

Properties of Proton Exchange Membranes Polyethylene Terephthalate (PET) Films Developed by Gamma Radiation Induced Grafting and Sulfonation Technique

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Abstract Proton exchange membranes (PEMs) were developed by radiation induced grafting of styrene onto polyethylene terephthalate (PET) and linear low density polyethylene (LLDPE) membranes using two steps technique. Subsequent sulfonation on the PET films was conducted by chlorosulfonic acid (ClSO₃H). The PET films in 45% styrene solution at 1500 krad dose has found to show the highest grafting (17.4%) in both techniques while the maximum degree of sulfonation was noticed to be 9% with a soaking time 150 minutes. Surface morphology was investigated from scanning electron microgram (SEM). Proton exchange capacity (PEC) was confirmed by pH change in 0.01 M NaCl solution. Optical and electrical characteristics of the PEMs were performed by the measurements of FTIR optical absorption, electrical impedance, and electrical resistance respectively.

Keywords: polymer electrolyte membrane, gamma radiation, grafting, sulfonation, styrene, poly (ethylene terephthalate), SEM, FTIR, impedance

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1. Introduction

The modification of the proton-exchange membranes (PEMs) for fuel cell performance has received with attention in the last few decades. Commercially expensive perfluorinated membranes as nafions are widely accepted for PEM of fuel cell though its operation is limited by temperature. Fluorine-containing polymers have been widely studied to develop proton exchange membranes by pre, post and simultaneous radiation induced grafting of different monomers. Several different polymers as poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP), polyvinyl-iodine fluoride (PVDF), poly (tetrafluoroethylene-co-perfluorovinyl ether), (PFA), PTFE-g-polystyrene, high-density polyethylene membranes (HDPE) etc. are widely used as fuel cell membrane instead of nafion but their proton exchange capacity is not satisfactory [1,2,3,4]. Yang et al. [5] reported the grafted polybenzimidazole (PBI) with benzimidazole pendant groups, however the degree of grafting was less than 6% [5]. The radiation induced technique is very promising because of easy to control the degree of grafting as well as ion exchange capacity, controlling the radiation dose. Gamma radiation

induced grafting on polymer membrane is an attractive method of most other methods because of high reactive energy of gamma-ray to initiate graft copolymerization reaction and allyl cetate, styrene, divinylbenzene etc are very commonly used monomers [6,7].

The silicon-based inorganic-organic membrane offers a number of advantages, but from the economic stand point, for proton exchange membrane fuel cell (PEMFC) highly stable membranes at fuel cell temperature with optimum proton exchange capacity (PEC) needed to be developed [8,9]. Thermal stability is the most important requirement because the physical and chemical properties are dependent on melting temperature and mechanical stability [7]. Experimentally radiation induced grafted sulfonic acid membranes based on commercial fluorinated ethylene propylene (FEP) films are stable for 1400 hours in PEMFC at operating temperature up to 80 °C and show better PEC [10]. Radiation induced technique graft monomer in one step and two step onto the poly (ether ether ketone) (PEEK) having high chemical resistance films effectively improve the stability and ion conductivity [11,12,13]. Sulfonation technique is widely used to modify the chemical structure of fuel cell membranes [14]. After sulfonation sulfur dioxide (SO₂) and sulfur trioxide (SO₃) complexes are added with

polymer chain of PEMs and PEMs showed proton conductivity as a function of degree of sulfonation [15]. Although, the polymer blends derived from sulfonated polystyrene ethylene butylene polystyrene (SPSEBS) and sulfonated polysulfone (SPSU) give better performance than nafion, it may time consuming and tedious [16]. Due to the presence of less functional groups, the melting temperature ($>250^{\circ}\text{C}$), chemical stability and radiation resistance of PET is very high [17,18]. Radiation induced grafting is very much effective technique in the field of copolymerization. Since the radiation has sufficient energy to copolymerize polymer bonding with monomer and the sulfonation conjugates sulfonate groups in the polymer bonding which accelerates proton exchange capacity of the membrane. Keeping these facts in mind, the present study aims to develop the proton exchange capacity of the PET membranes by radiation induced grafting of the monomer subsequently followed by a sulfonation technique.

2. Materials & Methods

The poly ethylene terephthalate (PET) used as the base film for gPETs and sPETs was prepared using PET granules purchased from MITSUIPET, Thailand. Styrene and chlorosulfonic acid (CSA) were purchased from BDH limited, Poole, England. Nafion film was purchased from [TekStakTM] Germany. All the ingredient and chemicals were used as received. The base PET films were made from PET granules of different masses, which were heated at 510°F or 265.55°C under 5 psi pressures for 5 minutes. The films were cut into suitable rectangles and washed with acetone to remove impurities on the film surface. The PET films were immersed in 100 ml methanol solution containing different concentrations (30, 35, 40, 45, 50, 55 and 60) of styrene under different dose (500, 1000, 1500, 2000 and 3000 krad) of ^{60}Co γ -radiation at room temperature. The samples were then treated with gamma radiation. The grafting of the samples were performed after 48 hours of gamma radiation induction. The grafted films were washed with a large amount of toluene vapor to remove the homo-polymer and the residual monomers. The degrees of grafting can be calculated using the relation, $G (\%) = (W_g - W_o) / W_o \times 100\%$, where W_o and W_g are the film weights before and after grafting respectively.

