Water management in alpha methyl styrene-butyl acrylate grafted and sulfonated PEEK membranes

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Received 2 February 2013 ; accepted 10 September 2013

Radiation grafted and sulphonated PEEK (poly ether ether ketone) membranes have been analyzed for water management within the matrix. Grafting is done using alpha methyl styrene-butyl acrylate (AMS/BA) mixture. Membranes exhibit enhanced water content with the increasing ionic content due to higher hydrophilicity. However, the water/ionic site ratio increases significantly with the increasing graft levels. The ionic mobility also increases with increasing graft levels. It is stated that the water management within the hydrophilic membrane matrix plays a key role and is responsible for the high proton mobility at higher graft levels in the membrane. This, in turn, is governed by the physiochemical changes taking place in membranes due to the grafting and sulfonation process. A correlation of the higher water/ionic site ratio arising out of the structural changes in the proton exchange membranes may be developed by radiation grafting of AMS/BA followed by sulfonation.

Keywords: Alpha methyl styrene-butyl acrylate, Grafting, Ionic mobility, PEEK membrane, Sulfonation

The development of new environmentally safe energy sources has become a subject of enormous interest. Fuel cells, in which the chemical energy of fuel is directly converted into electrical energy, belong to such energy sources1. Special attention is focused on the development of hydrogen–oxygen fuel cells based on the catalytic oxidation of hydrogen and the reduction of oxygen on a cathode and an anode respectively. A thin platinum layer supported on carbon electrodes is commonly used as a catalyst and water is formed as a result; thus fuel cells are environmentally clean energy sources. Considerable efforts have been made to the development of fuel cells for automobiles2,3.

A polymer membrane (solid polymer electrolyte) is the most important component of fuel cells. The main requirements for a functional membrane are high proton conductivity and capability to operate in an oxygen atmosphere at elevated temperatures for a sufficiently long time. Perfluorosulfonic acid, Nafion membrane (DuPont, USA) meets these requirements in terms of conductivity, water content and fuel cell performance. However, these membranes are expensive (about $800 per square meter), thus exactly enhancing the cost of fuel cell4.

It is, therefore, needed to develop membranes which are cost effective and close to Nafion in performance. The growing demand for high quality and cost effective proton exchange membranes for polymer electrolyte membrane (PEM) fuel cells needs more research efforts towards the development of new membrane materials5. Radiation grafted membranes bearing sulfonic acid groups are among the proposed alternative candidates6,7. Compared to other newly developed materials, these membranes have the advantage of well-controlled composition and properties through proper selection of grafting parameters5,9. Due to the chemical stability needed in PEM fuel cells, these membranes may be prepared by radiation grafting of styrene or its derivatives onto various fluorinated polymer films followed by a sulfonation reaction5,8. Radiation grafted membranes based on polytetrafluoroethylene (PTFE), poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly (tetrafluoroethylene-alt-ethylene) (ETFE) have been evaluated in PEM fuel cell and have been obtained to show stability up to 1000-1400 h (refs 10-12). However, one of the major problems that needs to be taken care to promote the practical application of these membranes is the oxidative degradation under the influence of chemical attack by hydroproxy radicals produced at the anode during the PEM fuel cell operation13.
Graft copolymers represent an interesting class of polymers in which two dissimilar polymer constituents may be combined\(^{14}\). Electrochemical application of ion exchange membranes requires graft copolymerization throughout the film thickness, which necessitates highly penetrating radiations such as gamma rays or electron beam. Radiation grafting is an interesting approach as it allows the grafting of polar monomers onto non-polar films\(^{15}\). For the application in fuel cells, perfluorinated or partially fluorinated films are used for reasons of chemical and thermal stability. Styrene and its derivatives are the most widely used grafting monomers, as the aromatic units are readily sulfonated to introduce ion exchange capacity (IEC)\(^{16}\).

Aromatic polymers such as poly(ether sulfone) (SPES), polyimide (SPI), polyimidazole, poly(aryl ether), polyphenylene, and polybenzimidazole are among those being investigated as potential PEMs\(^{17-28}\). However, to further simplify the preparation process and enhance performance of these materials, there are still some challenges, such as stereo-controllable chemical structures including easily controllable degree of sulfonation (DS), an sulfonation sites and well-refined microstructure\(^{29,30}\).

