

Preparation of Poly(ethylene terephthalate)-Based Proton-Exchange Membranes Through the Ultraviolet-Induced Graft Copolymerization of Allyl Methacrylate for Applications in Fuel Cells

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ABSTRACT: The ultraviolet-induced graft copolymerization of allyl methacrylate into poly(ethylene terephthalate) films and the subsequent sulfonation of the grafted film were performed to prepare a polymer electrolyte membrane (PEM). The sulfonation reaction occurred at the grafted chain under mild conditions; that is, the grafted film was easily transformed into a PEM. The mechanical, chemical, and thermal properties of the prepared PEM (i.e., the ion-exchange capacity, water uptake, tensile strengths at different water uptakes and temperatures, stability in hydrogen peroxide solutions, and proton conductivity) were measured with titrimetric and gravimetric

analyses; most were found to be better than those of Nafion. The maximum ion-exchange capacity and proton conductivity of the PEM were observed to be 0.072 mmol/g and 0.0458 S/cm, respectively. Because this PEM is inexpensive to prepare with available raw materials and has the properties required for fuel cells, it could be an attractive and suitable device for use in fuel-cell technology. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2442–2449, 2011

Key words: copolymerization; degree of polymerization (DP); electrochemistry; graft copolymers

INTRODUCTION

Fuel cells are being developed as a new, renewable source of energy because of the need to preserve the environment, reduce the dependence on fossil fuels as the main source of energy, and provide enough energy for the world's increasing population. Fuel-cell technology is very attractive because of its higher energy-conversion efficiency and cleanliness. Among the different fuel-cell technologies presently developed, polymer electrolyte membrane (PEM) fuel cells are among the best fuel cells because of their simplicity, which makes them interesting devices for vehicular transportation.¹ The advantages of PEM fuel cells are their lower operational temperatures, nonuse of corrosive fuels, good power-to-weight ratio, low sensitivity to orientation, and ability to be compacted.²

Nafion is the most frequently used PEM because of its good proton conductivity and excellent chemical stability.³ However, because of some disadvantages associated with Nafion [e.g., its high cost, high methanol (CH₃OH) permeability, and lower stability at higher temperatures], many approaches have been developed to prepare membranes with better performance and lower costs for fuel cells. Among them, the radiation-grafting technique is a versatile and potentially cost-effective method for preparing cell membranes.⁴ Graft-type PEMs can be prepared by radiation-induced graft polymerization and subsequent chemical modifications of the grafted chains.^{5–7} With the radiation-grafting process, the active functional groups can be introduced into inner polymer chains in films and can modify them into desirable multifunctional materials. To date, different types of PEMs have been developed by the radiation grafting of styrene derivatives (e.g., styrene, vinyl toluene, and divinylbenzene^{8–10}) and non-styrene monomers (e.g., methyl acrylate¹¹) onto polymer films and then sulfonation with chlorosulfonic acid (ClSO₃H). Because of the limited conditions of graft radical polymerization and the subsequent sulfonation reaction of the grafts, few non-styrene monomers have been radiation-grafted

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for PEMs until now. In this study, a poly(ethylene terephthalate) (PET)-based PEM was prepared successfully through the ultraviolet (UV)-radiation grafting of an allyl methacrylate (AMA) monomer onto PET films and then selective sulfonation by ClSO_3H . The effects of the monomer concentration and sulfonation on this grafted membrane of PET were observed in this study. The membrane was characterized with different chemical and physical parameters [e.g., water uptake, tensile strength, ion-exchange capacity (IEC), oxidative stability, proton conductivity, and Fourier transform infrared (FTIR) spectroscopy] and then was compared with Nafion. This PEM developed with new non-styrene, AMA grafts under UV radiation could be a graft-type PEM used in fuel-cell technology.

EXPERIMENTAL

Materials

The base PET film was prepared from PET granules (MITSUIPET Company, Thailand). The monomer AMA and the photoinitiator Darocur 1173 were purchased from Merck (Darmstadt, Germany). CH_3OH was used as a solvent for grafting and for the washing of the base film to remove impurities on its surface before grafting. Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) was used to remove the homopolymer after grafting. ClSO_3H was used for the sulfonation of the grafted membrane. Dichloroethane ($\text{C}_2\text{H}_5\text{Cl}_2$) was used as a diluent. CH_3OH , $\text{C}_6\text{H}_5\text{CH}_3$, and ClSO_3H were purchased from Merck. $\text{C}_2\text{H}_5\text{Cl}_2$, hydrogen peroxide (H_2O_2), and sulfuric acid (H_2SO_4) were provided by BDH, Ltd. (Poole, England); sodium chloride (NaCl) and sodium hydroxide (NaOH) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Preparation

PET granules of different masses were heated at different temperatures and cooled under different pressures with a heat-press machine and a cold-press machine (Shimadzu Corp., Japan), respectively. The homogeneous PET films were prepared with granules (4 g) at 490°F under 3500 psi of pressure for 8 min in each case. The PET films (thickness = 0.18 mm) were cut into 1 cm × 6 cm rectangles and were wiped with acetone for the removal of impurities on the film surface.