Water uptake and aging of the samples were calculated from the relation, water uptake (%) = $(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100\%$ where W_{wet} , the weight of the membranes after immersing in distilled water at required temperatures for different times (0.5, 1, 1.5, 2, 2.5, 3, 5, 10, 15 and 20h) and W_{dry} , the weight of the dried membranes. The surface morphology of the base, grafted and sulfonated films (irregular round shape) were studied using Scanning Electron Microscope (SEM) (Model: S-3400N, USA). For mechanical characterizations, the samples were cut into $2\text{cm} \times 5\text{cm}$ rectangles. Mechanical properties were performed in DIN 53455 and DIN 53452 standard methods using a universal testing machine (model H50 KS-0404, Hounsfield Series S, UK). The proton exchange capacity of the sPET films were determined by measuring the P^{H} change in 0.1M NaCl aqueous solution with time. Optical properties of the base-PET, and grafted sulfonated PET (sgPET) films were done using Fourier Transform

Infrared Spectrophotometer (FTIR) in the range of $400\text{-}4000\text{cm}^{-1}$. Sulfonated PET, sulfonated LLDPE and Nafion film were cut into rectangular shape and electric wire were coated in both surface of each sample with silver paste as contact material for dielectric measurements. Hewlett Packart Impedance Analyzer (HP 4291A, USA) was used for impedance measurements. For electrical measurements, the samples were rectangular in shape having 1mm length and 0.5-1.0 mm thickness. Silver paste was added on both sides of the samples together with two thin copper wires of 100-micron diameter for conduction. The samples were dried at 100°C to eliminate any absorbed moisture. Electrical measurements were carried out using Keithley Electrometer. The ac electrical resistance of the samples was measured as a function of frequency at a room temperature.

3. Results & Discussion

3.1. Grafting Optimization

Figure 1 show the optimization curves of monomer concentration and γ -radiation induced grafting. Firstly, the monomer concentration was optimized with higher degree of grafting shown in Figure 1 (a). The maximum degree of grafting has been obtained at 45% styrene concentration. According to the data presented in Figure 1 (b), it has been noticed that the γ -irradiation dose maximum degree of grafting for 35% and 45% monomer concentration. The γ -induced grafting by 45% styrene (monomer) concentration in methanol solution with 1500 Krads γ -irradiation dose was taken as optimum condition in which maximum degree of grafting G (%) was obtained (17.4%). The grafted PET films (gPET) were sulfonated by immersing in different concentrations (0.2, 0.1, 0.05, 0.03 and 0.01M) of chlorosulfonic acid (CSA) (ClSO_3H) in dichloromethane at different temperatures (30, 40, 50, 60, 70, 80 and 90°C) for different times (50, 80, 120, 150, 180 and 210 minutes) and then washed in distilled water to remove unreacted chlorosulfonic acid adhering on the films. The degree of sulfonation was calculated using the relation, $S (\%) = (W_s - W_o) / W_o \times 100\%$, where W_o and W_s are the film weights before and after sulfonation respectively.

Figure 2 shows the variation of the degree of sulfonation (adding sulfonate group ($-\text{SO}_3\text{H}$) in polymer membrane backbone) using chlorosulfonic acid (ClSO_3H) (CSA) at different sulfonation times. The different molar concentration of CSA with different soaking time was observed for better degree of sulfonation. From Figure 2, it is seen that the optimum sulfonation ($\sim 9\%$) was found for 0.05M ClSO_3H at a soaking time 150 minutes.

3.2. Water Uptake and Aging Tests

Figure 3 shows the water uptake (%) of the grafted and sulfonated PET films at working temperature of 80°C . Here we have considered 80°C as our working at because for most of the fuel cells the optimized temperature has been set to this temperature (or greater) [15]. Since the melting temperature of PET films is very high there was only small water uptake. According to the data presented in Figure 3, it is seen that with the increase in soaking time, the sPET films show higher water uptake than gPET films. Thus, we believe that sPET films might perform

better at 80°C and highly humid fuel cell working conditions. However, from Figure 4 it has been seen that the grafted films (gPET) show no longer stable performance at fuel cell operating temperature but the aging of the grafted sulfonated (sPET) films was stable [17].

