ISSN : 0974 - 7478 Volume 9 Issue 3

Trade Science Inc.

Macromolecules

An Indian Journal

Microreview

MMAIJ, 9(3), 2013 [102-110]

Properties of PEEK, preparation and characterization of SPEEK membranes for fuel cell applications: A review

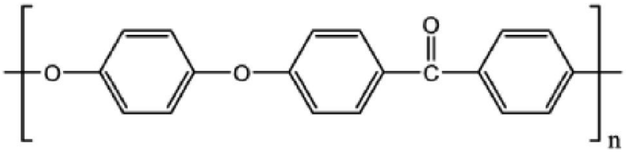
Hossein Mighani*, Negin Farshchi
Faculty of science, Department of chemistry, Golestan University, Gorgan, P.O. Box 155, (IRAN)
E-mail : h.mighani@gu.ac.ir

ABSTRACT

A review of the literature on the properties of Poly (oxy-1, 4-phenyleneoxy-1, 4-phenylenecarbonyl-1, 4-phenylene) (PEEK) and synthesis and characterization of SPEEK membranes for fuel cell application is presented. This paper provides an overview of the properties of general PEEK and synthesis and properties of sulfonated PEEK compositions membrane for fuel cell application. Based on this paper, PEEK is a high performance aromatic thermoplastic resin that can be used in different applications and sulfonated PEEK is the best alternative for Nafion membranes.

INTRODUCTION

PEEK is an abbreviation for PolyEtherEther-Ketone, a high performance linear aromatic semi-crystalline engineering thermoplastic which has a high melting temperature of 649°F (343°C). It has a glass transition temperature at 289°F (143°C). The material was invented and patented in 1978 by the Imperial Chemical Industries (ICI) Company[1]. PEEK's characteristics include high temperature performance, excellent wear properties, superior chemical resistance, hydrolytic stability and outstanding toughness and strength. PEEK grades offer chemical and water resistance similar to PPS (PolyPhenylene Sulfide), but can operate at higher temperatures. PEEK can be used continuously to 480°F (250°C) and in hot water or steam without permanent loss in physical properties and is a dimensionally stable material that offers an excellent tensile rating with an operating temperature up to 500°F (260°C). For hostile environments, PEEK is a high strength alternative to fluoropolymers. PEEK is halogen free and carries a UL94V-0 flammability rating and exhibits very low smoke and toxic gas emission when exposed to flame contributing to improved workplace safety. It has excellent chemical resistance to almost all organic and inorganic chemicals and is extremely resistant to high levels of gamma radiation for a long-term bundling solution. Hydrolysis resistance is high even at elevated temperatures. PEEK meets many aerospace, automotive, fire, smoke and toxicity, food/water, and military approvals and standards. And unfilled PEEK is approved by the FDA for food contact applications (since 1998).



PEEK chemical structure

Fuel cell field is the most investigated field of the eco-friendly energy source for the next generation and the development of a proton exchange electrolyte membrane which is an indispensable part for the actual driving of the fuel cell can be achieved by solving the problems regarding the technical aspect in technical field. Among the portable electronic equipments of the fuel cell application, the direct methanol fuel cell (DMFC) is the most accessible and promising. The direct methanol fuel cell (DMFC) offers the potential of high-energy efficiency and near-zero emissions in comparison to internal combustion engine. The methanol cross over is the key problem for the direct methanol fuel cell among conductivity, the stability and the thickness of the membrane. The most common proton exchange membrane for the direct methanol fuel cell is Nafion which is a perfluorosulfonic acid-type electrolyte membrane. While the perfluoro-type polymer electrolyte membrane provides higher conductivity and chemically stability, the performance of the membrane is lowered in a long time running because the membrane is thick and the degree of methanol permeability is relatively high, therefore the membrane also has problems in practical applications. Generally, the thinner membrane leads to the smaller over-voltage by the resistance, and the heavier equivalent weight provides the smaller ion conductivity. Therefore, the thinner polymer electrolyte having lighter equivalent weight is the preferable electrolyte membrane. However, a membrane having an excessively thin thickness raises not only the problem of mechanical strength, but also the problem of methanol crossover, which permits the permeation of gas for each pole of the cell from one pole to the other pole through the membrane, which leads to considerable loss of the performance of the fuel cell.

TABLE 1: Presents physical property information that is based on typical values of the base PEEK resin as well as test results obtained from actual film testing.

