Physical Properties Analysis of UV-Crosslinked Sulfonated Poly Ether Ether Ketone and Methyl Cellulose

Nordiana Nabilla Ramly, Ab Malik Marwan Ali,
Nursyahida Sahli, Nazli Ahmad Aini
Faculty of Applied Sciences, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
Institute of Science, Universiti Teknologi MARA, 40450
Shah Alam, Selangor, Malaysia

Muhd Zu Azhan Yahya
Faculty of Science and Defense Technology, Universiti
Pertahanan Nasional Malaysia, 57000 Kuala Lumpur,
Malaysia
Institute of Science, Universiti Teknologi MARA, 40450
Shah Alam, Selangor, Malaysia

Siti Fatimah Aminuddin
Centre of Foundation Studies, Universiti Teknologi
MARA, 42300 Puncak Alam, Selangor, Malaysia

Nur Adyanie Mohamad
Department of Electronic and Mechanical Engineering,
Dundalk Institute of Technology
Country Louth, Ireland

ABSTRACT

Proton exchange membrane materials based on sulfonated Poly Ether Ether Ketone with Methyl Cellulose are developed in this study. The hybrid membrane is exposed to UV radiation with photoinitiator to improve the membrane dimensional stability up to 50%. The hybrid membranes characterized by FTIR shows the crosslinking occurs by formation of C-C bond from BEE instead of the consumption of SO_3H group. This new crosslinked hybrid membrane shows good prospect for the use as proton exchange membrane in fuel cell.

Introduction

At present, the most widely commercialized proton exchange membranes, PEMs are Nafion-based perfluorinated ionomer polymers. Despite of having outstanding performance such as good conductivity, excellent mechanical and chemical stability, the membrane suffers from high fuel crossover and is difficult to synthesize. This shortcomings lead to research on alternative new PEM materials that have adequate electrochemical properties but more economic such as Sulfonated Poly Benzimidazoles (SPBI), Sulfonated Poly Ether Ether Ketone (SPEEK) and Sulfonated Polyimides (SPI) [1]. Among these potential candidates, SPEEK is most promising because it has high thermal stability, good mechanical strength and high conductivity [2]–[5]. However, SPEEK is too dependable on its degree of sulfonation (DS), too high DS can cause excessive membrane swelling leading to membrane dissolution while too low DS can lead to insufficient conductivity hence becomes impractical for PEMFC application [6].

Much effort has been made to rectify these problems. According to H. Hou et al. one of the solutions that have gained attention is UV-crosslinking [7]. This simple but powerful method is able to improve the dimensional stability of PEM. The down side of UV-crosslink technique is the consumption of $-SO_3H$ groups that leads to lower proton conductivity compared with the non-crosslinked PEMs. To overcome this issue photoinitiator Benzoin Ethyl Ether (BEE) is introduced in the polymer to initiate crosslink by the formation of a C-C bond instead of consuming $-SO_3H$ group.

Previous studies show UV-crosslinking SPEEK polymer with biodegradable polymer modifies the hybrid membrane by restricting the mobility of polymer chains hence forming more compact network [8]–[10]. Chitosan and cellulose acetate are one of the biodegradable polymers that have been made into crosslinked hybrid membrane. In this study Methyl Cellulose (MC) is chosen as it is abundant in nature and for its ability to retain water and form membrane easily. It is a modified type of cellulose with a tendency to form crosslinked three-dimensional network hydrogels that tend to swell in water or biological fluids [11]. To evaluate the physical properties of Sulfonated Poly Ether Ether Ketone-Methyl Cellulose (SPEEK-MC), several characterizations has to be taken into consideration i.e. the hybrid membrane water uptake, the solubility test, the Fourier Transform Infra Red Spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance (^{1}HNMR) spectra.