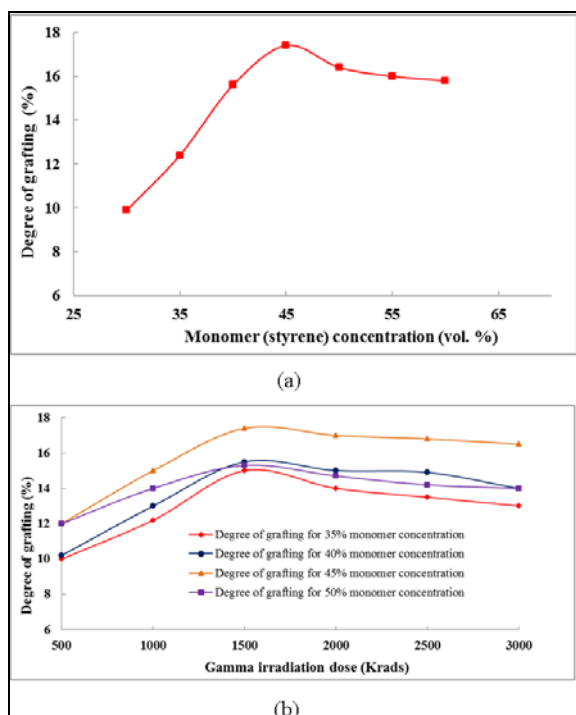


Figure 1. Grafting optimization curves (a) for monomer concentration and (b) for gamma-radiation dose

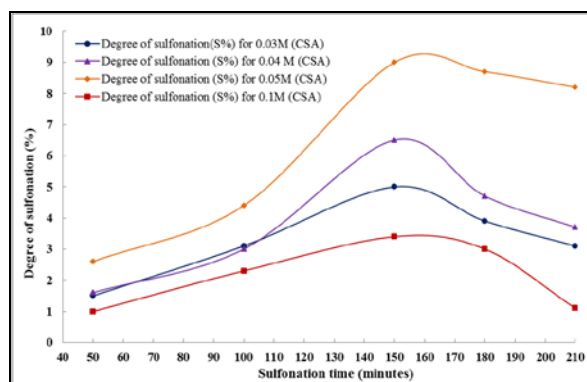


Figure 2. Sulfonation optimization with soaking time

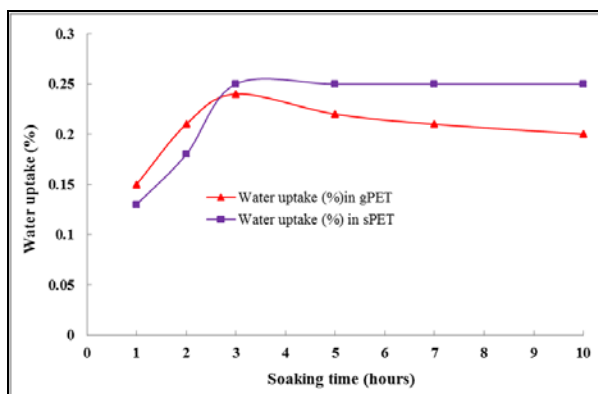


Figure 3. Water uptakes of grafted films (gPET) and sulfonated films (sPET) films as a function of soaking time

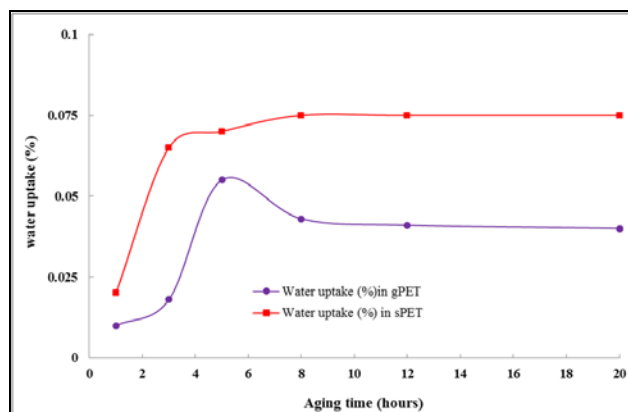


Figure 4. Water uptakes grafted films (gPET) and sulfonated films (sPET) films as a function of soaking time

3.3. Surface Morphology of the Films

Figure 5 shows the scanning electron micrograph (SEM) images of different films. Figure 5 (a) depicts the surface morphology of base PET film which is smooth and may not contain any porosity or crystallinity while the Nafion is crystalline porous film in Figure 5 (b) shows lots of pores along with the elongated shape particle morphology. In addition to the existence of pores in Nafion films there are repeated arrangements all over the surface might be due to the crystalline structure of the polymer chains. Figure 5 (c) shows the surface morphology of the post γ induced grafted sulfonated PET film (degree of sulfonation less than 5%) while Figure 5 (d) represents the simultaneous γ induced grafted PET films. Porosity of PET film was increased by grafting and sulfonation which was confirmed by impedance analysis. However, the improved crystalline structure was formed only in simultaneous γ induced grafted film by further sulfonation as shown in Figure 5 (e) which is our desired finding.