Test	Units	ASTM Test	Result
Mechanical			
Tensile Strength @ yield	psi	D882	17.400
Elongation @break	%	D882	50
Tensile Modulus	psi	D882	391.500
Flexural Modulus	psi	D790	531.000
Tear Strength – prop.	$\frac{g}{mil}$	D1004	35
Thermal			
Continuous Use Temp - UL	° F	–	464
Heat Deflection Temperature @264 psi	° F	D648	330
Melt Temp - DSC	° F	–	644
Glass Transition Temp	°F	D3418	289
Flammability			
UL Rating – UL94	–	–	$VTM-1$
L.O.I	*%*	D2863	23
NBS Smoke	*Dmax*	E662	1
Electrical			
Surface Resistivity	*Ohms*	D257	1.8×10^{15}
Dielectric Strength @.003"	*V/mil*	D149	3.200
Dielectric Constant	*1KHz*	D150	3.30
Dissipation Factor	*10KHz*	D150	0.0026
Other			
Specific Gravity	–	D792	1.256
Water Absorption	*%/24hr*	D570	0.5
Refractive Index	–	–	–
Haze	*%*	D1003	0.4
Area Factor	$In^2/lb/mil$	–	20.900

In this regard, the recent investigation have increasingly concerned with the polymer electrolyte composite membrane which has reduced thickness. The polymer electrolyte composite membranes have proper supports and mechanical properties comparable to Nafion membrane. Further, advanced countries, such as USA, Japan and European countries have carried out a number of investigations, however, resulting in no prominent outcome, and if any, the results would be tightly secured, therefore it is not easy to access the information. For example, the Max-Plank institute, German has investigated the development of polymer membrane with PEEK.

Wide water channels are provided by aggregation of hydrophilic domains in hydrophilic polymer in the presence of water which is generated from the driving of fuel cell and it is known that such a channel is caused by high hydrophilic-hydrophobic minute phase separation associated with hydrophilic sulfonic acid groups and hydrophobic tetafluorobackbones. Consequently, methanol and water are easily transported across membranes through those channels. On that occasion, the methanol transported from anode to cathode causes the oxidation reaction to take place not only in anode but also in cathode, resulting in defects such as low performance of 35% in total, mixed potential, and loss of fuel. Further, the high water permeability lowers the performance of the cathode. Therefore, it is necessary to develop a novel membrane which is not expensive, and to solve the technical problems such as methanol crossover which is the representative defect of the preexisting Nafion membrane, stability at high temperature and conductivity. High proton conductivity and low methanol crossover of sulfonated polyether ether ketones (PEEK) and their composites qualify these membranes to be considered as an alternative for application in DMFCs.

PEEK GRADES

PEEK (Unfilled)

This general purpose grade is unreinforced and offers the highest elongation and toughness of all PEEK grades. Unfilled PEEK is available in sheet and rod forms in natural (a very light brown or tan) color (Figure.2) and is also available in black**.** Black PEEK is ideal for instrument components where aesthetics are important, as well as for seal components where ductility and inertness are important. All unfilled PEEK grades comply with FDA regulation 21CFR 177.2415 for repeated food contact.

PEEK (30% Glass filled)

The addition of glass fibers significantly reduces the expansion rate and increases the flexural modulus of PEEK. This grade is ideal for structural applications that require improved strength, stiffness, or stability, especially at temperatures above 300°F (150°C). Glass-filled PEEK is light brown or tan in color.

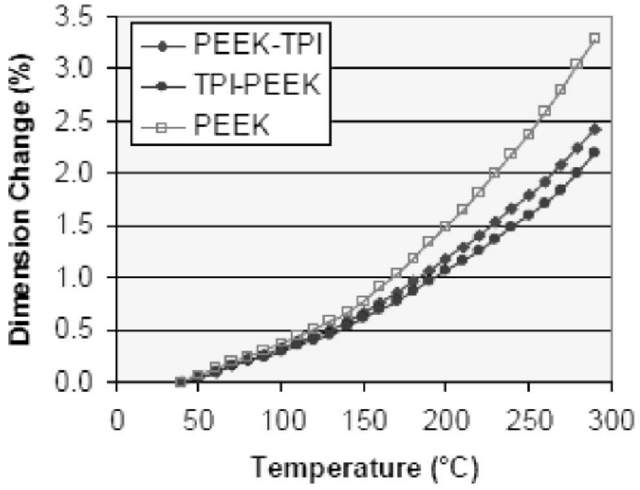


Figure 2

PEEK (30% Carbon filled)

The addition of carbon fibers enhances the compressive strength and stiffness of PEEK, and dramatically lowers its expansion rate. It offers designers optimum wear resistance and load carrying capability in a PEEK-based product. This grade provides 3½ times higher thermal conductivity than unreinforced PEEK — dissipating heat from the bearing surface faster. Carbon-filled PEEK is black in color.