After drying, the washed films were immersed for graft copolymerization in 25-mL CH_3OH solutions with different concentrations of the AMA monomer (21, 26, 32, 37, 42, and 47 vol %) and 2% photoinitiator under UV radiation (Shimadzu) for different times (1, 2, 3, 4, 5, and 6 h). After graft copolymerization, the grafted films were washed with a large amount of

$\text{C}_6\text{H}_5\text{CH}_3$ to remove the homopolymers and residual monomer by a Soxhlet extraction process.

The degree of grafting was calculated as follows:

$$\text{Degree of grafting}(\%) = (W_g - W_0)/W_0 \times 100 \quad (1)$$

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

The grafted films were sulfonated by immersion in different concentrations of ClSO_3H (0.2, 0.15, 0.1, 0.08, 0.05, 0.02, and 0.01M) in $\text{C}_2\text{H}_4\text{Cl}_2$ at different temperatures for different times and were washed in distilled water for the removal of unreacted ClSO_3H adhering to the films. The degree of sulfonation of the dried sulfonated films was calculated as follows:

$$\text{Degree of sulfonation}(\%) = (W_s - W_g)/W_g \times 100 \quad (2)$$

where W_s and W_g are the weights of the sulfonated and grafted films, respectively.

Characterization of the membranes

The IEC of the PEM was determined by titrimetric analysis. The dried membrane in the protonic form was immersed in a 0.1M NaCl aqueous solution for 24 h at room temperature (30°C). The solution was titrated with a 0.05M NaOH solution. The IEC of the membrane was calculated with the titration results as follows:

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

where C_{NaOH} (mol/L) and V_{NaOH} (mL) are the concentration and volume of the NaOH solution required for neutralization of the residual solution, respectively, and W_{dry} is the weight of the dry sulfonated membrane in its protonic form.

The water uptake of the sulfonated membranes was calculated as follows:

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

where W_{wet} is the weight of the PEM after the immersion of the dry membrane in distilled water at different temperatures for different times and W_{dry} is the weight of the dried PEM.

The H_2O_2 tolerance of the sulfonated membranes was calculated as follows:

$$\text{H}_2\text{O}_2 \text{ tolerance}(\%) = 100 \times (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \quad (5)$$

where W_{wet} is the weight of the PEM after the immersion of the dry sulfonated membrane in H_2O_2 solutions of different concentrations for different times and W_{dry} is the weight of the dried PEM.