3.4 Proton Exchange Capacity of PEMs

The phenomenon of proton exchange capacity of sulfonated PETs in 0.1M NaCl aqueous solution has been depicted in Figure 6. From Figure 6, it has been observed that when the sulfonated PET films (sPET) dipped into 0.1M NaCl aqueous solution, the p^H of the solution found to be decreased. This may be due to the presence of sulfonate group ($-\text{SO}_3\text{H}$) in sPET membrane backbone. In the mother aqueous solution there are four ions Na^+ , Cl^- , H^+ and OH^- (NaCl has been dissociated into Na^+ and Cl^- ions while water, H_2O forms the H^+ and OH^- ions). When sPET films dipped into the mother solution, then sulfonate group ($-\text{SO}_3\text{H}$) is exposed. H^+ of $-\text{SO}_3\text{H}$ can easily be replaced by Na^+ to show much negative polarity than the hydroxyl group ($-\text{OH}$) presence in NaCl aqueous solution. Thus in 0.1M NaCl aqueous solution Na^+ is attracted by ($-\text{SO}_3^-$) and H^+ is released in solution and p^H of the solution is decreased as shown in Figure 6. p^H is decreased up to 20 minutes i.e., all protons are exchanged in solution within 20 minutes then it becomes steady. This reflects the fact that the sPET shows significant proton exchange capacity (PEC) in NaCl aqueous solution. According to our experiment, the proton exchange capacity of sPET was found to be $1.256 \times 10^{-4} \text{M}$ per minute in 0.1M NaCl aqueous solution.

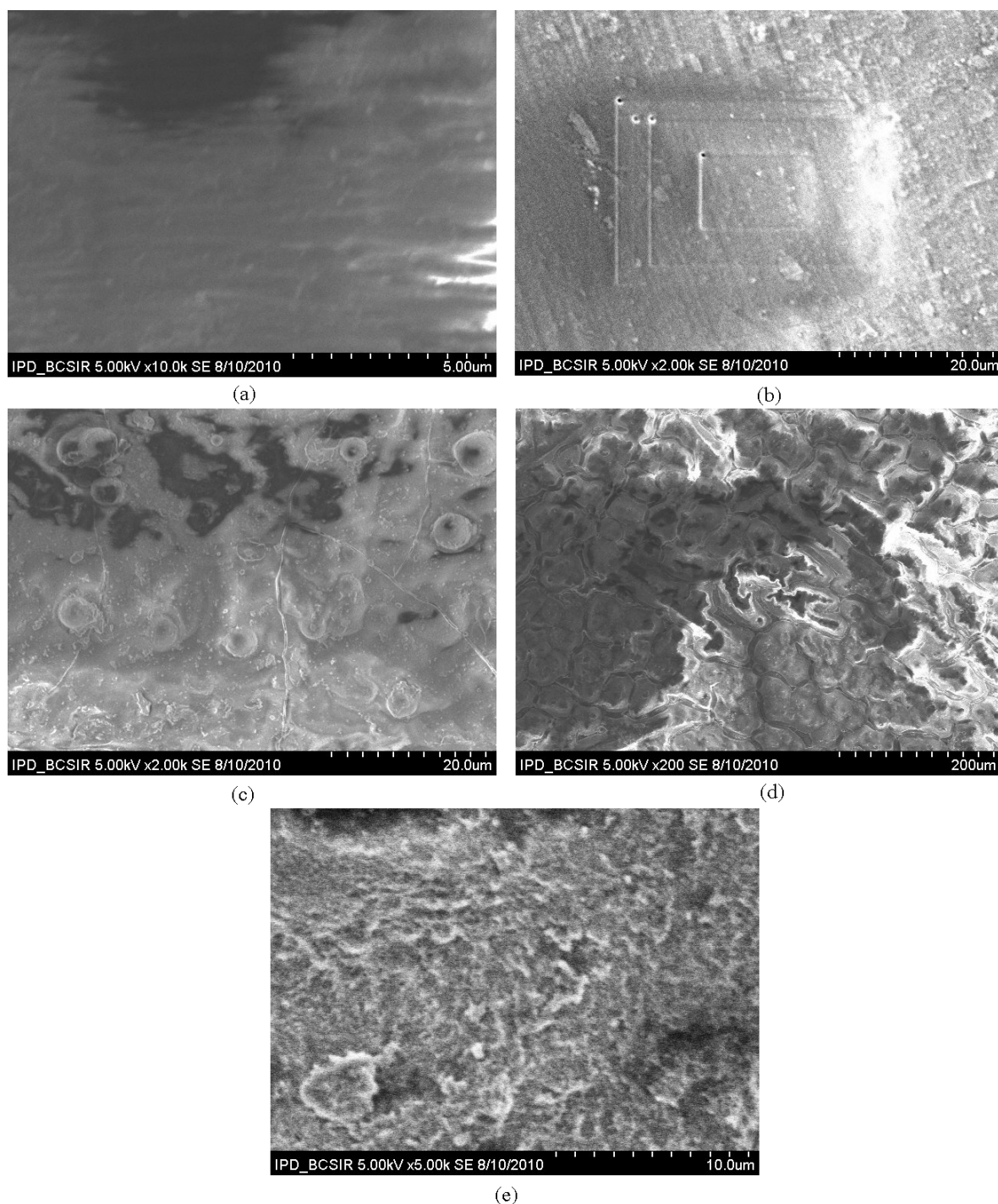


Figure 5. SEM (a) base PET (b) Nafion film (c) post γ induced sPET (d) simultaneous γ induced gPET and (e) simultaneous γ induced sPET