PEEK (Bearing grade, ketron HPV)

This grade of PEEK, containing carbon fiber reinforced with graphite and PTFE lubricants, offers the lowest coefficient of friction and the best machinability for all PEEK grades. Bearing grade PEEK has an excellent combination of low friction, low wear, high limiting PV, low mating part wear, and easy machining. Bearing grade PEEK is black or dark grey in color.

Other specialty grades now available

High-temperature PEEK HT, bearing grade Ketron HPV, static-dissipative Semitron ESd 480, Ceramic-Filled PEEK, and T-Series PEEK-PBI (also, these new medical grades: PEEK-LSG, PEEK-CA30 LSG, PEEK-GF30 LSG and PEEKCLASSIX LSG.)

Thermal stability

Practical use temperature for any load-bearing application of a semi-crystalline resin is typically limited to its Tg due to significant dimensional changes and loss in stiffness above the Tg. For PEEK, such practical use temperature under load is around 150ºC. This deficiency can be improved by the addition of reinforcements such as glass fibers and mineral fillers. Unfortunately, these changes, while improving one property, adversely affect other properties. For example, addition of glass fibers increases weight, reduces flow and induces anisotropy in molded parts. In some instances the fiber additives can interfere with the surface smoothness of the shaped parts causing uneven surface properties. Addition of reinforcing filler to PEEK can also make it difficult to extrude thin films and fibers.

Another approach to improve the practical use temperature of PEEK is to blend it with a high temperature (e.g., Tg > 200ºC) amorphous resin. Many blends of PEEK with resins such as polyetherimides, polyimides and aromatic sulfones have been reported[2-4]. Blends of PEEK with a polyetherimide (e.g., ULTEM* 1000 resin) have been extensively studied[4-8]. ULTEM 1000 and PEEK form a miscible blend across the entire composition space as evidenced by one-phase morphology and by a single Tg. Such a high extent of miscibility slows down the crystallization of PEEK and these blends are more or less amorphous as processed under typical conditions. Upon annealing at temperatures above the Tg of PEEK, crystallization of PEEK is feasible[8].

Recently a new thermoplastic polyimide polymer (TPI) has been commercialized by SABIC Innovative Plastics as EXTEM* UH resin[9-10]. It is the highest glass transition temperature, amorphous thermoplastic resin available commercially. EXTEM UH resin offers good dimensional stability, high temperature strength, creep resistance and flame resistance. A new class of high temperature TPI-PEEK blends has been developed by alloying PEEK with the new EXTEM UH resin. PEEK is not fully miscible with this new TPI and the blends demonstrate a two-phase morphology and two Tg's. One of the advantages of these phase-separated EXTEM UH-PEEK blends compared to the ULTEM-PEEK blends is that PEEK can crystallize fast and no annealing of parts is needed. PEEK also improves the melt process ability of the TPI. These TPI-PEEK blends combine strengths of both PEEK and TPI to perform in the most demanding environments, specifically in applications requiring a combination of high temperature mechanical performance and dimensional stability. These blends are designed to fill the performance gap found in many of today's high temperature materials with ability to perform at temperatures in the range of 150-275ºC. Co-efficient of thermal expansion of PEEK improves a little with the addition of the TPI (below the PEEK Tg). Substantially lower expansion (i.e. better dimensional stability) is seen for the TPI-PEEK blends above the PEEK Tg as shown in Figure 2.Typical datasheet properties of TPI-PEEK blends compared to PEEK are shown in TABLE 2.

TABLE 2

ASTM Testing			– PEEK	– PEEK
PROPERTY				
Tensile Modulus,23°C	**MPa**	4300	4200	4100
Tensile Strength,23°C	**MPa**	100	90	95
Flexural Modulus,23 °C	**MPa**	4000	3800	3800
Flexural Strength,23°C	**MPa**	170	160	170
Izod Impact,unnotched,23°C	$\frac{J}{m}$	*NB*	640	1230
Izod impact,notched,23°C	$\frac{J}{m}$	59	32	48
CTE,23°C to 125°C,flow	$\frac{ppm}{°C}$	47	44	39
HDT,0.45MPa,3.2mm (as-molded)	°C	156	260	280
HDT,1.82MPa,3.2mm (as-molded)	°C	146	160	230
Density	$\frac{g}{cc}$	1.32	1.34	1.38
Limiting Oxygen Index (LOI)	%	35	41	42