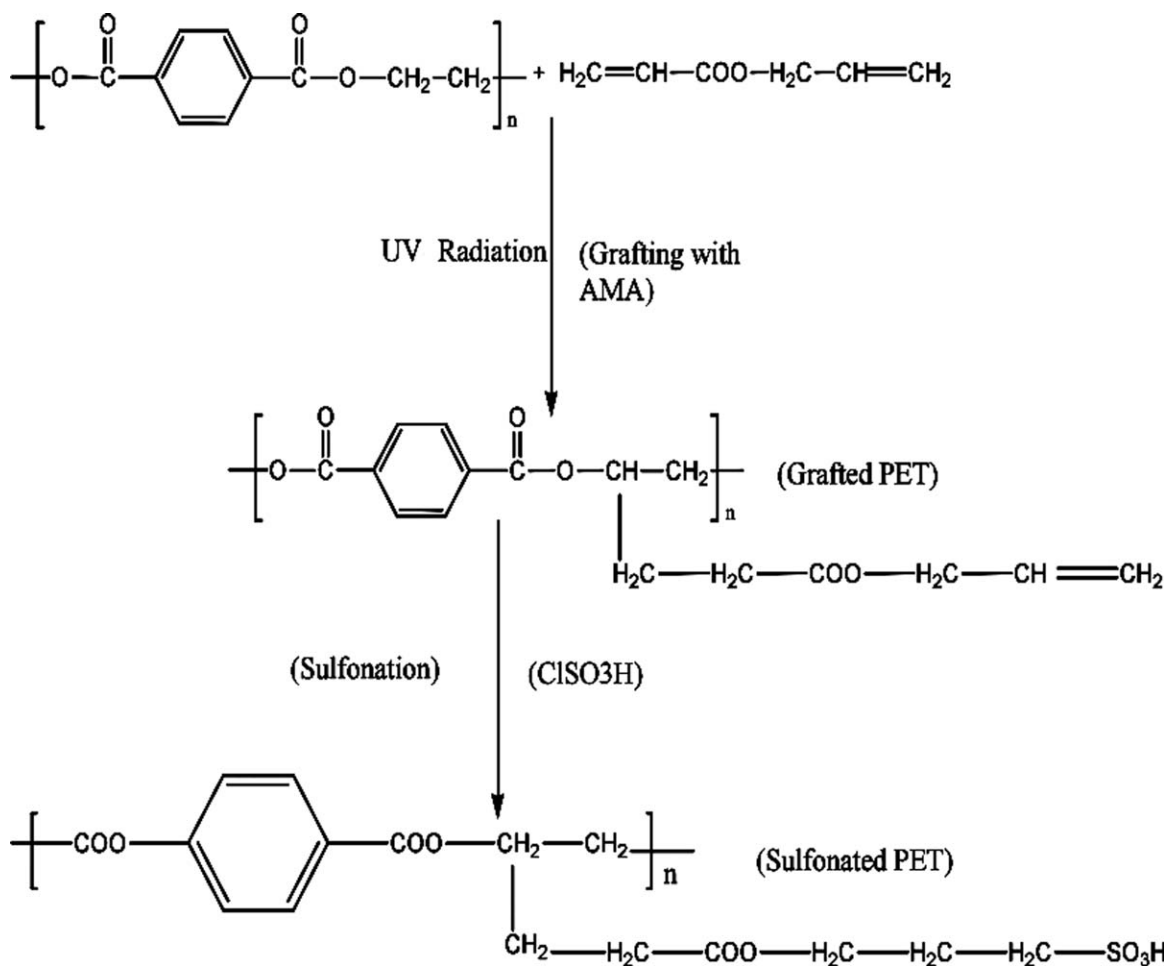


Figure 1 Proposed reaction mechanism for the grafting of AMA onto the PET film under UV radiation and for the sulfonation of the grafted film.

The proton conductivity of the PEM was calculated as follows:

$$\text{Proton conductivity (S/cm)} = l/R \times S \quad (6)$$

where R is the resistance of the membrane (Ω), l is the thickness of the membrane (cm), and S is the contact surface area of the electrode (cm^2).

IR spectra of the original, grafted, and sulfonated PET films in the range of $400\text{--}4000\text{ cm}^{-1}$ were measured with an FTIR spectrophotometer (Shimadzu). The tensile strengths of the sulfonated films were determined with a tensile strength testing machine (Instron Ltd., High Wycombe, Bucks, U.K.). For the measurement of the resistance, the membrane was soaked in water at 95°C for 36 h. Then, the hydrated PEM was platinized with Pt/C (acting as an electrode) and was connected with copper wire to an impedance analyzer (Shimadzu). The membrane/electrode assembly was placed in a thermal controlled-humidity chamber. The resistance of the membrane was read from the impedance analyzer at room temperature (30°C) and at a relative humidity of 70%.

RESULTS AND DISCUSSION

Graft copolymerization

The radiation-induced graft copolymerization of AMA onto PET films was carried out with a simultaneous UV-radiation technique. During the radiation-induced graft copolymerization, active sites (radicals) were generated on the polymer backbone with UV radiation. The irradiated PET polymer was then allowed to react with the monomer AMA units, which propagated to form side-chain grafts (Fig. 1). After the grafting, the thickness of the grafted PET films increased by 13–15%, and this indicated that grafting occurred throughout the films. Furthermore, the transparent PET films became opaque and white after grafting, and this suggested the penetration of the monomer (AMA) throughout the films.

Optimization of the grafting conditions

The degree of grafting of the AMA monomer onto the PET films was studied as a function of the monomer concentration (Fig. 2). With the monomer

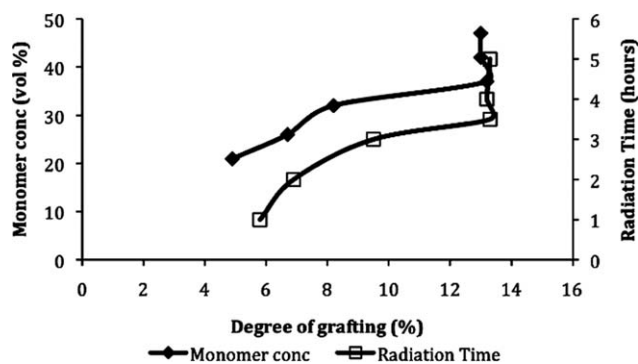


Figure 2 Degree of grafting of AMA on the PET film as a function of the monomer concentration and radiation time.

concentration increasing, the degree of grafting increased rapidly initially while the propagation process dominated and then fell more slowly as termination became more frequent. In this study, the degree of grafting reached a maximum of 13.2% with a monomer concentration of 37 vol %. The increase in the degree of grafting with the monomer concentration increasing could be attributed to the increases in the monomer diffusion and concentration in the grafted PET films. As the monomer concentration increased, homopolymer formation was enhanced, and the diffusion of the monomer was hindered.¹²

The influence of the radiation time on the degree of grafting of AMA onto PET films with a 37 vol % monomer concentration was also investigated (Fig. 2). The grafting steadily increased initially and tended to level off beyond 4 h; that is, after 4 h of radiation, there was no significant change in the level of grafting. A previous study also suggested that a grafting time of 4 h was sufficient to achieve nearly the maximum degree of grafting of styrene onto PET films.¹³ The increase in the irradiation time led to the enhancement of the homopolymerization effect.¹² Therefore, the degree of grafting tended to level off with higher irradiation times.

