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Preparation and Characterization of UV Irradiated SPEEK/Chitosan Membranes

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Cross-linked composite membranes of sulfonated poly(ether ether ketone) (SPEEK) with a chitosan content up to 50 wt%, were prepared by solution cast technique and ultraviolet (UV) curing. A mixture of sulfonated poly(ether ether ketone)-chitosan (SPEEK-CS) membranes was prepared by dissolving SPEEK in dimethyl sulfoxide (DMSO) and chitosan (CS) in acetic acid. The homogen formed was later irradiated with an UV source to induce crosslinking. The membranes were then characterized by evaluating infrared spectra, proton conductivity, water uptake, degree of swelling and ion exchange capacity (IEC). The Fourier transform infrared (FTIR) study revealed considerable interaction between the sulfonic acid functions of SPEEK and amino groups of chitosan. Proton conductivity decreases with increasing of chitosan content from 8.51 x 10^{-3} to 2.85 x 10^{-7} S cm^{-1}. Meanwhile, water uptake decreases with increasing of chitosan content from 52% to 29% and IEC 0.188 to 0.018 mequi. However, the swelling properties unchanged as the chitosan content increases.

Keywords: Chitosan (CS), SPEEK, SPEEK/CS, UV curing, Crosslinking.

1. INTRODUCTION

Fuel cells such as proton exchange membrane fuel cells (PEMFC) have emerged strongly as a viable option for electrical power due to their high energy efficiency, environmental friendly and highly promising alternative for future energy needs, especially for portable power applications [1, 2]. Perfluorosulfonic polymers, such as Nafion®, are the primary polymeric materials used as electrolytes in polymer electrolytes membranes owing to their high proton conductivity and good chemical and thermal stability but the main weaknesses are their high cost and fuel crossover which not only reduces fuel efficiency but also decreases the cathode performance [3-5].

The major function of the membrane can be classified as: i) a proton conductor, ii) a fuel barrier and iii) a mechanical separator between the anode and cathode [6]. Sulfonated polymembrane such as SPEEK is most promising candidate as an alternative to Nafion membrane because it is cheap, possesses good mechanical properties and high thermal stability. However the highly sulfonated membrane tends to swell excessively under the humidified conditions and lose their dimensional stability [7].

To overcome these problems, attempts to crosslink the SPEEK with CS via different techniques are proposed. Zhong et al. [8] introduced SPEEK/CS in the form of two-layer composite membranes by coating CS with the SPEEK substrate. The resultant SPEEK/CS composite membranes then were submersed in acetone solution containing glutaraldehyde and H_2SO_4 to crosslink and protonate the CS layer. The crosslinked SPEEK/CS membrane showed good result in thermal stability (above 240 ^oC) and significantly stronger methanol barrier property. The thickness of this CS layer had also no obvious effect on water uptake.

CS is widely used in membrane based applications due to its high hydrophilicity, in which a good CS has both reactive amino and hydroxyl groups that can chemically react to form salts. The hydrophilic nature of these groups are considered to play an important role in preferential water sorption and diffusion through the CS membrane [9]. CS is a potential candidate because of it is cheap and able to maintain its chemical and thermal stability until 200 ^oC with an acceptable mechanical strength. According to literature on suitable modification, polymers containing hydroxyl and amine groups exhibit good conductivities [6, 10]. UV irradiation - induced crosslinking technique is one of the most effective methods due to easiness in application, cheaper to operate and takes shorter time. It is also solvent free and therefore safer, environmental friendlier [10, 11]. The objective of this work is to study the fundamental characteristics (such as proton conductivity, water uptake and ion exchange capacity) of SPEEK crosslinked chitosan membranes prepared via UV irradiation - induced crosslinking technique.

2. EXPERIMENTAL

2.1 Materials

DMSO and CS were obtained from Sigma Aldrich chemical company Ltd. PEEK G90P was purchased from Victrex. SPEEK was prepared by dissolving PEEK in sulfuric acid (98% purity).