PEEK excellent thermal properties are attributed to the stability of the aromatic backbone, which makes up the bulk of the monomer unit[11,12] The heat of combustion of PEEK, measured using Oxygen Bomb Calorimetry, is 31.28 kJ/g.[13] However, in a real fire scenario, the polymer leaves a substantial (~70%) char residue. Specific Heat Release Rate for Several Polymers is shown in Figure 3[14]

PEEK has superior thermal degradation resistance, with a continuous use temperature of 260°C and a melting point of 343°C. The onset of thermal degradation resulting in mass loss occurs between 575-580°C.[18].As shown in TABLE3, this number is quite noteworthy in comparison to the other polymers listed.

Methods of film production

PEEK as a high performance, aromatic thermoplastic resin can be melt extruded into both amorphous and crystalline films. PEEK has a high melting temperature and is typically processed at melt temperatures of between 380-400°C (710-750°F).while these operating temperatures are much higher than most conventional polymer processes, PEEK can be run on such equipment whit a few miner modification. The most significant aspect is to upgrade the heater bands to be capable of running at this high temperature. Single screw extruders are used for melting the polymer and form a thin film through a casting die with appropriate thickness. The product is passed through a series of heated rollers to form the final film product. The actual temperature of the rollers is the key process parameter which determines whether the film is amorphous or crystalline[15].

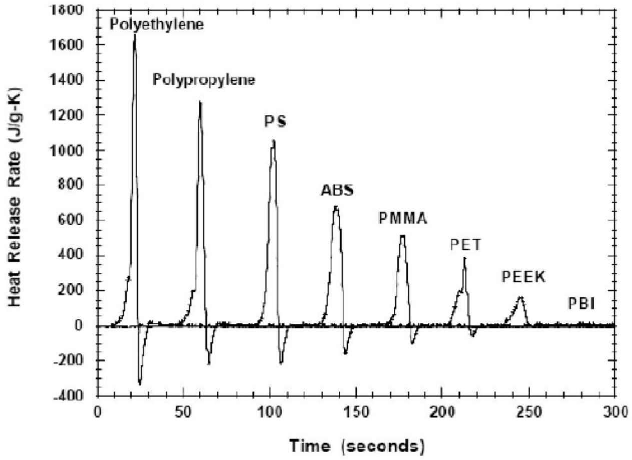


Figure 3

TABLE 3

Polymer	Decomposition Onset Temperature (°C)
Polyethylene (PE)	335
Polypropylene (PP)	328
Polyvinyl chloride (PVC)	200
Polystyrene (PS)	285
Polymethyl methacrylate (PMMA)	170
Polyethylene terephthlate (PET)	283
Polycarbonate (PC)	420
Polytetrafluoroethylene (PTFE)	508
PolyEtherEtherKetone (PEEK)	575

Sulfonated PEEK

Sulfonation is a desirable and versatile process, which can be used to simultaneously render the polymer proton conductive as well as hydrophilic in nature. Sulfonated polymers can be prepared in the form of a free acid (-SO, H), a salt (e.g.,-SO,-Na') or an ester (-S03R)[16]. The degree of sulfonation can be controlled as desired and the polymers can be sulfonated in the initial stages of synthesis or in their final form. Introduction of clusters of hydrophilic sulfonic acid groups in the hydrophobic PEEK matrix yields selective regions of water absorption (with limited swelling), and good proton conduction.

Preparation of sulfonated Polymer

According to procedures described in the literature[17], the polymer (60g) was dissolved in 95–97% H_2SO_4 (330ml) at room temperature for 24hrs and raised to 70°C for 20mins. The reaction temperature was decreased to 60°C and the reaction mixture stirred for a further 6 hrs. The sulfonated polymer was precipitated in 5 l water, filtered off and washed in (1) 1 M HCl at 80°C and (2) H_2O at 50–60°C until a pH of 7 was attained. The polymer was dried to constant weight at 80°C.

Membrane formation

A polymer solution was prepared by dissolving SPEEK in NMP in a ratio of 0.12 (weight/volume). The solution was stirred at room temperature for at least three days. In case of poorly dissolving polymers (low degree of sulfonation), the solution was heated to 120 °C for 3 h. Polymer membranes were prepared by a casting and solvent evaporation process[18]. Before casting, a glass plate was cleaned with NMP followed by acetone. Then, a film of polymer solution was cast with a 0.6 mm doctor blade. The solvent was evaporated by drying in an oven at 70 °C for 20 h followed by drying in a vacuum oven (100 °C/<100 mbar) for 20 h. The membranes, which adhered to the glass plates, were soaked in a deionized water (DI water) bath for 2 h. In this step, the remaining solvent was eliminated and the membranes were peeled off from the glass plate. Protonation was carried out in 1 M HCl for 1.5 h followed by soaking the membranes again in DI water for 2 h. The membranes were air dried and stored until further characterization. The thickness of the membranes varied between 30 and 40 μm.