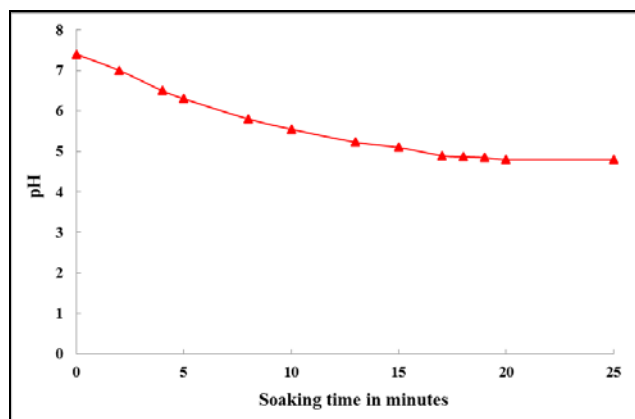


Figure 6. Proton Exchange Capacity of PEMs in 0.1M NaCl aqueous solution

3.5. FTIR Studies of PEMs

Figure 7 show the FTIR spectra as absorption for various PET films in the range of $400\text{--}4000\text{ cm}^{-1}$. As is observed from Figure 1 and Figure 2, for gamma-induced grafted PET films, the degree of grafting 17.4%; for gsPET films, the degree of grafting 17.4% and the degree of sulfonation 9%; for UV-induced grafted PET films, the degree of grafting 12%; for UV-induced gsPET films, the degree of grafting 12% and the degree of sulfonation 5%; and for UV-induced grafted- CCl_4 sulfonated PET (coloration) films, the degree of grafting 12% and degree of sulfonation 3%. For the base PET films of spectrum A has been found to contain strong functional groups by the existence of strong bands at 1741.52 and 733.88 cm^{-1} for stretching vibration of ester group ($\text{C}=\text{O}-\text{O}$) and

absorption bands at 2888.84 and 2965.62 cm^{-1} , for the symmetric and asymmetric stretching vibration of the CH_2 group of ethylene, respectively. The $=\text{CH}$ stretching vibration at 3053.75 cm^{-1} confirmed the benzene ring at PET films and the skeletal $\text{C}=\text{C}$ in-plane stretching vibrations at 1579.77 and 1502.70 cm^{-1} respectively. The Para disubstitution of benzene ring is represented by the band at 873.67 cm^{-1} [10,11,12,13]. Gamma induced styrene grafting onto PET film is confirmed in spectrum B where broad peaks are detected at 2929.70 and 1708.64 cm^{-1} . Due to styrene grafting $\text{C}=\text{C}$ converged to C-C and peaks are detected 1608.58-1574.14 cm^{-1} . After sulfonation of the samples for spectrum B considerable peaks are detected in C. Since films were sulfonated by chlorosulfonic acid (ClSO_3H) most of the peaks observed at C in the range from 4459.30 cm^{-1} to 1697.56 cm^{-1} were decreased. However, above 1697.56 cm^{-1} peaks were identified to be increased and new broadening peaks were found in the range 1328.19 cm^{-1} to 511.95 cm^{-1} . The peaks found at 1328.19 cm^{-1} might be due to the presence of $-\text{SO}_3$ and the peak at 1096.05 cm^{-1} for the presence of $-\text{SO}_2$ which indicates sulfonate groups were bonding properly. From spectrum D, it is observed that the UV-induced AA monomer grafted successfully. However, no remarkable peaks for sulfonate groups were noticed with further sulfonation in the sample for spectrum E. In spectrum F there is no significant improvement (similar as base PET) but during sulfonation yellow in coloration was observed which became ash blue in CCl_4 indicated sulfonation [18]

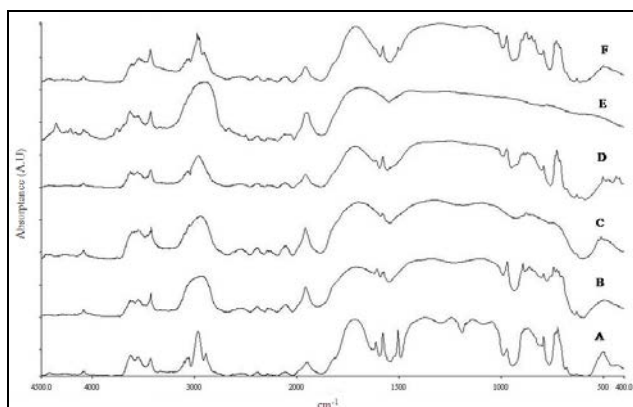


Figure 7. FTIR spectra for (A) base PET films, (B) for simultaneous γ -induced grafted PET (gPET) films, (C) γ -induced grafted sulfonated (gsPET), (D) UV-induced grafted PET (gPET) films, (E) UV-induced grafted sulfonated PET (gsPET) films, and (F) UV-induced grafted- CCl_4 sulfonated PET (coloration) (gsPET) films