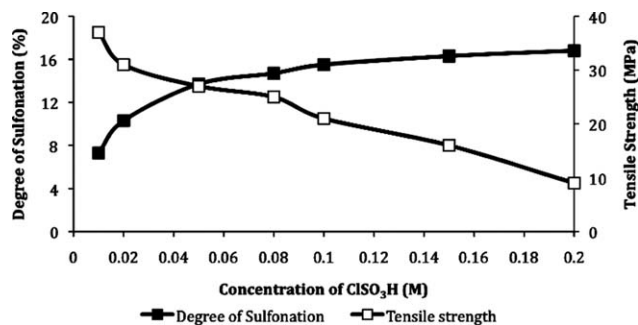


Figure 3 Degree of sulfonation and tensile strength with different concentrations of ClSO₃H at room temperature (30°C).

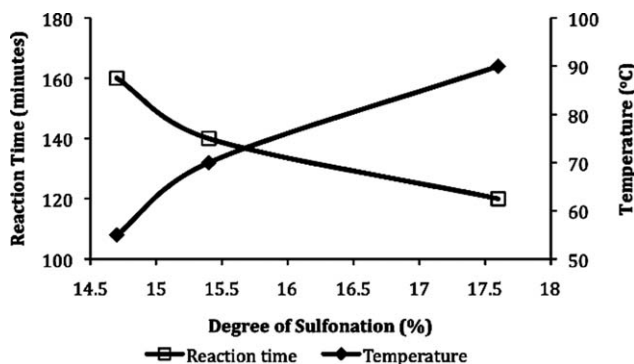


Figure 4 Maximum degree of sulfonation of the grafted film with different reaction times and temperatures.

Sulfonation

The sulfonation was performed with ClSO₃H; -SO₃H was added to the ethylenic carbon of the grafted film to yield a new proton-conducting membrane (Fig. 1). The degree of sulfonation is defined as the molar ratio (%) of sulfonic acid to monomer units of the grafted polymer chain (the SO₃H ratio). Increasing the ClSO₃H concentration diminished the time necessary for full sulfonation; however, the tensile strength of the film decreased with increasing concentration (Fig. 3). This may have been due to side reactions (i.e., the formation of sulfonyl chloride and crosslinking by sulfone formation) that made the film more fragile.^{14,15} Homogeneous grafting and sulfonation of the film surface produced a more rigid structure with a higher tensile strength, so the sulfonation of the grafted PET film was performed under mild conditions (i.e., 0.05M ClSO₃H). The grafted PET film (grafting degree = 13.2%) exhibited a maximum sulfonation degree of 14.7%, and this suggested that the degree of sulfonation was proportional to the degree of grafting in the sulfonated membrane.

Effects of the sulfonation condition

For determining the influence of the reaction conditions on the properties of the membrane, the effects of the reaction time and temperature were investigated in ClSO₃H solutions. Figure 4 shows the effects of the temperatures (55–90°C) and reaction times (100–160 min) on the maximum degree of sulfonation for each temperature and time. This study suggests that at higher temperatures, the maximum degree of sulfonation was obtained in a shorter reaction time. An elevated temperature increased the sulfonation reaction rate and thus facilitated maximization of the sulfonation reaction in a shorter reaction time.¹⁵ Extending the sulfonation reaction time beyond the time needed to reach full sulfonation did not seem to have any effect. The sulfonation degrees

of the films—14, 15, and 18%—were reached after 140 min at 55, 70, and 90°C, respectively.

Characterization of the sulfonated films

IEC

The structural changes in AMA-grafted PET by sulfonation were identified by the quantitative determination of sulfonic acid in the membranes with titrimetric analysis. The IEC is an important property that governs the hydrophilicity and water content of membranes to a large extent. The IEC of the membranes was found to be progressively increased with increasing sulfonation (Figure 5), due to increased incorporation of sulfonic acid groups in the grafted PET film.¹⁶ In this study, with a 14.7% degree of sulfonation, the IEC reached a maximum of 0.072 mmol/g; however, it was very low in comparison with the Nafion membrane (IEC = 0.91 mmol/g). Because of the repulsion forces existing between the condensed sulfonic acid groups at a high degree of sulfonation,¹⁶ the IEC tended to level off in this study.