2.2 Synthesis and Characterization of SPEEK

2.2.1 Sulfonation of PEEK

PEEK was sulfonated as reported by Aini et al. [2]. 10 g PEEK was dissolved in 250 ml sulfuric acid and stirred until completely dissolved for 50 h. The solution was then poured into ice-cold distilled water to stop the reaction. The formed SPEEK fiber was later washed using distilled water until pH closed to 7 and dried in oven for 24 h at 100 °C. The degree of sulfonation (DS) was determined by ^{1}H NMR as described by Gaowen et al. [5].

2.2.2 ^{1}H NMR Spectroscopy

The ^{1}H NMR spectra were recorded using a Brucker 200 MHz spectrometer. The spectra were recorded at 60 °C, without internal standard and using deuterated dimethyl sulfoxide (DMSO-d6) as a solvent, with a polymer concentration of about 30 mg ml^{-1}. Experimental data were elaborated with a 1D Win-NMR software, applying the Lorentze Gauss enhance function and using appropriate Line broadening and Gaussian broadening parameters in order to improve the peaks resolution as reported in [12].

2.3 Membranes preparation

Blends of SPEEK/CS with different ratio were prepared by physically mixing both solutions in a container using sonochemistry equipment. The solutions were then irradiated under 300 Watt UV source (λ ~ 320 – 390 nm) for 120 minutes [2]. After that, the solutions were cast onto a clean glass plate and dried in vacuum oven at 80 °C. The composition between SPEEK and CS of all samples are recorded in Table 1.

Table 1. Sample composition

Sample	SPEEK (%)	Cs (%)
S1	100	0
S2	90	10
S3	80	20
S4	70	30
S5	60	40
S6	50	50
S7	0	100

2.4 FT-IR Analysis

The FTIR spectra of all crosslinked SPEEK/CS membranes were scanned using a Perkin-Elmer-283B FT-IR Spectrometer with a resolution of 2 cm^{-1}.

2.5 Proton conductivity

The proton conductivity of the membrane was measured using electrochemical impedance spectroscopy technique over frequency range of 10 Hz to 1 MHz with oscillating voltage of 10 mV.

The measurement was carried out using EIS WonATech impedance analyzer. The membrane was sandwiched between two stainless steel electrodes with diameter of 6 mm and kept in a temperature and humidity chamber with constant relative humidity of 80%. The measurement was performed at room temperature of 30 ^{o}C. The conductivity of the membrane was calculated from the impedance data, using relation $\sigma = d/RS$, where d and S are the thickness and the surface area of the sample respectively as well as R is defined from the low intersection of the high frequency semicircle on a complex impedance plane with the $R_e(z)$ axis [5].

2.6 Water uptake

In order to determine water uptake percentage, the membrane was dried in a vacuum oven at 100 ^{o}C overnight until constant weight is obtained. Each dried membrane was subsequently weighed (W_{dry}) and soak in distilled water for 24 h. The membrane was then taken out and immediately weighed (W_{wet}) after wiping out water at the surface. Water uptake was calculated using the following equation:

$$\text{Water uptake} = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \text{X } 100 \qquad (1)$$

2.7 Ion exchange capacity (IEC)

The ion exchange capacity (IEC) was measured by the titration method. The dried membrane in the protonic form was immersed in a 1M NaCl aqueous solution for 24 h at room temperature (30 ^{o}C). The H^+ ions, substituted by Na^+ ions, were released into the solution. The solution was then titrated by a 0.012 M NaOH solution using phenolphthalein as an indicator. The IEC of the membranes were calculated using the following equation:

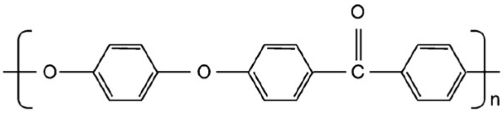
$$\text{IEC} = \left(\frac{C_{NaOH} \times V_{NaOH}}{W_{dry}}\right) \qquad (2)$$

where C_{NaOH} (mol L^{-1}) and V_{NaOH} (mL) are the concentration and volume of NaOH solution required for neutralization of the residual solution, and W_{dry} is the weight of the dry sulfonated membrane.