3.6. Frequency Dependence Electrical Properties Measurement of PEMs

The ac electrical resistivity various films have been presented in Figure 8. From Figure 8, it has been observed that the resistance decreases with the increase in frequency. It was also observed that the resistance decreases slowly with increasing frequency up to 1500 kHz then it remains almost constant with further increase of frequency for the Nafion and sulfonated PET films. This decrease in

resistance might be due to the presence of the porosity in the films. This reflects the fact that at higher frequency every pore of the film develops a capacitor and the reactance of the capacitor decrease with frequency [19]. Thus, without coatings, the nafion and sulfonated PET show same porosity which was great findings for fuel cells because of the increased porosity results the higher performances [20]. However, the sulfonated LLDPE films show the dissimilar electrical property than Nafion and sulfonated PET films that mean its structural property is not approval for PEMFC. The maximum value of resistance at minimum frequency for Nafion film was found 0.255K Ω at 5 KHz, for sulfonated PET film was 0.455K Ω at 60 kHz and for sulfonated LLDPE film was 0.82K Ω at 4000 KHz. Sulfonated LLDPE film attributed no significant improvement of the resistance with comparison to nafion film.

3.7. Electrical Impedance of the PET Films

Figure 9, Figure 10 and Figure 11 show the variation of the real and imaginary parts of the electrical impedance with frequency. According to the data presented in Figure 9, it is clear that real part of the electrical impedance increases at lower frequency side and at a certain frequency, so called threshold frequency, the impedance becomes almost invariant with the further change of frequency. Thus, at threshold frequency the films act as resistors. However, in the case of the grafted and sulfonated films the electrical impedance decreases with the increase in frequency which is depicted in Figure 10 and Figure 11. This reflects the capacitive behavior of the grafted and sulfonated films. If there are having some porosity in polymer film, the porous portion acts as dielectric medium while the rigid portion acts as conducting plate of a capacitor [21]. The impedance decreasing rate with increasing frequency is higher in case of grafted sulfonated PET (sPET) film, which proves that the better compatibility of sulfonated film for an ideal fuel cell [21]. Moreover, according to these data it has been also observed that the polymer crystallinity of all the films is increased significantly after chemical treatment of the films as grafting and sulfonation.