Experimental

Sample preparation

The synthesis of hybrid membrane involves two stages. The first stage is the synthesis of SPEEK membrane and the second stage incorporates SPEEK with MC by UV-crosslinking [2,10]. For synthesis SPEEK membrane, the Poly Ether Ether Ketone (PEEK) underwent a sulfonation process by dissolving it in concentrated H_2SO_4 (95% - 98%) with continuous vigorous and constant stirring at room temperature for 84 hours. The ratio of the polymer with the acid is 10g:25mL. Then the polymer was washed with distilled water and filtered. The washing and filtering steps were repeated until the acidic polymer's pH turned neutral (Ph 7). After that the polymer was dried in an oven at 50°C for 8 to 10 hours. The DS of the resulted membrane was determined with 1HNMR [10]. The second stage is the synthesis of Sulfonated Poly Ether Ether Ketone–Methyl Cellulose (SPEEK-MC) hybrid membrane. Each of SPEEK and MC was dissolved in DMSO separately to become solutions before mixing them together. For this study the desired composition for a membrane was 1.7g with thickness ranges from 1.3 to 1.7mm and the composition ratio used was $SPEEK_{(1-X)}MC_{(X)}$ (X=2,4,6,8,10). The homogeny solution was crosslinked with UV-irradiation technique for desired period (15 and 30 minutes) with 5wt%, 10wt% and 15wt% Benzoin Ethyl Ether (BEE) as photoinitiator and was let dry in an oven at 50°C for 48 hours [12,13].

Characterization

The ^{1}HNMR spectra were used to measure the DS. The concentration of the polymer was 30mg ml^{-1} and deuterated dimethyl sulfoxide (DMSO-6) was used as solvent. The ratio between the peak area of Hs and the integrated peak area of all the proton signals (Hx; x = a, b, c, d, a', b', c', d') was expressed as Equation (1).

$$\frac{peak\ area\ (Hs)}{\Sigma\ peak\ area\ (Hx)} = \frac{y}{12(1-y)+10y} = \frac{y}{(12-2y)} \qquad (1)$$

$$total\ DS = y \times 100$$

Solubility for SPEEK membranes with varied DS is tested to analyze the membrane behavior in certain type of solvent. The obtained SPEEK membranes are immersed in selected solvent i.e. DMSO, DMF, methanol and hot water.

To check the membrane dimensional stability, water uptake test was essential. The pre-weighed membranes were immersed in distilled water for

24 hours and weighed after mopping with plotting paper. The percent water absorption capacity was determined with Equation (2) [3]:

$$\frac{Wwet - Wdry}{Wdry} \times 100 \tag{2}$$

Where W_{wet} is the weight of the wet membrane sample and W_{dry} is the weight of the same membrane sample placed in an oven at 100 °C for 24 hours.

The FTIR spectra of the membranes for MC, SPEEK, SPEEK-MC and SPEEK-MC-BEE PEM are analysed with Perkin Elmer 283B FTIR spectrometer in the wavenumber range of 500–4000cm^{-1} with resolution of 2cm^{-1} [6].

Result and Discussion

Degree of Sulfonation

Degree of sulfonation is determined by 1HNMR. The hydroquinone segment of the PEEK is introduced with sulfonic groups ($-SO_3H$). Figure 1 shows the structure of PEEK polymer prior and after sulfonation process. Non 1HNMR spectra for pristine PEEK is recorded as it is only soluble in strong acid. Table 1 shows 60 hours of sulfonation in room temperature produce DS of 68%. The sulfonation causes a total of 0.20ppm down field shift between the hydrogen of H_S and $H_{C'}H_{D'}$ in the hydroquinone ring. The $H_{B'}$ and $H_{C'}$ signals that are associated with hydroquinone ring show doublets at 7.8ppm and 8.0ppm respectively. While 72 hours of sulfonation produces DS of 88% and 84 hours produces DS of 95%. The H_C and H_B' intensities increase proportionally with DS. Sulfonation time, temperature and the amount of H_2SO_4 used affect the resulted DS. Sulfonation proceeds in slow rate at room temperature and needs more than 48 hours just to reach above 50% DS [14]. Thus 60 hours of sulfonation of PEEK at room temperature produces SPEEK with the total DS of 68% indicating the SPEEK polymer is suitable for further test [10,15].