3. RESULTS AND DISCUSSION

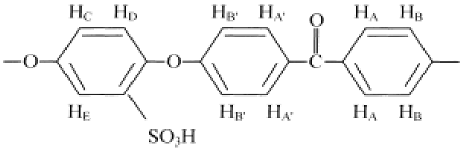
3.1 Degree of sulfonation

Upon sulfonation process the structure of PEEK has changed into SPEEK which can be visualized as shown in Figure 1. This is in agreement with the organic structures of PEEK before and after the sulfonation process as reported by Lau et al. [13, 14] and Zaidi et al. [13, 14]. Degree of sulfonation (DS) of SPEEK is defined as the percentage of repeating units of PEEK that has been sulfonated [15]. In this work, NMR spectrometer is used to determine the degree of sulfonation. The presence of the $–SO_3H$ group would result in a distinct signal of protons H_E at 7.5 ppm [13].



(a) PEEK

Sulfonation
↓



(b) SPEEK

Figure 1. Structure of PEEK before (a) and after sulfonation (b)

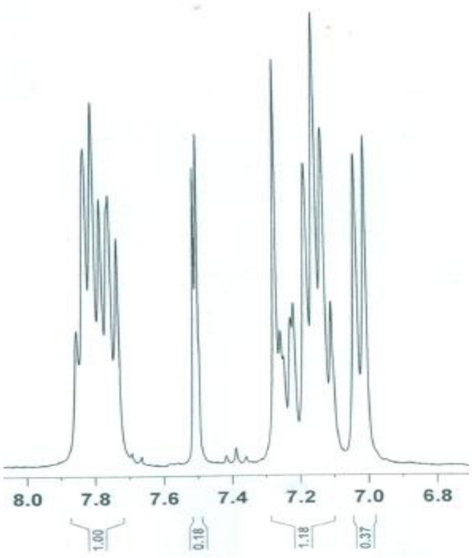


Figure 2. ^{1}H NMR Spectroscopy of sulfonated PEEK

According to Paik et al. [16], since the numbers of H_E and $–SO_3H$ groups are equivalent to each other, the DS is calculated from the peak area of H_E relative to the integral of the peak areas of all the other proton signals (H_x : x = a, b, c, d, a', b', c', d'). Using the following mathematical expressions [13]:

$$DS/(12 - 2DS) = AH_E/\Sigma\, AH_x \quad (0 \leq DS \leq 1) \qquad (3)$$

where AH_E is the integral of H_E and AH_x is the integral of H_x (x = a, b, c, d, a’, b’, c’, d’). By inserting the data of integral area that were obtained from ^{1}H NMR spectroscopy in Figure 2 into equation (3), The determined DS of SPEEK is 74%.

3.2 FTIR analysis

It is well known that functional groups and intermolecular interaction between two polymers can be determined by FTIR spectra. Comparative FTIR spectra of CS, SPEEK and SPEEK crosslinked CS are shown in Figure 3. The presence of amine I (O=C-NHR) and NH_2 of CS represented by peaks at 1650 and 1550 cm^{-1} respectively.

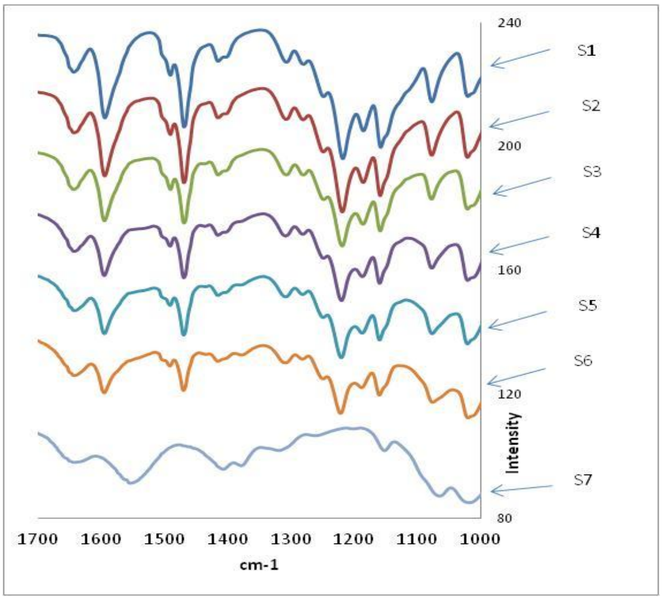


Figure 3. FT-IR spectra of CS, SPEEK and SPEEK/CS

Meanwhile, the peak of symmetric and asymmetric stretching vibrations of the sulfonic acid group $–SO_3H$ of SPEEK at 1024 and 1080 cm^{-1} respectively [17, 18]. It can also be clearly observed that a new broad peak at 1540 cm^{-1} in the spectra of the crosslinked SPEEK/CS blend membrane has formed. This may be assigned to the symmetric $–NH_3^+$ deformation resulting from the crosslinking reaction occurs between amino groups of CS and sulfate ions of SPEEK which have a Coulombic interaction [2, 6]. Thus, it can be concluded that the SPEEK was successfully crosslinked with CS.

