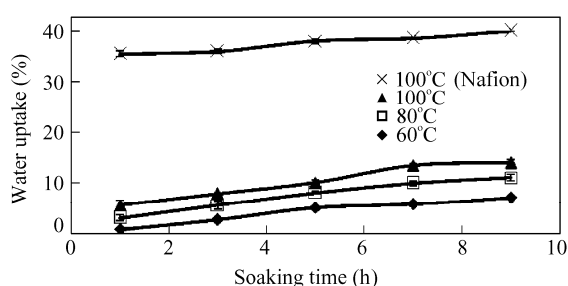


Fig. 6 Water uptake of the sulfonated membrane as a function of soaking time at 60°C, 80°C and 100°C and that of Nafion 117 at 100°C for the same soaking time

Water Uptake

The water within the membrane provides a carrier for the proton and maintains high proton conductivity in the PEM. Figure 6 shows the water uptake of the sulfonated membrane as a function of soaking time (1–9 h) at different temperatures (60°C, 80°C, 100°C) of the medium. The water uptake of Nafion 117 at 100°C for same soaking time was also shown for comparison. In this study, water uptake increased with increasing soaking time and temperature of the medium. This can be explained by the fact that the polymer chain mobility and the free volume for water absorption increased at elevated temperatures. The maximum water uptakes were found to be 14.1% and 40% for the prepared PEM and Nafion 117, respectively at 100°C for 9 h soaking time. It is noteworthy that all the membranes maintained their dimensional stability at 80°C. This suggests that they could meet the demands for operation at elevated temperatures as PEMs for using in fuel cell^[17].

Proton Conductivity

The proton conductivity is one of the key properties of a polymer electrolyte membrane affecting directly the performance of a fuel cell through ohmic losses and therefore in order to attain a high power density, the area resistance of the membrane should be low. The proton conductivities of PEMs containing different IEC have been presented as a function of different frequencies in Fig. 7. The proton conductivities increased with increasing frequency and IEC in this study. The maximum proton conductivity was found to be 0.035 S cm^{-1} at the highest frequency of 13000 kHz and IEC of 0.04125 mmol g⁻¹.

The proton conductivity of sulfonated film is known to be associated with the IEC and water uptake of the membranes. Generally, the density of available sulfonic acid groups and their dissociation capability in water are the main factors for showing the proton conductivity of the membrane. The attachment of water to the acid functionality in the membrane induces a modification of the cluster structure which becomes spherical water pools in order to minimize the interfacial energy. Water and hydrophilic solvents can penetrate the membrane through water channel and it can also provide the passage of protons. But, excessive water uptake in a PEM leads to unacceptable dimensional change which could lead to weakness or dimensional mismatch when incorporated into a membrane electrode assembly^[2, 17]. Therefore, optimized water uptake is important for membrane materials for fuel cell systems.

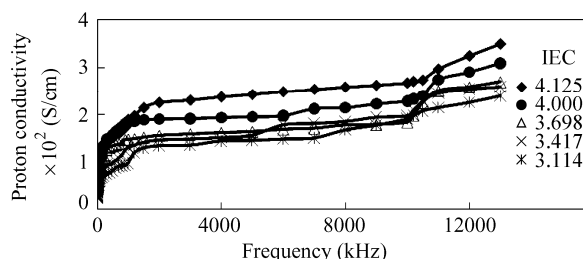


Fig. 7 Proton conductivity of PEMs having different IEC as a function of frequencies at 30°C and at RH of 60%

If we compare the proton conductivity of AA-grafted PEM of 0.035 S cm^{-1} (at 30°C and 60% RH) with some other studied PEMs we find that although the proton conductivity of AA-grafted PEM is lower than that of Nafion® 117 but it is quite satisfactory with respect to acrylic acid (AAc)- and *N,N*-dimethylacrylamide (DMAA)-grafted membranes^[4] and amidated pectin (AP) based polymer electrolyte membrane^[18] that show proton conductivity of $< 0.001 \text{ S cm}^{-1}$. Besides, in this study the measurement of proton conductivity was taken under a RH of 60% rather under hydrous condition (RH of 100%). In that respect, the AA-grafted PEM can perform as a good membrane under hydrous condition in fuel cells.