Ion exchange capacity and degree of sulfonation

The ion exchange capacity and the degree of sulfonation of the polymers and the membranes are determined by titration. In addition the DS of the polymers is measured by NMR. Huang et al.[19] reported a kinetic study on the sulfonation of PEEK. DS was related to sulfonation time with:

$$-\ln(1-DS) = K \times C.H2SO4 \times t.sulfonation \quad (1)$$

This is valid with the assumption that the sulfonation is a second order reaction and that at first all monomers must be sulfonated (DS = 1) before further substitution on the sulfonated monomers can take place. The concentration of sulfuric acid in the solution is obviously much higher than the concentration of PEEK and is 18.0 M (assumption: 96 % H2SO4). When –ln (1-DS) is plotted against sulfonation time, a linear dependency must be found according to Eq.1.The reaction rate coefficient is 3.13·10-3 L mol-1 h-1. Huang et al. found 5.05·10-3 L mol-1 h-1 (at 36 °C) with the sulfonation of PEEK (Victrex, 38.400 g mol-1, powder). They first solved the PEEK powder in 1 h at 22 °C and found an intercept with the y-axis at –ln (1-DS) = 0. The presented experimental data are obtained with PEEK pellets, where a longer dissolving time is expected in comparison to PEEK powder (presented in literature). The intercept with the x-axis in Figure 4.3 is 5.1 h. representing the practical dissolving time for PEEK pellets at 35 °C.

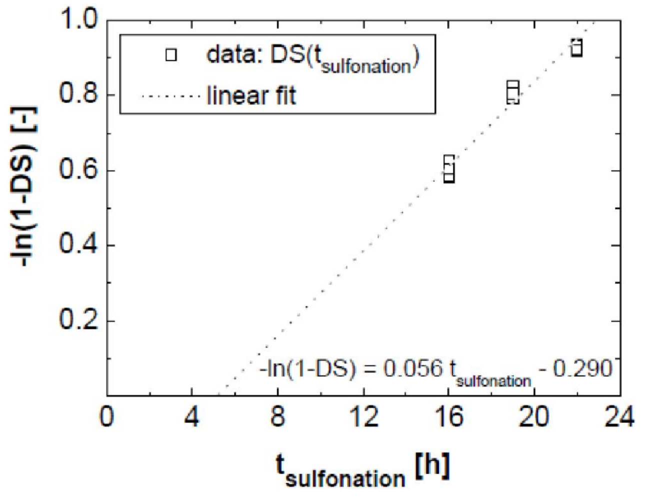


Figure 4

Determination of the reaction rate coefficient

The sulfonation proceeds with dissolving PEEK in sulfuric acid at 25 °C followed by sulfonation at a certain sulfonation temperature. This is a similar approach as described by Do et al.[20] In the dissolving step, sulfonation takes place to a small extent. The amount of ion exchangeable groups is measured with titration and is 0.177 mmol g-1. DS and IEC of the final membranes as a function of the sulfonation temperature are shown in Figure 5. There is a linear relationship in that temperature interval and the DS can be well controlled or predicted. In all cases the values measured by NMR are slightly higher. With a different titration method Huang et al.119 determined values which are consistent with the presented results. It is remarkable, that they also observed a constant difference between both methods, but in all cases the titration values were slightly higher. For all further calculations, the titration values are used. Reasons for this are:

- A lower measureable DS limit with titration and, therefore, avoiding difficulties of dissolving low sulfonated polymers in case of NMR sample preparation.
- Time, effort and expenses, because the NMR-measurements are performed externally and the titration measurements in our own laboratory.
- Expected complications when these polymers should be compared to inorganic-organic hybrid materials, where dissolving in a solvent in case of NMR sample preparation is complicated or not possible

The reaction rate coefficient is dependent on temperature and therefore described by the Arrhenius equation:

$$K = \mathrm{K}_0 e^{-\frac{\mathrm{E}_a}{RT}} \rightarrow \ln K = \ln \mathrm{K}_0 - \frac{\mathrm{E}_a}{\mathrm{RT}} \qquad (2)$$