Water uptake

Sufficient water content within a PEM is necessary for adequate ionic conductivity in fuel cells. For an ideal fuel-cell membrane, higher proton conductivity with a lower water uptake is expected. The proton-transport mechanism for a wet membrane is similar to that for an aqueous solution.¹⁷ The water uptake was measured as the percentage increase in the weight of the dry membrane. The water uptake of membranes with the soaking time at different temperatures is presented in Figure 6. A remarkable increase in the water uptake with soaking times up to 8 h was observed for the membrane. After 8 h, we observed no significant increase in the water uptake. The overall water uptake of the film was low (maximum = 8%), but it was ideal for facilitating proton transport in the fuel cell. As the sulfonic acid group was partly responsible for the high ion exchange and water uptake in the sulfonated mem-

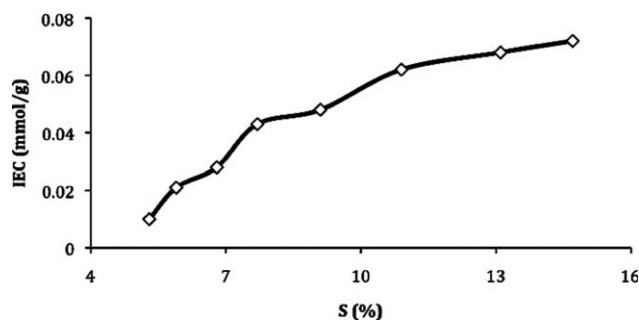


Figure 5 IEC as a function of the degree of sulfonation (S).

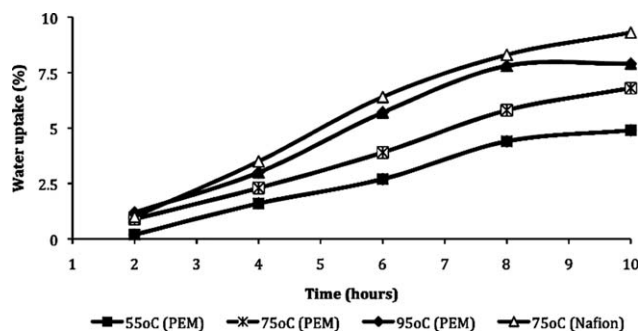


Figure 6 Water uptake of PEM and Nafion with respect to time at different temperatures.

brane, the lower water uptake of the membrane was observed because of the low degree of grafting and sulfonation. The higher water uptake of the membrane activated CH_3OH crossover, which resulted in a loss of fuel, reduced fuel efficiency, reduced cathode voltage, and excess thermal load on the cell.¹⁸ We suggest that the low swelling (lower water uptake) of the prepared PEM gives the membrane excellent dimensional stability in the hydrated state, makes the water management of the relevant PEM fuel cell far easier, and prevents the activation of the CH_3OH crossover. In this study, the lower water uptake of the PEM was also responsible for the lower IEC of the membrane.

We observed higher swelling of the membrane at a higher temperature. Park et al.¹⁹ also discovered that the water uptake of PEMs increased with increasing temperature at a constant relative humidity. The radiation-grafted membrane can be assumed to have a larger hydrophilic part with more dispersed water channels at higher temperatures, which might facilitate water transport together with the protons.

Mechanical stability

The mechanical stability of the membranes was determined with a tensile test. The water uptake of the membrane and the temperature of the environment have a large impact on the mechanical properties, so the tensile strengths of the membrane and Nafion (for comparison) were determined for different water uptakes at different temperatures (Fig. 7). In comparison with Nafion, the membrane had higher mechanical stability for different water uptakes, and this confirmed the toughness of the membrane.

As the temperature increased, the tensile strength of the membranes decreased (Fig. 7). For Nafion, the temperature effect is more drastic, so Nafion cannot be used in fuel cells that operate above 80°C. The characterization of the PEM by tensile strength measurements demonstrated its good thermal stability even above 100°C. The high thermal stability of the membrane was due to the presence

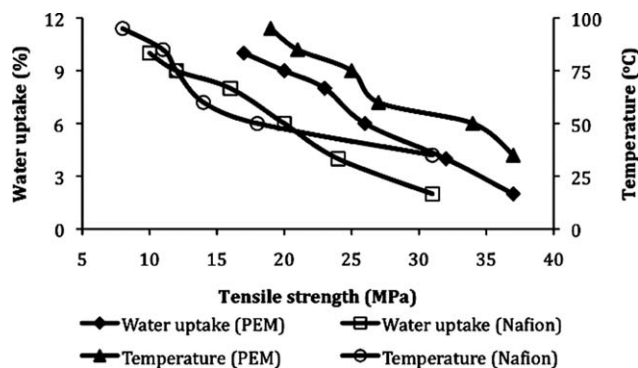


Figure 7 Tensile strengths of PEM and Nafion with different water uptakes of the membranes and at different temperatures.

of an aromatic ring in the polymer and the electrolyte membrane.²⁰

Hydrolytic stability

The tensile strength of the sulfonated film was also observed as a function of the soaking time of PEMs in aqueous media at 80°C for 9 days (Fig. 8). In this study, the tensile strength slightly decreased from 27 to 23 MPa with the soaking time increasing from 1 to 6 days, and after 6 days of soaking, the tensile strength remained constant; this confirmed the hydrolytic stability of the PEM.