Oxidative Stability

H₂O₂ can be produced as a very low degree in hydrogen fuel cell, so the oxidative stability of PEMs is especially important for fuel cell applications. The formation of HO or HO₂ radicals is considered as the key reason for

membrane degradation^[19]. Therefore, the stability of the prepared sulfonated membrane in such an environment was investigated using different concentrations of H_2O_2 at 80°C for 10 days (Fig. 8). For comparison, the oxidative stability of Nafion 117 was also investigated using 0.05 mol/L H_2O_2 solution under the same condition. In this study, there were no significant changes (maximum 1.4% weight loss) in the prepared sulfonated membrane even after treatment with 0.05 mol/L H_2O_2 for 10 days confirming the excellent oxidative stability.

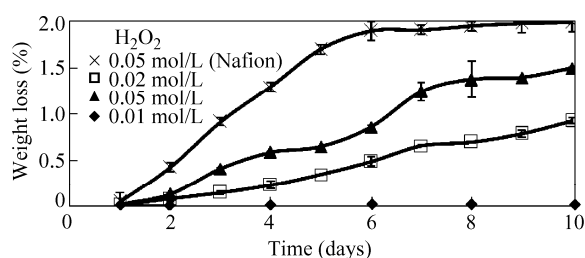


Fig. 8 The stability of the sulfonated membranes in different concentrations of H_2O_2 as a function of reaction time

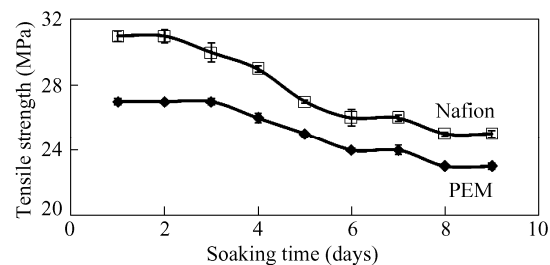


Fig. 9 Tensile strength versus soaking time of the sulfonated film and Nafion 117 in H_2O at 80°C for 9 days