Table 1**:** Sulphonation time and degree of sulfonation

Sulphonation time (hours)	Degree of sulphonation, DS (%)
60	68
72	88
84	95

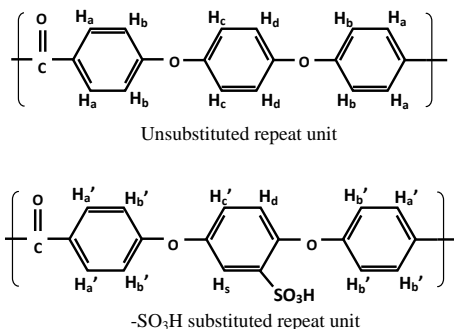Unsubstituted repeat unit

-SO$_3$H substituted repeat unit

Figure 1: Nomenclature of PEEK and SPEEK

Solubility Test

PEEK can withstand a broad range of chemical reagents. The sturdy intercrystalline forces cause the polymer to only dissolve in strong acids. Sulfonating the polymer PEEK makes the polymer soluble in many other solvents such. The dissolution properties of SPEEK are dependent with its degree of sulphonation, DS. The solubility test is carried out in search of the most suitable solvent to cast SPEEK membranes. Table 2 summarizes SPEEK solubility with varied sulphonation period. For SPEEK with DS below 30% at non-extreme temperature the samples are insoluble in most solvents except in strong acid. Those with DS higher than 30% are soluble in hot DMF, DMAc and DMSO while for DS above 40% SPEEK become soluble in DMF, DMAc and DMSO at room temperature. At 80% of DS, the SPEEK became soluble in methanol and at 100% of DS it is soluble in hot water and these results are in agreement with L. Li et al. [16]. In conclusion that the most suitable solvent to cast SPEEK membrane are DMF and DMSO because SPEEK polymer retains good solubility in them. As for crosslinked sulphonated membranes, they are insoluble in DMF and DMSO however became soluble in water and methanol.

Table 2: Solubility test of SPEEK polymer with various DS and solvent

Sulphonation period (hours)	DS ± 5 (%)	Solvent
40	30	DMSO, DMF
45	40	DMSO, DMF
50	50	DMSO, DMF
55	60	DMSO, DMF
60	70	Methanol
65	80	Methanol
70++	90	Hot water

FTIR results

Figure 2 shows the FTIR spectra for PEEK and SPEEK membrane. The sulphonation process of PEEK leads to significant differences in the IR spectrum between sulfonated PEEK (SPEEK) and pristine PEEK. The presence of SO_3H groups is observed with the absorption bands at 3400, 1248, 1078, 1022, and 706cm^{-1}. The broad band at 3500–3300cm^{-1} can be assigned as the O–H vibration of the sulfonic acid group and is in agreement with S. M. J. Zaidi et al. [5] and J. Xi et al [17]. The other bands are assigned as various sulfur-oxygen vibrations; asymmetric O=S=O stretch (1248cm^{-1}), symmetric O=S=O stretch (1078cm^{-1}), S=O stretch (1022cm^{-1}), and S–O stretch (706cm^{-1}).
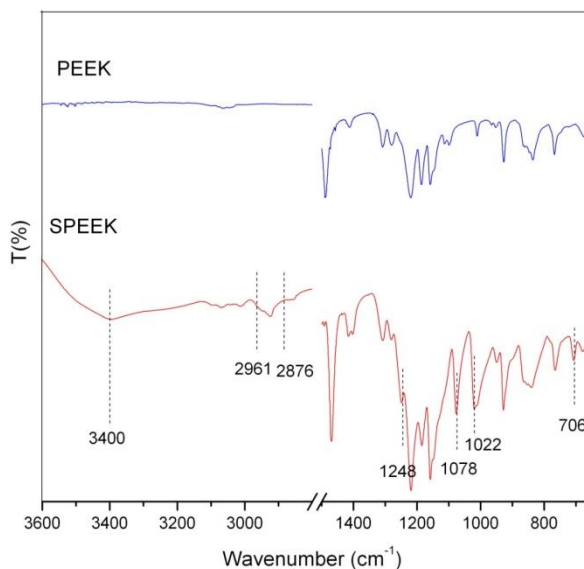