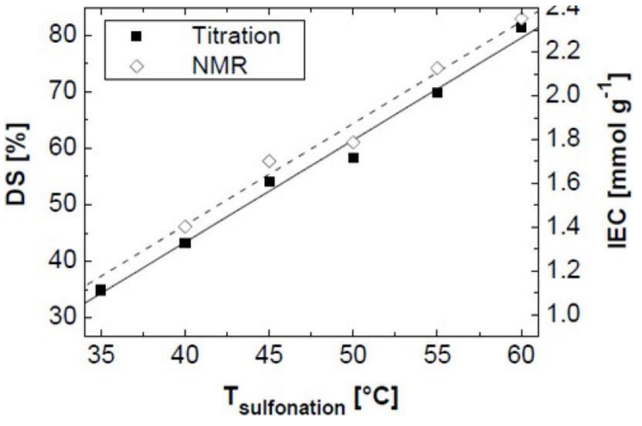


Figure 5

FTIR analysis

Figure 6 shows the FTIR spectra of sulfonated and unmodified PEEK membranes from which it can be seen that the sharp peaks, due to monosubstitution occurring at 700, 780 cm^{-1}, and noticed with the unsulfonated PEEK disappeared after sulfonation. Appearance of new peak at *e20* cm^{-1}, indicating para substitution, was observed. This shows that after sulfonation, the –SO$_3$H groups are Introduced at the para position only. A peak at 1360 cm^{-1}, identified in the spectra is due to the asymmetric stretching of the S=O bond[21]. The symmetric vibration of this bond produces the characteristic split band of absorbance at 1150 and 1185 cm$^{-1,}$ No other significant changes were observed in other regions.

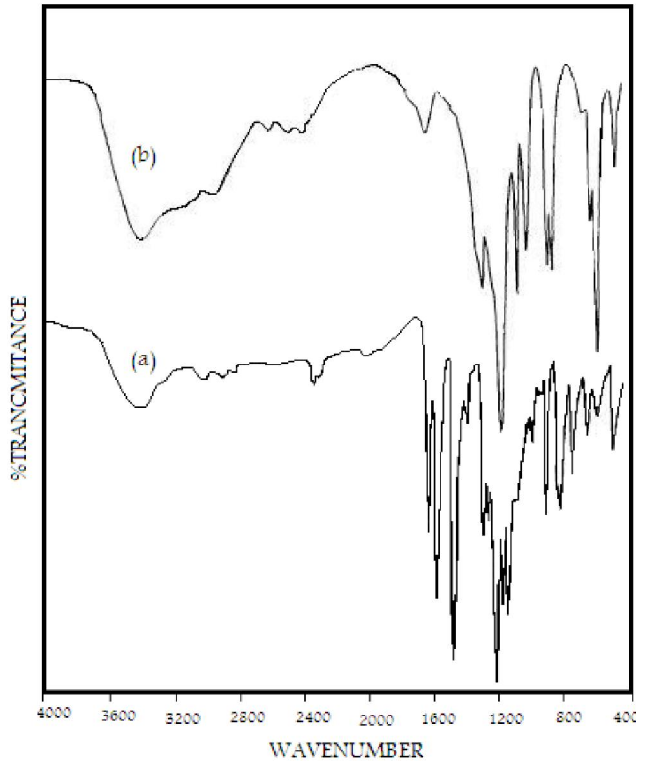


Figure 6

Water absorption

It is known that the presence of water facilitates proton transfer and increases the conductivity of solid polymer electrolytes. The enhancement of hydrophilicity by sulfonation of PEEK polymer can be determined by absorption of water in the SPEEK membrane as a function of sulfonation time. Figure 7 shows the plots of water uptake and methanol uptake of SPEEK against the sulfonation time. It can be noticed that the water uptake increases linearly with degree of sulfonation and reaches a maximum of 67% after the polymer was sulfonated for a period of 80 hrs.

The water absorption increased gradually, when the sulfonation time ranged between 5-12 hrs and very rapidly thereafter. This may be due to the formation of clustered ionomers in the highly sulfonated polymer. Clustered ionomers absorb more water, therefore, a large water uptake is suggestive of the presence of ion-rich regions where proton transfer is particularly rapid[22].

Unlike water absorption, not much change was evidenced in the case of methanol absorption. It clearly indicates that the sulfonated polymer is not highly permeable to methanol even at higher degrees of sulfonation thereby ensuring a high efficiency of methanol utilization.