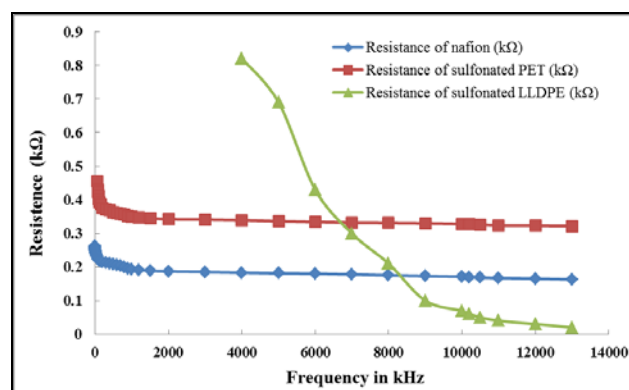


Figure 8. Effect of frequency on resistance of different films

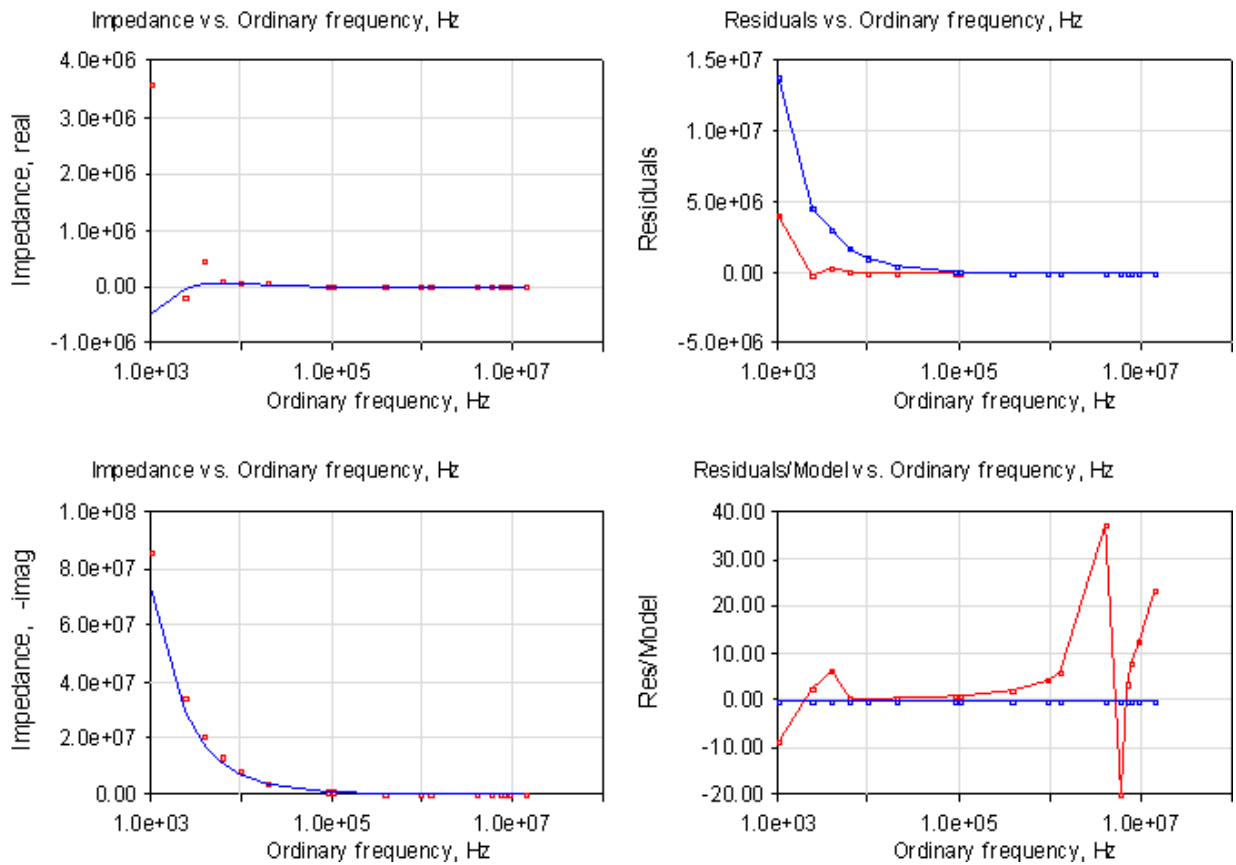


Figure 9. Effect of frequency on impedance of base PET films

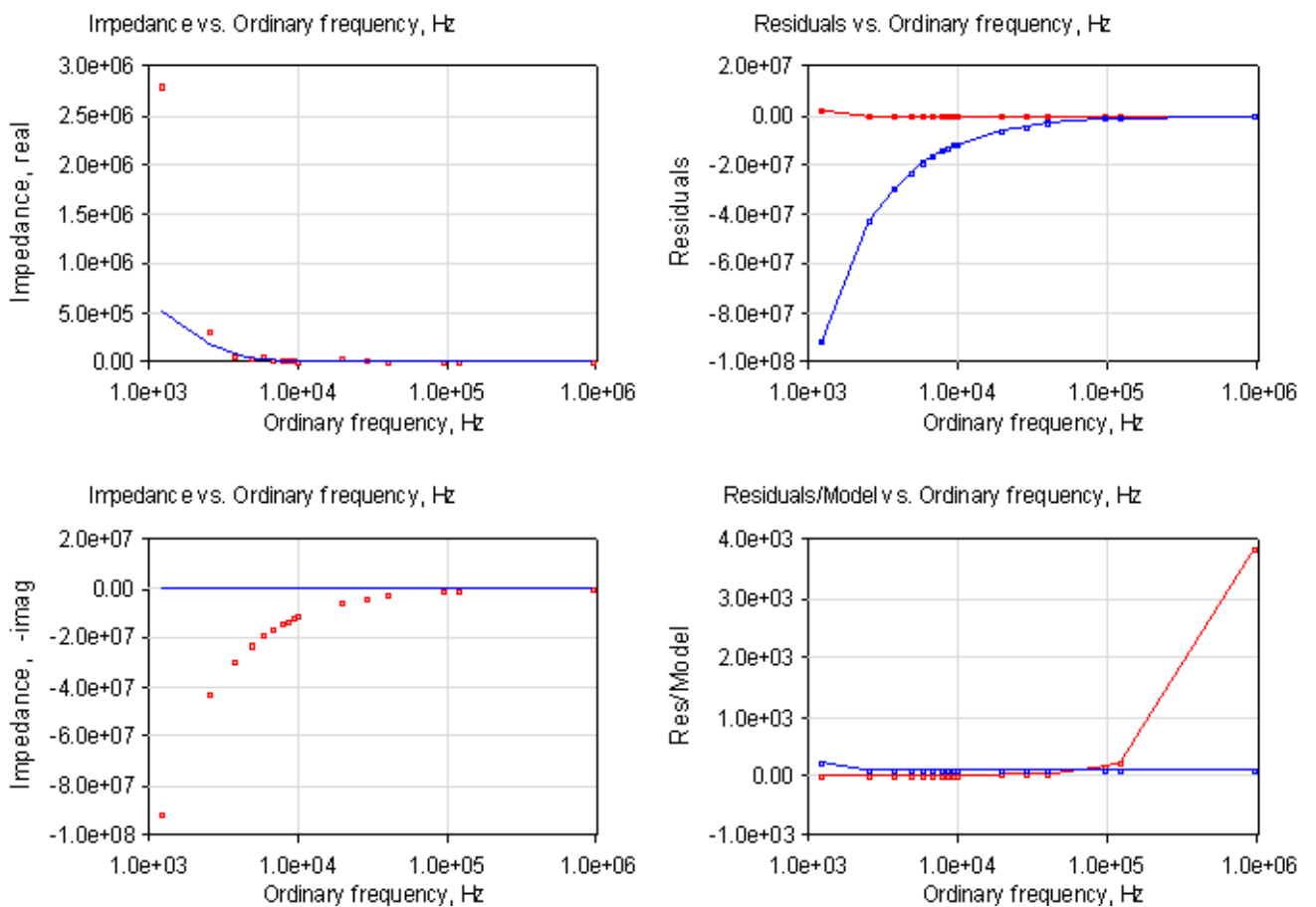


Figure 10. Effect of frequency on impedance of grafted PET films

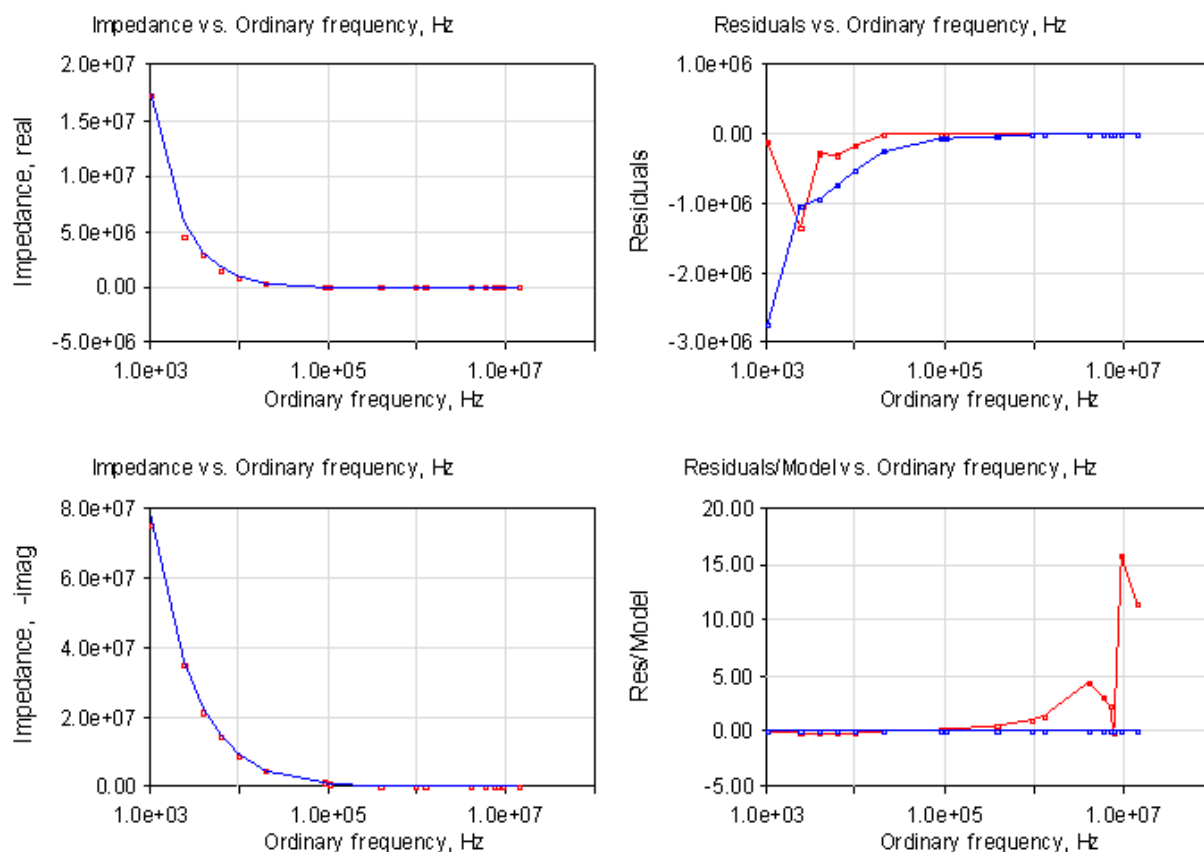


Figure 11. Effect of frequency on impedance of grafted PET films after sulfonation

4. Conclusions

Various types of proton exchange membrane PET films were successfully prepared by two step method (radiation induced grafting and then sulfonation) and hence various properties were investigated. The optimum grafting condition was found at 45% styrene in methanol solution at 1500 krad γ -radiation dose and the maximum degree of grafting was reported to be 17.4%. The optimum sulfonation condition was found at 0.05M ClSO₃ H with soaking time 150 minutes and maximum degree of sulfonation was recorded as 9%. Crystallinity and particle morphology of the samples were investigated by SEM investigation. SEM micrographs show that the crystallinity of the films is increased significantly after grafting and sulfonation. However, the LLDPE films could not be accepted because of their high crystallinity and less porosity. PETs found to contain less chemically active group and thus show moderate degree of grafting. Moderate crystallinity is required with grafting functional group for PEMFC that has been successfully observed in the present study. PEMs PET films found to show a proton exchange capacity (PEC) of 1.26×10^{-4} M per minute in 0.1M NaCl aqueous solution. Throughout the study it has been observed that surface morphology, proton exchange capacity, optical absorption and electrical properties of the PET films are improved significantly with the grafting subsequently followed sulfonation.

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