3.3 Proton conductivity

Proton conductivity is one of the most important properties of PEMFC. Conductivity curve in Figure 4 shows proton conductivity decreases with increasing of chitosan content from 8.51×10^{-3} to 2.85×10^{-7} S cm^{-1}. During crosslinking, amino groups ($-NH_2$) in CS interacting with the sulphonic groups (-SO_3H) in SPEEK compound to form –NH_3 [2]. Number of -SO_3H species decreases when number of –NH_2 species (consumed amount of sulphonic acid groups) increased. It is well known that proton transfer between ionic clusters consisting of polar groups such as –SO_3H. The number of ionic clusters decreases with decreasing of the number of -SO_3H species and water content in the membrane. By crosslinking, the structure of membranes become more compact which leads to the reduction of the mobility of H^+ and space of retaining water around sulfonic acid groups [19]. Therefore less -SO_3H species and water content in membranes might limit protons to move easily and hence contributed to the decrease of proton conductivity.

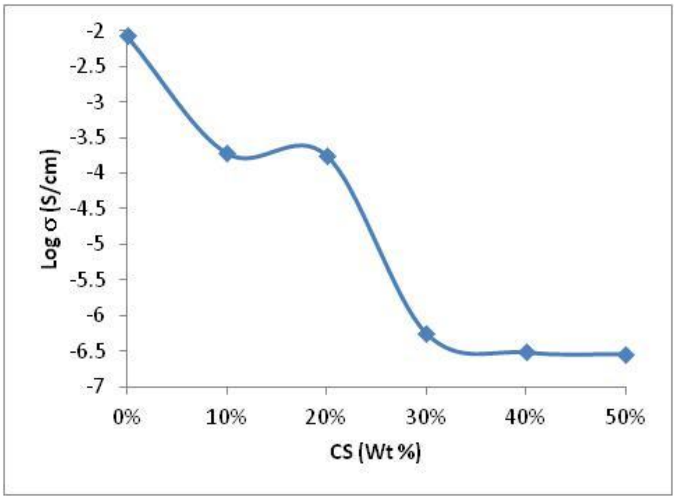


Figure 4. Conductivity versus chitosan content

3.4 Water uptake

Figure 5 shows water uptake decreases with increasing of chitosan content from 52% to 29%. After that water uptake increases parallel to the CS content. This can be best explained that amount of ionic interaction between –SO_3 and –NH_3 also increased, thus it has led amount of free amine and sulfonic groups decreased. This factor has decreased water sorption capability of membrane. Meanwhile, as crosslinking density increased it limits the polymer chains mobility and leads towards a denser membrane structure. This would mean smaller free volume which resulted in smaller hydrophilic channel and therefore reduced water uptake [2, 10]. Beyond 30% water uptake starts increasing and no more ionic interaction between –SO_3 and –NH_3. This is because of limitation of –SO_3H which leads to lower ionic conductivity. Thus, this result is in fully agreement with the conductivity curve as shown in Figure 4. Moreover, CS is highly hydrophilic polymer. The increase in water uptake occurred when amino groups of CS have combined with water molecule and assisted the formation of continuous hydrophilic region [2].