PEEK films are known for their excellent thermal stability, mechanical strength and high chemical resistance. PEEK films have been modified by thermal grafting of divinylbenzene (DVB) followed by radiation grafting of ethyl styrene sulfonate (ETSS), to develop a membrane for use in direct methanol fuel cells (DMFCs)\(^{31-33}\). In another development, PEEK film was crosslinked by the electron-beam irradiation to enhance its insolubility and divinylbenzene (DVB) was added to enhance the radiation-induced styrene grafting\(^2\). The subsequent sulfonation resulted in lower methanol permeability and higher mechanical properties Hasegawa et al.\(^{33}\) carried out the grafting of styrene into PEEK films and subsequently sulfonated it to introduce sulfonic acid groups into the matrix\(^33\). The radiation grafting of PEEK films has been investigated recently in such a way that the copolymers with desired functionality are developed\(^{34,35}\). In our previous work, we have carried out the synthesis and characterization of radiation grafted PEEK membranes\(^{34,35}\). PEEK films were graft with alpha methyl styrene-butyl acrylate (AMS-BA) mixture by pre-irradiation grafting process. The graft films with varying degree of grafting were sulfonated using chlorosulfonic acid to introduce sulfonic acid groups. However it is found that the membranes exhibit higher water uptake and conductivity is the function of the degree of grafting. It is therefore intend to investigate the influence of the structural changes on the water management of these membranes. Membranes are being analyzed for the structural-property correlation in this investigation. The findings of these studies are reported in this paper.

**Experimental Procedure**

**Materials**

PEEK films (50 µm thickness) were obtained from Solvay Solexis Inc., USA. Alpha methyl styrene (Sigma Aldrich) and butyl acrylate (Sigma Aldrich) were purified by vacuum distillation. Ethyl methyl ketone (Merck) was used as solvent for grafting. 1,2 dichloroethane (Merck), sodium hydroxide (Merck) hydrochloric acid (Merck) and chlorosulphonic acid (Merck) were used. Deionised water (18 MΩ resistivity) was used\(^{36}\).

**Irradiation**

A $^{60}$Co gamma radiation source (dose rate 0.16 kGy/h), supplied by Bhabha Atomic Research Centre, India, was used for the irradiation of the samples. Irradiations were carried out at 100 KGY in air under ambient conditions.

**Graft copolymerization**

Graft copolymerization of AMS-BA mixtures on the PEEK film was carried out by pre-irradiation grafting as per the method reported earlier\(^{34}\). The irradiated samples were placed in a reaction tube containing aqueous monomer solution. The tube was deaerated by bubbling nitrogen and was placed in a thermostatic water bath at 50°C for a desired period. After the reaction, samples were washed with toluene repeatedly at room temperature to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The degree of grafting was determined gravimetrically as per the following expression\(^36\):

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100 \quad \ldots (1)$$

where $W_o$ and $W_g$ are the weight of the ungrafted and grafted films respectively.

**Sulfonation of grafted PEEK**

PEEK-$g$-AMS-BA films were cut into $2.5 \times 2.5$ cm\(^2\) size and were sulfonated in 1,2 dichloroethane with 0.05 M chlorosulfonic acid at 0°C for 120 h\(^{36}\). The resulted membranes were washed several times
with deionised water until the pH was neutral. Finally, membrane was dried under vacuum for 8–10 h at 80°C.

**Water uptake**

Pre-dried sample was immersed in milliQ water for 16 h ambient temperature followed by the boiling for 6 h. The sample was taken out from water and weighed after blotting out the excess of water from the surface of sample with tissue paper. The swelling behavior of the sample was measured as amount of water per unit weight of the membrane.

Water uptake \(= \frac{W_s - W_d}{W_d} \times 100 \quad \ldots \ (2)\)

where \(W_s\) and \(W_d\) are the weight of the samples in the swollen and dry states respectively. The wet membrane volume was measured by taking into account, the thickness of the fully swollen membrane.

**Determination of ionic content**

The ionic content of the samples was determined by titrimetric analysis. Dry sulfonated membranes in proton form were immersed in 20 mL aqueous 3 M NaCl solution and equilibrated for 24 h. The remaining solution was titrated with a 0.02 M NaOH solution using phenolphthalein as indicator.

**Determination of amorphous content from X-ray diffraction**

X-ray diffraction patterns of the samples were recorded on PHILIPS, Holland, CuKa X-ray generator. Scanning was carried out in 2\(\theta\) range of 10°–40° and at the wavelength of 1.54 Å, filament current of 30 mA and voltage of 40 kV, as shown below:

Amorphous contents (%) = 100-% Crystallinity

**Hydration and ionic mobility**

Hydration of the membrane was determined from molar ratio of the sulfonic acid content (mmol/g) and water uptake of membrane (mmol/g), as shown below:

Hydration = \(\frac{\text{Sulphonic acid content (mmol/g)}}{\text{Water uptake (mmol/g)}} \times 100\)

Membrane samples were equilibrated in 0.1 M potassium chloride solution over night at ambient temperature and then specific resistivity of samples was measured by placing the swollen membrane between two circular electrodes 2x2 cm². Conductivity was measured using conductivity meter. Ionic mobility was calculated as per the following equation:

\[ \mu = \sigma e_0 n \]

where \(\mu\) is the ionic mobility \((\text{cm}^2/\text{VS})\); \(\sigma\), the conductivity \((\text{S/cm})\); and \(e_o\), the elementary charge. A defined size of wet membrane was taken and exchanged with 0.5 KCl solution. In order to determine \(n\), a defined size of the wet membrane was taken and exchanged with 0.5M KCl solution. The protons released into the medium were titrated with 0.05 M KOH and then calculated as meq/cm³ of the wet membrane. The value of \(n\) was obtained by multiplying the mmol/cm³ value with Avogadro's number.