Oxidative stability

Several chemical and electrochemical degradations of PEMs can occur under fuel-cell operating conditions. Chemical attacks against PEMs are usually attributed to OH_· and OH₂ radicals (precursors of

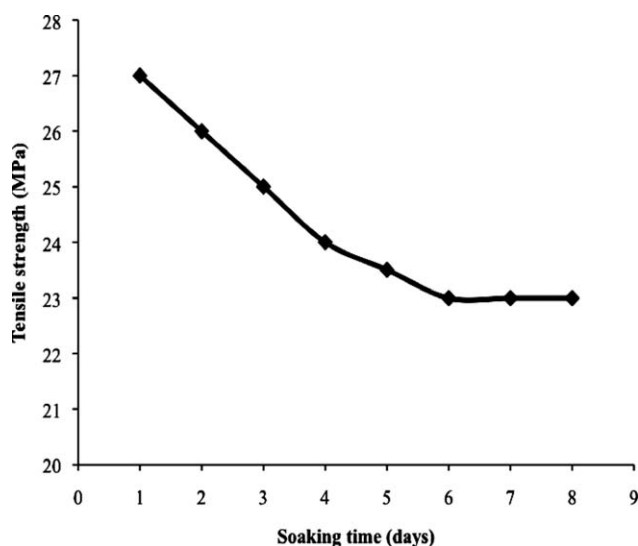


Figure 8 Tensile strength of the sulfonated film with different soaking times in water at 80°C.

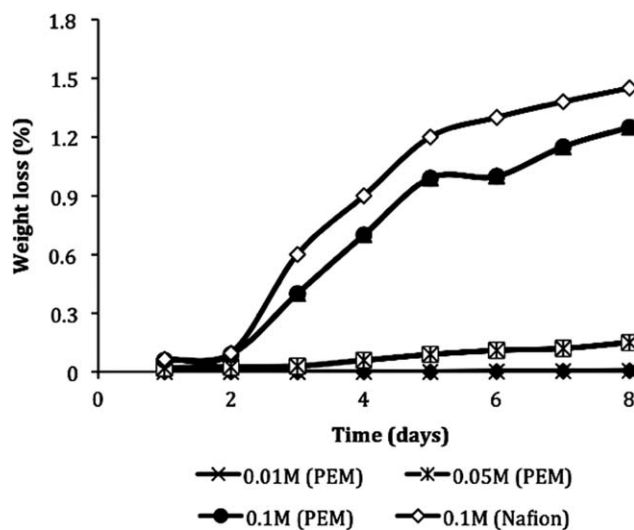


Figure 9 Tolerance of the sulfonated film in H₂O₂ solutions of different concentrations. Nafion is shown in a 0.1M H₂O₂ solution for comparison.

H₂O₂) can be formed on top of the platinum catalyst surface in both the anode and the cathode.²¹ Therefore, the oxidative stability of the membrane was investigated with different concentrations of H₂O₂ at 30°C for 8 days. The degradation of the membrane was evaluated by weight loss and by visual observation. No significant changes (maximum weight loss = 1.2%) were observed in the membrane even after treatment with 0.1M H₂O₂ for 8 days (Fig. 9); this showed that no polymer degradation occurred and supported the excellent oxidative stability of the PEM. This study also showed that the oxidative stability of the PEM was slightly higher than that of Nafion (Fig. 9).

Proton conductivity

For fuel-cell applications, a graft-type PEM has a homogeneous distribution of sulfonic acid in a direction perpendicular to the film surface and thus exhibits higher proton conductivity between the two electrodes in a fuel-cell device.¹⁴ In this study, the proton conductivity of the membrane increased with frequency, and this increase was drastic in the beginning, tended to level off, and attained a magnitude of 3×10^{-2} S/cm (Fig. 10). For comparison, the proton conductivity of Nafion was measured under the same conditions. The proton conductivity of the membrane was slightly lower than that of Nafion but was better than that of a membrane previously prepared with styrene monomer.¹³ The proton conductivity was directly dependent on the degree of sulfonation,²² so the AMA-grafted PEM with a low degree of sulfonation had lower proton conductivity than Nafion.