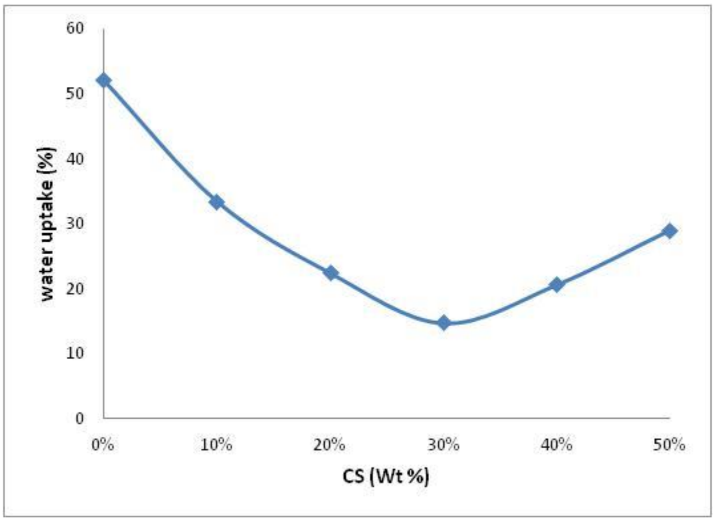


Figure 5. Water uptake of SPEEK/CS membranes

3.5 Ion exchange capacity (IEC)

Ion-exchange capacity (IEC) indicates the amount of the ion exchangeable groups present in a polymer matrix which are responsible for proton transfer, and thus is an indirect and reliable approximation of the proton conductivity [17]. Figure 6 shows the relationship between ion-exchange capacity (IEC) and the CS at room temperature. It can be observed that IEC decreases from 0.188 to 0.018 mequi. The results reveal that IEC decreases as the weight content of CS (%) increases. Decreasing IEC is due to the decreased $–SO_3H$ groups with a higher degree of crosslinking that consumed part of the ion-exchange groups.

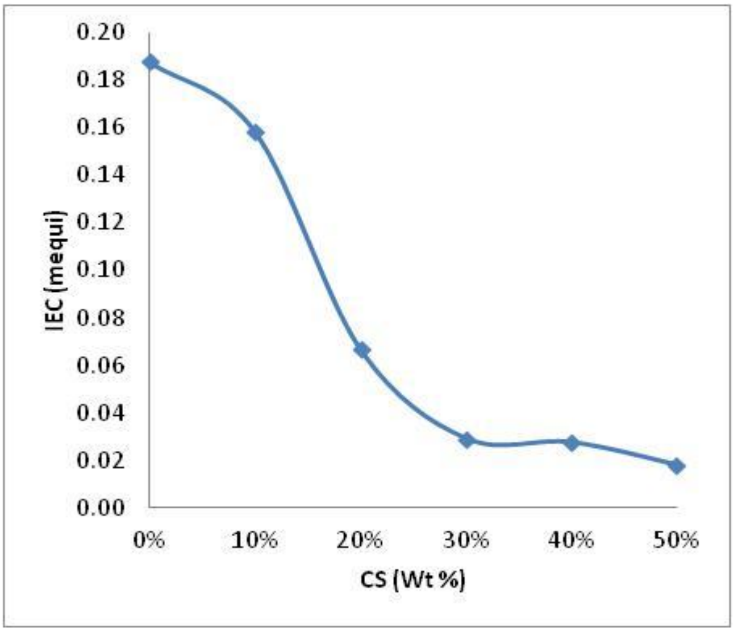


Figure 6. IEC versus CS at room temperature.

The amount of SO_3H groups is responsible for the ion exchange and the water uptake in the sulfonated membranes [20]. With increasing the degree of crosslinking between $–SO_3H$ and amino groups (NH_2), more NH_2 are introduced in the SPEEK/CS film, and accordingly the equivalent sulfonic acid group is incorporated. Due to the repulsive forces between the condensed sulfonic acid groups at a higher degree of crosslinking, the water uptake tends to reach a saturated level and hence slowing the increase of IEC [20].

4. CONCLUSION

UV irradiation induced crosslinking technique is one of the most effective technique to crosslink SPEEK and CS which is confirmed by FTIR spectrum. As CS increases, the conductivity in trend decreases. This is due to the increase of ionic interaction between $–SO_3$ and $–NH_3$ which leads to the lack of $–SO_3H$ species. Water uptake decreases as CS increases because of the rising of ionic interaction activities which implying the decrease of $–SO_3H$ species. After that water uptake increases as CS increases. This is due to the increase of amino groups of CS that have combined with water molecule. The decrease of IEC as CS increases is due to less of $–SO_3H$ species which responsible for the ion exchange.

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