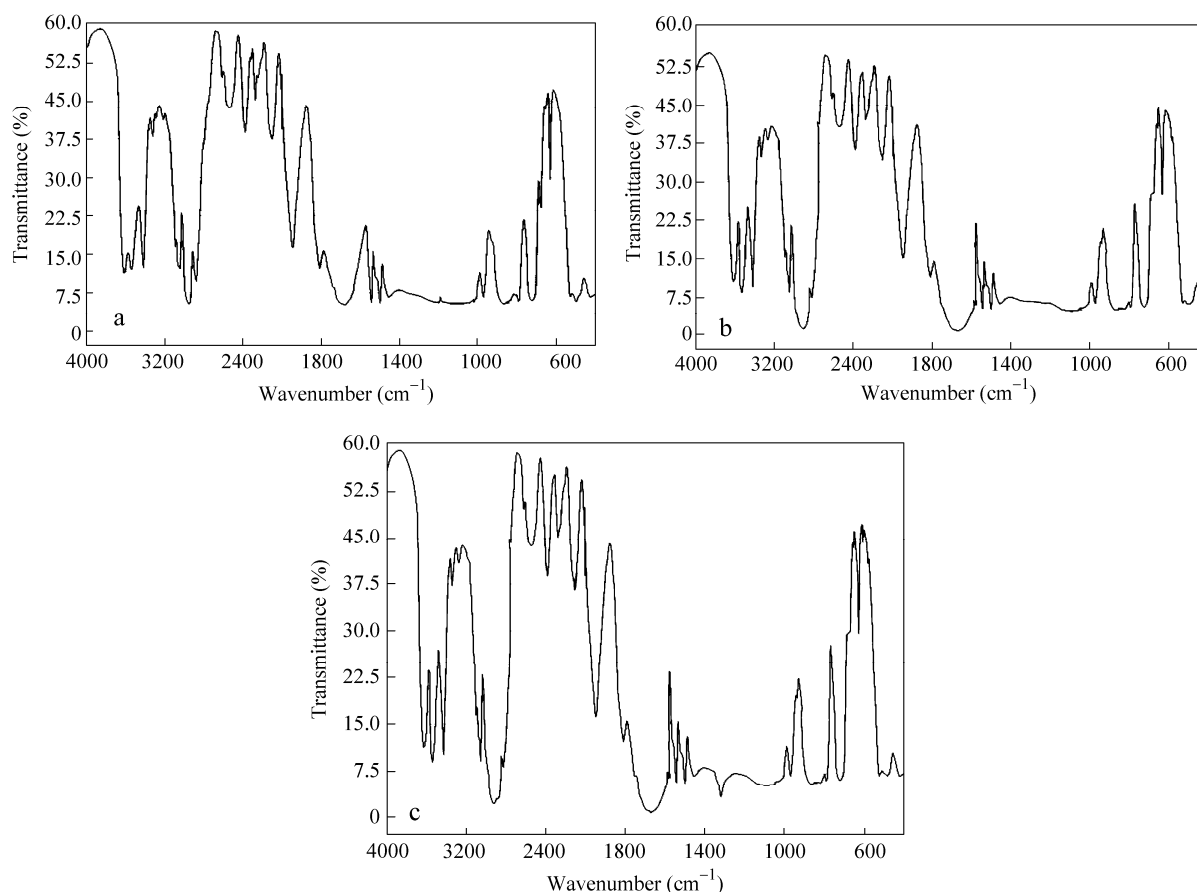


Fig. 10 IR spectra of PET (a), grafted PET (b) and sulfonated PET film (c)

Mechanical Stability

Figure 9 shows the tensile strengths of PEMs and Nafion 117 as a function of soaking time in aqueous media at 80°C for 9 days. In this study, tensile strength slightly decreased with increasing soaking time in water

confirming that the prepared membrane has a very good mechanical stability (although somewhat lower value than Nafion 117) for using in fuel cells.

FTIR Analysis

Figure 10 represents FTIR spectra of original, grafted and sulfonated PET films. The FTIR spectrum of ungrafted PET film shows distinctive absorptions at 1720, 1550–1650, 2960–2910 and 3060 cm^{-1} that are typical of C=O, C=C, aliphatic C–H and aromatic C–H stretching, respectively. After grafting AA monomer on the PET film, the peaks at 1550–1750 and 2960–2910 cm^{-1} caused broadening in the FTIR spectrum of the grafted PET film due to the overlapping of the C=O (esters) groups, C=C (alkene) and aliphatic C–H peaks of the monomer. Sulfonation at the grafted PET films was confirmed by showing peaks at 1300–1350 cm^{-1} for sulfonic acid group.

CONCLUSIONS

Proton exchange membranes (PEMs) for fuel cells have been successfully prepared by simultaneous UV radiation-induced graft copolymerization of AA monomer onto PET films and consequent selective sulfonation by chlorosulfonic acid at the grafting chains in the film state. A maximum grafting value of 12.8% was found for 35 vol% allyl acetate and 3 h radiation time. Optimum concentration of ClSO_3H was selected as 0.05 mol/L based on tensile strength and degree of sulfonation. The maximum degree of sulfonation was found to be 12.1% at 60°C for 95 min. The electrolyte properties of the sulfonated membranes were investigated where maximum IEC, water uptake (at 100°C for 9 h) and proton conductivity (at 30°C and 60% RH) were found to be 0.04125 mmol g^{-1} , 14.1% and 0.035 S cm^{-1} , respectively. Besides, the prepared membranes were found with high thermal durability (at 100°C) and high mechanical stability (23 MPa in H_2O at 80°C for 9 days). The PEMs were found to possess high oxidative stability (max. weight loss 1.4% in 0.05 mol/L H_2O_2 at 80°C for 10 days). It is suggested that the prepared PEMs can contribute a very significant improvement in nonfluorinated membrane science to function in fuel cells as an alternative of Nafion.

ACKNOWLEDGEMENT We thank staffs of Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission for technical support and advice throughout the work. We also thank Bangladesh University of Engineering Technology for using their impedance analyzer.

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