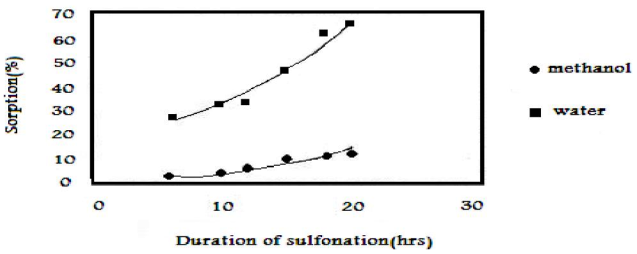


Figure 7

Mechanical properties

The tensile strength of the sulfonated polymer is reported in Figure 8 and elongation at break percent in TABLE 4. It can be observed that there is a decrease in the tensile strength of PEEK, and an enhancement in percent elongation after sulfonation. This reduction may be attributed to the increasing degree of substitution with sulfonation, which causes the swelling of the polymer. This swelling permits increased chain movements which in turn makes the polymer softer and more flexible. This greater chain movement means that the material changes from glassy state (hard and brittle) to rubbery state (flexible and soft), thereby reducing the tensile strength and elongation under stress. On increasing the duration of sulfonation, a reduction in the tensile strength of the polymer was evidenced. PEEK, sulfonated for a period of 12 hrs showed a tensile strength of 168 N/mm^2, and an elongation of 20%. TABLE 2 gives the tensile strength and percent elongation at break for different sulfonation times.

Conductivity measurements

The proton conductivity in water measured with the platinum wire configuration (PWC) is similar but always higher than the values measured with the spring tips configuration (STC) the average value of the absolute difference between both methods is 4.6 ± 0.6 m S.cm-1. This deviation is dedicated to differences in experimental setup and membrane geometries.

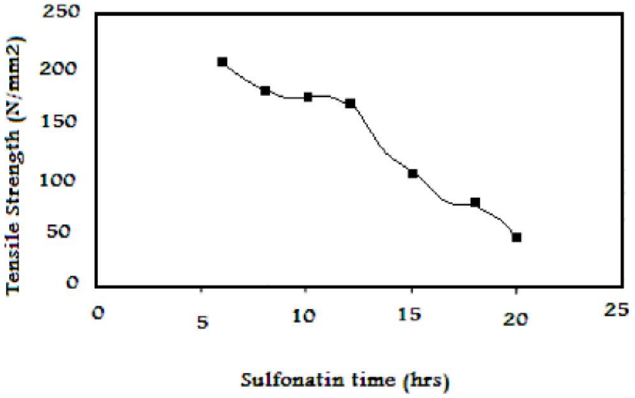


Figure 8

TABLE 4

Duration of sulfonation (h)	Tensile strength(N/mm$^{2)}$	Elongation at break(%)
6	205	32
8	181	33
10	174	27
12	168	20

Prior to conductivity measurements, the SPEEK membrane was fully hydrated. The influence of temperature on the conductivity of SPEEK membrane, sulfonated for a period of 12 hrs (with a degree of sulfonation of 60%) in comparison to commercially used Nafion 117, is shown in Figure 9. The conductivity of Nafion 117 increased steeply in the range of 30-40°C from 0.086 to 0.1 0 S.cm^{-1} and then gradually in the range of 40-100°C and showed a conductivity of 0.17 S.cm^{-1} at 100°C. On the other hand, the conductivity of SPEEK increased slowly in the range of 30-50°C from 1.2 x 10^{-2} S.cm^{-1} to 2.5 x 10^{-2} S.cm^{-1}, more rapidly between 50 -100°C, at trained a maximum conductivity of 5.8 x 10^{-2} S.cm^{-1} at 100°C, and dropped gradually thereafter. This rise and fall of conductivity suggests two competing trends, one, which enhances the conductivity and other that reduces it. As ionic conductivity of electrolytes is in general thermally stimulated, a rise in proton conductivity with temperature is expected. The fall in conductivity curve above a certain temperature suggests that dehydration of polymer occurs during measurement. Jones et al attained a conductivity of 0.04 S.cm^{-1} for a 65% sulfonated PEEK at 100°C/100%R.H.