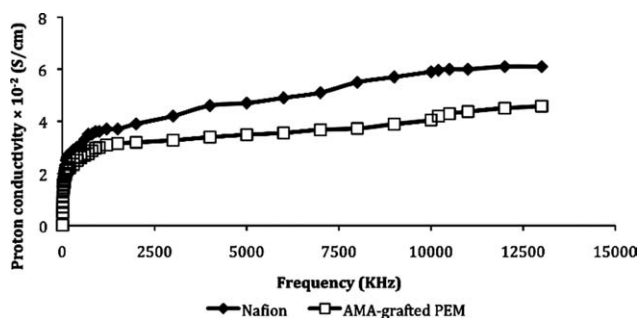


Figure 10 Proton conductivity of the sulfonated PET film and Nafion versus different frequencies.

In fuel-cell operations, the membranes should be as thin as possible when they are acting as electrolytes for proton transport. However, at the same time, they should be strong enough to avoid damage during the fabrication of the membrane electrode assembly and to act as barriers to provide effective

separation between the anode and the cathode. In this study, the prepared PEM had considerably higher mechanical strength than Nafion, although the proton conductivity was slightly lower than that of Nafion.

IR spectroscopy

The structural characterization of the sulfonated membranes by titrimetric analysis was confirmed by FTIR spectroscopy. The character of the PET spectrum was determined by the group contents: several peaks in the range of $1500\text{--}1600\text{ cm}^{-1}$ for C=C (aromatic ring), in the range of $1700\text{--}1800\text{ cm}^{-1}$ for C=O (ester), and in the range of $3000\text{--}3100\text{ cm}^{-1}$ for C—H (aromatic ring). A comparison of the FTIR spectrum of the starting PET film with the spectra of the AMA-grafted PET and sulfonated AMA-grafted PET (Fig. 11) showed that for the most part, a marked change in the absorption bands took place in the