**Results and Discussion**

The sulfonation of the radiation grafted PEEK films leads to the development of ion exchange membranes with varying ionic content. This leads to the PEEK films with hydrophilic matrix and ionic structure: significant structural changes take place during the grafting and sulfonation process. The membranes developed by the two-step process exhibits high degree of swelling in water as observed in our earlier publication. This is the indication of the enhanced hydrophilicity of membranes with the increasing degree of grafts. Our interest is to look at the water management within the membrane matrix with respect to the ionic content. The structure-property correlation of these membranes has been studied here as a function of the changes occurred in membranes during the grafting and the sulfonation process.

Interestingly, the molar ratio of water and sulfonic acid shows a sharp increase as the grafting increases (Fig. 1). This ratio increases very rapidly in range of

![Fig. 1—Variation in molar ratio of water and the sulfonic acid with the degree of grafting](image-url)
4-13% grafting, and then slows down. The interesting aspect is that this ratio increases from 16 to 38 water molecules as per ionic site with the increase in the grafting from 4% to 27%. An increase in water content is expected to increase due to the increase in the hydrophilicity by virtue of ionic content of the membrane at high graft level, but this ratio may not change much such behaviour.

This suggests that some additional factors are also responsible along with hydrophilicity which contributes to the large increase in H$_2$O/SO$_3$H ionic site ratio and these factors facilitate the membrane structure to imbibe more water. These physicochemical changes which take place during the membrane preparation, grafting and sulfonation are responsible for such behaviour. Since these changes are specific for each graft level and vary with the sulfonic acid content, a significant change in membrane behaviour with the increase in grafting is observed. There is a combination of three factors which are responsible for observed behaviour such as enhanced hydrophilicity, increase in amorphous content and increase in chain mobility (Fig. 2). Each of these factors contributes to this hydration behaviour independently. One such factor may be the increase in amorphous content as the grafting increases from 4% to 27%. The variation in the water ionic site ratio with amorphous content is presented in Fig. 1. This contribution will be in addition to the influence of increasing sulfonic acid on enhancing the hydrophilicity. The results on ionic mobility with degree of grafting also show a sharp increase in ionic mobility beyond 8% grafting, indicating the creation of the structure which favours the ionic movement (Fig. 3). This is particularly interesting to see that ionic content per unit volume of the wet membrane decreases beyond 8% grafting, but the mobility still increases. This suggests the role of water domains in managing the channels for the ionic. Moreover, this decrease in the amorphous content makes the matrix with low crystalline regions. Crystallites are known to behave almost like crosslinks in a matrix. The decrease in the crystallinity facilitates the water movement.

Under the circumstances, where the ionic distribution is homogenous across the matrix irrespective of the graft level, it may be stated that at low graft level of 4%, the sulfonic acid groups are distributed randomly but far from each other. Therefore, the water molecule associated with these ionic group form micro domains being sparingly distributed within the matrix (Fig. 4.). As the grafting increases, the distribution of sulfonic acid group becomes closer to each other but also forms macro domains of water within the hydrophilic network. This reduces the pathway for ionic transport and resistivity thereby increasing the ionic mobility (Fig. 3). In the other words, the inter-networking of water domains is facilitated in such a way that the percolating behaviour originated within the membrane structure in-sites of ionic content remains almost constant at high graft levels (Fig. 2).

Based on the schematic representation (Fig. 4), it may be proposed that the membranes developed by radiation grafting of AMS-BA into PEEK film and subsequent sulfonation are excellent materials, with good water uptake and reasonable conductivity. The water management in these membranes is very much governed by the ionic site distribution in a homogenous manner. The hydration of ionic site is
significantly enhanced due to the highly amorphous structure of the membrane at high graft level. We also observed similar trend in the FEP-g-PSA membranes, where contribution of different factors in water management was observed and it makes an excellent material for the fuel cell applications.

Conclusion
This work is related to the structure inter-management and property correlation of the membranes. Membranes exhibit enhanced water content due to the increase in the ion exchange capacity in the membrane. However, the water/ionic site ratio increases at high graft levels. The ionic mobility also shows more in the membrane with higher graft level. Physical factors such as high amorphous nature and enhanced networking of water domains facilitate the higher water/ionic site ratio in these membranes. These results lead to the fact that proton exchange membranes may be developed by radiation grafting of AMS/BA followed by sulfonation. These membranes seem to be interesting material for fuel cell application.

Acknowledgement
One of the authors (Deepti Gautam) is thankful to University Grants Commission (UGC) for the award of senior research fellowship (SRF) to carry out this work.

References