Figure 2: FTIR spectra of PEEK and SPEEK membranes

For MC, FTIR technique is used to study the hydrogen (H$_2$) bonds and hydroxyl (OH) stretching. Cellulose is the main constituent in natural fibers. Its strong crystalline structure is made of extensive hydrogen bonding within the cellulose chain. In the original data set i.e. Figure 3, the OH sub peaks are not visible individually. Thus they need mathematical method i.e. deconvolution to find the exact peak for hydrogen bonding and is shown in Figure 4. The regions of hydroxyl stretching are between 3800cm^{-1} and 3000cm^{-1} and the stretching was observed at 3445cm^{-1}. After deconvulated, the sub peaks positions are found at 3547cm^{-1}, 3414 cm^{-1}, 3289cm^{-1} and 3162cm^{-1}. These bands are associated with the valence vibration of hydrogen

bonded OH groups. The first band at 3547cm^{-1} is related with the intra molecular hydrogen bond of O_2H---O, second band at 3414cm^{-1} is related with the intra molecular hydrogen bond of O_3H---O, third band at 3289cm^{-1} is related with intermolecular hydrogen bond of O_6H---O and last band at 3162cm^{-1} is related with the O-H stretching. The composition of MC does not have any effect at this peak position [18].
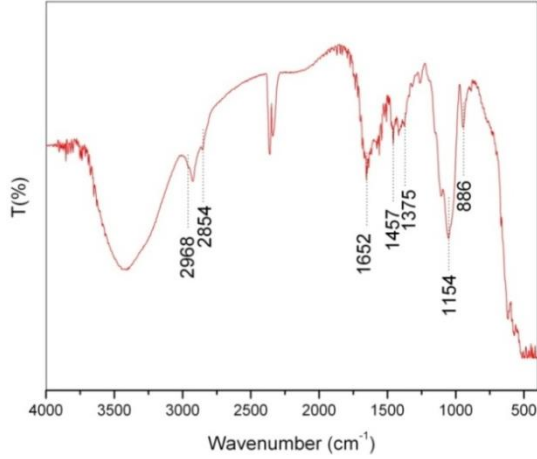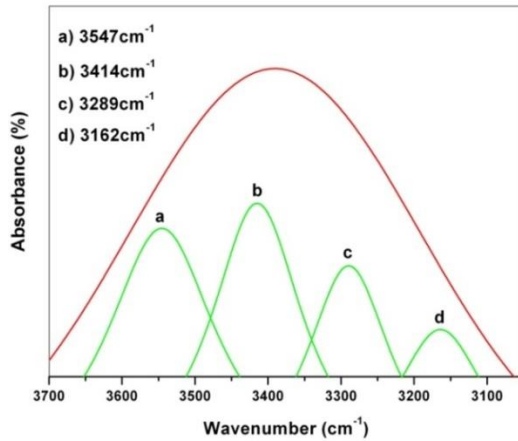