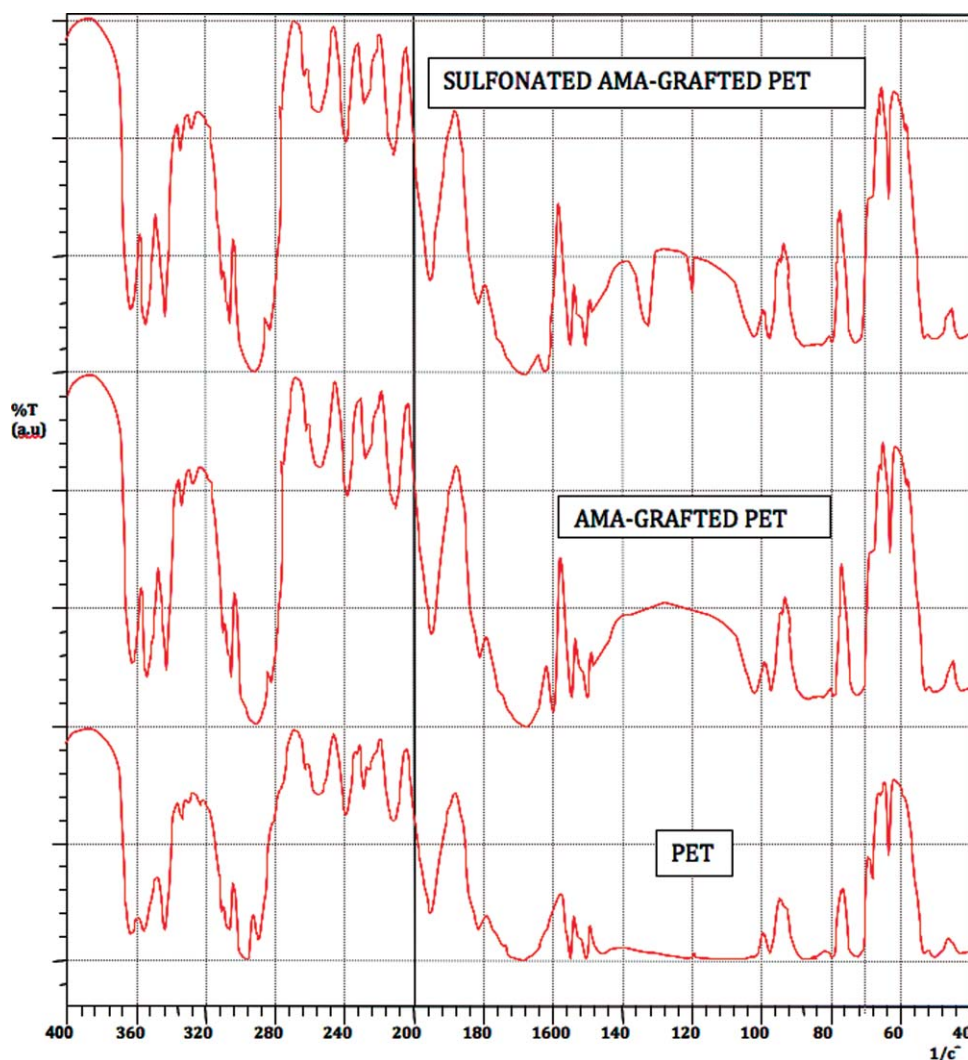


Figure 11 IR spectra of the original, grafted, and sulfonated PET films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1600–1700-cm⁻¹ region. The absorption band at 1650 cm⁻¹ was absent in the IR spectrum of the starting PET; however, it was detected in the spectrum of AMA-grafted PET. The presence of the band at 1650 cm⁻¹, which was due to the stretching vibrations of the C=C (alkene) bond of the AMA monomer, confirmed that the monomer was grafted. In the FTIR spectrum of the sulfonated membrane, the band of the sulfonic acid group was confirmed by two peaks at 1380 (asymmetrical stretching) and 1180 cm⁻¹ (symmetrical stretching) for the sulfonic acid group. The significant decrease in the band intensity at 1650 cm⁻¹ for the sulfonated film also confirmed the sulfonation of the grafted film.

CONCLUSIONS

A PEM for fuel cells was successfully prepared by UV-radiation grafting of AMA onto PET films and subsequent selective sulfonation by ClSO₃H. The maximum degree of grafting was found with a 37% monomer concentration after 4 h of UV radiation. The irradiation, grafting, and sulfonation conditions could easily be changed to obtain membranes with different IECs and properties. The IEC of the PEM was 0.072 mmol/g at its highest sulfonation. The lower water uptake of the PEM in comparison with Nafion gave dimensional stability to the membrane. The water uptake and proton conductivity of the PEM increased with increasing temperature. The excellent thermal, mechanical, and chemical stability of the prepared PEM suggests that it could be used in fuel cells. The preparation method is very simple and inexpensive, and this also makes the PEM more attractive for use in fuel-cell technology.

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References

1. Reinholdt, M. X.; Kaliaguine, S. *Langmuir* 2010, 26, 11184.
2. Badaru, A. A. Ph.D. Thesis, Florida State University, 2010.
3. Schmidt, T. J.; Simbeck, K.; Scherer, G. G. *J Electrochem Soc A* 2005, 152, 93.
4. Sone, Y.; Ekdunge, P.; Simonsson, D. *J Electrochem Soc* 1996, 143, 1254.
5. Dargaville, T. R.; George, G. A.; Hill, D. J. T.; Whittaker, A. K. *Prog Polym Sci* 2003, 28, 1355.
6. Nasef, M. M.; Hegazy, E. *Prog Polym Sci* 2004, 29, 499.
7. Chen, J.; Asano, M.; Yamaki, T.; Yoshida, M. *J Membr Sci* 2005, 256, 38.
8. Chen, J.; Asano, M.; Yamaki, T.; Yoshida, M. *J Power Sources* 2006, 158, 69.
9. Chen, J.; Asano, M.; Maekawa, Y.; Sakamura, Y.; Kubota, H.; Yoshida, M. *J Membr Sci* 2006, 283, 373.
10. Chen, J.; Asano, M.; Yamaki, T.; Yoshida, M. *J Membr Sci* 2006, 269, 194.
11. Wu, S.; Jin, Z.; Kim, J. M.; Tong, Q.; Chen, H. *Carbohydr Polym* 2009, 76, 129.
12. Nasef, M. M. *J Appl Polym Sci* 2000, 77, 1003.
13. Ahmed, M.; Khan, M. B.; Khan, M. A.; Alam, S. S.; Halim, M. A.; Khan, M. A. H. *J Power Sources* 2011, 196, 614.
14. Takahashi, S.; Okonogi, H.; Hagiwara, T.; Maekawa, Y. *J Membr Sci* 2008, 324, 173.
15. Kang, K.; Kang, P. H.; Nho, Y. C. *J Appl Polym Sci* 2006, 99, 1415.
16. Nasef, M. M.; Saidi, H.; Yahaya, A. H. *J Appl Membr Sci Technol* 2005, 2, 47.
17. Carrette, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* 2001, 1, 5.
18. Sankir, M. Ph.D. Thesis, Virginia Polytechnic Institute and State University, 2005.
19. Park, M. J.; Downing, K. H.; Jackson, A.; Gomez, E. D.; Minor, A. M.; Cookson, D.; Weber, A. Z.; Balsara, N. P. *Nano Lett* 2007, 7, 3547.
20. Itoh, T.; Hamaguchi, Y.; Uno, T.; Kubo, M.; Aihara, Y.; Sonai, A. *Solid State Ionics* 2006, 177, 185.
21. Mittal, V. O.; Kunz, H. R.; Fenton, J. M. *J Electrochem Soc B* 2007, 154, 652.
22. Glipa, X.; Haddad, M. E.; Jones, D. J.; Roziere, J. *Solid State Ionics* 1997, 97, 323.