CONCLUSIONS

The water uptake, proton conductivity, and methanol permeability for sulfonated PEEK membranes with different DS were discussed. The membrane thermal stability up to 250 °C makes them suitable candidates for fuel cell applications. The proton conductivity is also sufficiently high for fuel cells. It was demonstrated that the water uptake of the membranes increased with increasing temperature and DS. The degree of sulfonation must be controlled and terminated as soon as the most desirable IEC and mechanical strength are attained, since the resulting enhanced hydrophilicity can lead to increased softness of the polymer, irreversible swelling, and solubility in water which are not desirable. Sulfonation of PEEK for a duration of 12 h at 55°C appears viable as it yields comparatively good IEC values (0.9 meq/g), water sorption of 33% and a proton conductivity at 80°C (0.046 S.cm^{-1}) which are comparable to Nafion 1 17 respectively (IEC-0.863, water absorption 30%, proton conductivity at 30°C-0.07 S.cm^{-1}). The desulfonation/ decomposition of SPEEK occurs at 360°C, which indicates that SPEEK can be safely used at operating temperatures normally recommended for PEMFC. However, the long term in situ stability in particular, of SPEEK membranes in DMFCs still needs to be assessed in practice, to establish that it can be deployed as a suitable alternative to commercially Nafion membrane.

REFERENCES

[1] F.Yao, J.Zheng, M.Qi, W.Wang, Z.Qi; The Thermal Decomposition Kinetics of Poly (Ether-Ether-Ketone) (PEEK) and its Carbon Fibre Composite, Thermochimica Acta, **183**, 91-97 **(1991)**.

[2] L.A.Utracki; Commercial Polymer Blends, Chapter, **21**, 441 **(1998)**.

[3] R.Androsch, H.J.Radusch, F.Zahradnik, M.Muenstedt; Polymer, **38(2)**, 397 **(1997)**.

[4] L.M.Robeson, M.Matzner, L.M.Maresca, U.S.Patent, **4**, 293,670 **(1981)**.

[5] J.E.Harris, L.M.Robeson, M.D.Cliffton, B.H.Eckstein, M.Matzner, U.S.Patent, **5**, 171,796 **(1992)**.

[6] J.E.Harris, L.M.Robeson; J.Applied Poly.Sci., **35(7)**, 1877 **(1988)**.

[7] X.Kong, F.Teng, H.Tang, L.Dong, Z.Feng; Polymer, **37(9)**, 1751 **(1996)**.

[8] H.S.Lee, W.Kim; Polymer, **38(11)**, 2657 **(1997)**.

[9] S.Lee; Plastics Technology Magazine, (http://www.ptonline.com/articles/200701fa6.html) January **(2007)**.

[10] EXTEM; Resins from SABIC Innovative Plastics. (http://www.geplastics.com/gep/Plastics/en/ProductsAndServices/ProductLine/extem.html)

[11] S.K.Yesodha, C.K.S.Pillai, N.Tsutsuni; Stable Polymeric Materials for Non-Linear Optics: A Review Based on Azobenzene Systems, Progress in Polymer Science, **29(1)**, 45-74 **(2004)**.

[12] M.P.Stevens; Polymer Chemistry: An Introduction. Third Edition. Oxford University Press, New York, USA, **(1999)**.

[13] R.N.Walters; Molar Group Contributions To The Heat Of Combustion. Fire And Materials, **26**, 131-145 **(2002)**.

[14] R.Walters, R.E.Lyon; Calculating Polymer Flammability from Molar Group Calculations. US Department Of Transport, Report Number: DOT/FAA/AR-01/31 **(2001)**.

[15] Mike Percy, Victrax Plc, Thronton Celevelays, Lanchashire; London, Comparison of Crystalline PEEK Films to PTFE and Polyimide Films for Pressure Sensitive Tape Application.

[16] C.Lopatin, H.A.Newey; Polym Preprint, **12(2)**, 230 **(1971)**.

[17] W.Cui, J.A.Kerres, G.Eigenberger; Separation and Purification Technology, **14**, 145–154 **(1998)**.

[18] C.S.Karthikeyan, S.P.Nunes, L.A.S.A.Prado et al.; Polymer nanocomposite membranes for DMFC application, J.Membr.Sci., **254**, 139 **(2005)**.

[19] R.Y.M.Huang, P.Shao, C.M.Burns et al.; Sulfonation of poly (ether ether ketone) (PEEK): Kinetic study and characterization, J.Appl.Polym.Sci., **82(11)**, 2651 **(2001)**.

[20] K.N.T.Do, D.Kim; Comparison of homogeneously and heterogeneously sulfonated polyetheretherketone membranes in preparation, properties and cell performance, J.Power Sources, **185(1)**, 63 **(2008)**.

[21] D.P.Wilkinson, J.St.Pierre; Chem, Eng.Tech., **25(4)**, **(2002)**.

[22] C.D.Bailly, D.J.Viilliams, F.E.Karzarid, W.I.McKnight; Polymer, **8**, 1009 **(1907)**.