Figure 3: FTIR spectra of Methyl Cellulose

Figure 4: FTIR deconvolution spectra of MC polymer

Figure 5 depicts the spectra of SPEEK PEM after MC is incorporated for enhancing the binding capacity of the water. Hydrocarbons containing methyl groups showed at two distinct bands at 2961cm^{-1} and 2876cm^{-1}. At 2961cm^{-1}, the peak corresponds to asymmetrical (as) stretching mode i.e. v_{as} CH$_3$ which the two C-H bonds of the methyl groups are extending and the third C-H bond is contracting.   At 2876cm^{-1}, the peak arises from symmetrical (s) stretching i.e. (vsCH$_3$) in which all three of the C-H bonds contract and extend in phase. The presence of methyl groups should result in strong absorption at positions discussed, however only small amount of MC i.e. 0.04g to 0.2g are added thus resulting in tentative absorption.
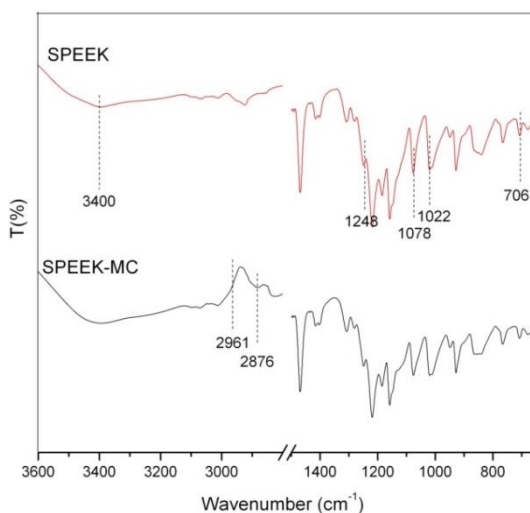

Figure 5: FTIR spectra of SPEEK-MC and SPEEK-MC-BEE

Both SPEEK and MC polymer are not photo responsive types thus they need photoinitiator to crosslink with each other. In this study, Benzoin Ethyl Ether used as photoinitiator decomposes into active radical. While exposed to UV light, the energy is transported to other molecules thus producing crosslinking reaction[19,20]. Figure 6 shows the addition of BEE and UV-crosslink technique could alter the functional group and the structure of the SPEEK-MC membrane. The difference period time for UV irradiation and amount of BEE effects on the membrane structure are shown in Figure 7 and Figure 8. The C=C double bonds peak at became less apparent with increasing UV irradiation period due to carbons are mainly used in crosslinking process. It can be concluded that very few chemical structure was formed as PEEK has high resistance to irradiation even after increasing doses of photoinitiator and longer exposure of membrane to UV-light.
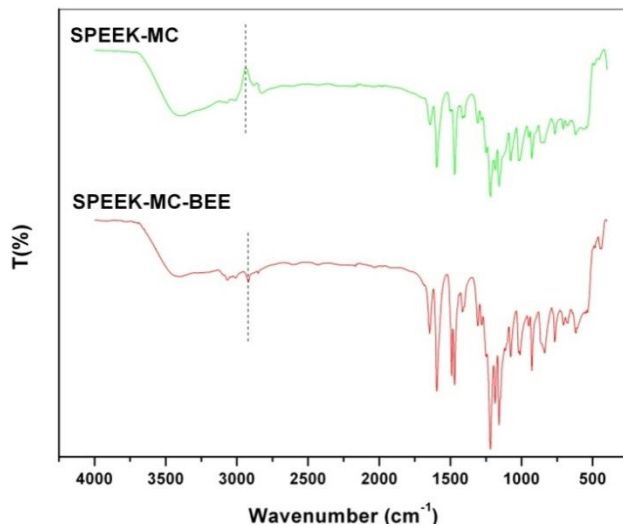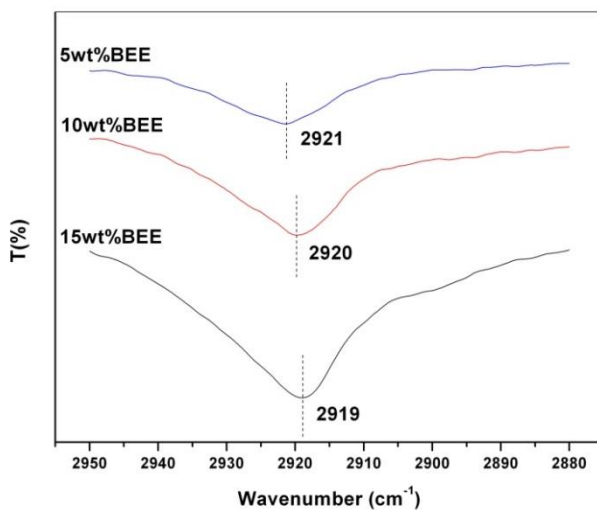
Figure 6: FTIR spectra of SPEEK-MC and SPEEK-MC-BEE

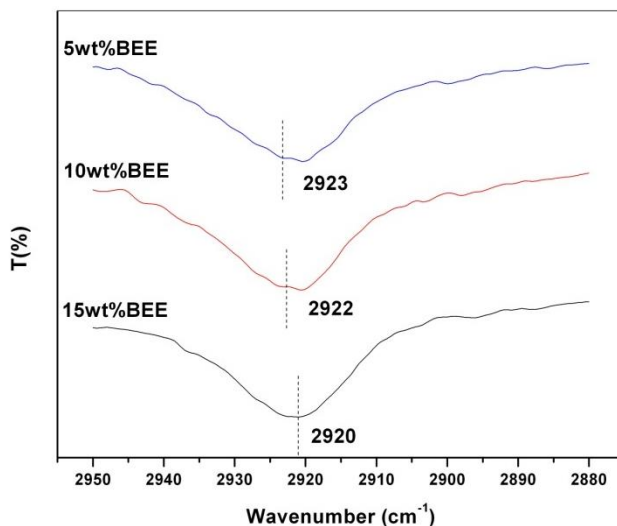Figure 7: FTIR Spectra of 15 Minutes UV-Crosslinked SPEEK-MC-BEE

Figure 8: FTIR Spectra of 30 minutes UV-Crosslinked SPEEK-MC-BEE

Water Uptake

The sulfonation of PEEK introduces hydrophilicity properties in polymer electrolyte. Table 3 summarizes the water uptake for both crosslinked and non-crosslinked membranes. The water uptake for pure SPEEK is 27%. After the incorporation of MC into the membrane, the water uptake continues to increase with increasing amount of MC. Thus, leads to membrane dissolution in water. Contrary to non-crosslinked membrane, the water uptake for crosslinked membrane is acceptable. The water uptake for (98%)SPEEK(2%)MC, (96%)SPEEK(4%)MC, (94%)SPEEK(6%)MC and (92%)SPEEK(8%)MC are 25%, 27%, 32% and 39% respectively thus indicating they are suitable for further use. The water solubility of MC is primarily due to the reduced number of inter-chain hydrogen bonds. Water molecules are prone to form a cage like structure around the hydrophobic substituent on MC thus can attract more water. High water uptake leads to high conductivity but can lead to low dimensional stability and solubility in water if exceeded. Adaptation of crosslinking method results in denser structure and smaller free volume membrane [21]. Therefore decreases the membrane ability to absorb water. In hydrous condition the water molecule can help to dissociate sulfonic acid group and facilitate proton mobility which is an advantageous to the PEM.

Table 3: water uptake at room for SPEEK and SPEEK-MC membranes with and without UV-crosslink

Membrane	Water uptake (%)	
	Non-crosslinked	Crosslinked
(98%)SPEEK(2%)MC	51	25
(96%)SPEEK(4%)MC	55	27
(94%)SPEEK(6%)MC	61	32
(92%)SPEEK(8%)MC	78	39
(90%)SPEEK(10%)MC	>100	67
Pure SPEEK	27	-

Conclusion

Proton exchange membrane composed of SPEEK and MC are synthesized then are modified by UV-crosslinking. The effect of UV-irradiation period and photoinitiator BEE composition on the proton exchange membrane is examined. The outcome indicated that both stirring and drying period play crucial role in determining the sulfonation degree of a PEM. 60 hours of sulfonation produces degree of sulfonation 68%. FTIR result proves the occurrence of sulfonation when new peaks of $-SO_3$ groups appear and proves crosslink reaction is initiated by C-C bonds instead of $-SO_3$ groups consumption when using BEE as photoinitiator. Methyl Cellulose when crosslinked to SPEEK membrane enhances its binding capacity of water and improves its conductivity but at the same time maintains the membrane dimensional stability.

Acknowledgment

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