Effects of sulfonation process on thermal behavior and microstructure of sulfonated polysulfone membranes as a material for Proton Exchange Membrane (PEM)

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Abstract

This paper reports the effect of sulfonation processon thermal behavior and microstrucutre of sulfonated polysulfone membrane. Various degree of sulfonation reactin has been conducted and the sulfonated membranes were characterized by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), x-ray diffraction (XRD) and scanning electron microscopy (SEM). Modifications of the origin polysulfone polymer resulted in an increment value of glass transition temperature (Tg) due to the introduction of sulfonic acid group to the polymer backbone. However, due to some hindrance such as trace amount of organic solvent left during solvent evaporation and high hydrophilicity of the produced sulfonated membranes resulted in decreasing values of Tg. The polymer membrane showed lower degradation temperature as a function of degree of sulfonation. From XRD analysis, it was found that the membrane shows slight crystalline behavior after the sulfonation reaction. Detail discussions and observation of the alteration in microstructure of the sulfonated membrane were supported by SEM micrograph.

Keywords: Polysulfone, polymer electrolyte membrane, sulfonated polysulfone, thermal behavior

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1. Introduction

Thermal stability of sulfonated polymer is very critical in determining the best possible material to apply in real fuel cell operating condition. Degradation behavior and glass transition temperature are among the important parameters to be considered. The glass transition temperature (Tg) is the temperature at which large-scale (translational and rotational) molecular motion of chains begins and is used as a measure of chain flexibility. Thus, at any temperature above the Tg value, the molecular chains possess more mobility than below Tg value. To be used in the intended application, a polymer should be chosen with Tg significantly above the operating temperature.

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There are various factors affecting the glass transition temperature of polymer. Some of them are polymer structure, molecular symmetry, molecular weight, structural rigidity and the presence of secondary forces[1]. The secondary forces may be due to the presence of polar groups introducing interaction such as hydrogen bonding. For sulfonated ionomer-type

polymers, the addition of the sulfonic acid group usually has an additional effect. The introduction of the sulfonate group raises the glass transition temperature (Tg) by increasing bulkiness to the polymer chain unit, thereby increasing the barrier to the rotation of the chains; this influences the ability of segmental motion within the polymers[2].

Sulfonation reactions are also believed to cause an increase in Tg value of the base polymer. Noshay and Robeson[3] reported that sulfonation had increasing the Tg of the sulfonated polysufone membrane by as much as 130ºC and is proportional to the degree of sulfonation. However, they found out that the free acid form (-SO$_3$H) membrane displays lower Tg value than that in sodium salt form, i.e. 230ºC for a 1.0 -SO$_3$H/PSU compared to 310ºC for 1.0 –SO$_3$H/PSU. This demonstrates the importance of ionic intermolecular interaction in increasing Tg via an ionomer effect.

Sivashinsky et al.[4] have studied the effect of the ion concentration of sulfonic group on Tg value for sulfonated polysulfone membrane. Some important conclusions are made indicating that if single Tg is present, it explains that only small fraction of ions can exist in the form of large ionis domains. Meanwhile, if two Tg values are detected, they represent the nonpolar phase devoid of ion content and another for ionic phase. They also thought that the deviation from linearity in the dependence on Tg vs. ion content may be interpreted as evidence of some changes in the state of ion aggregation e.g. transition from multiplets to clusters has occurred at this ion content. However, it is difficult to decide whether the increase in Tg is only due to a change in composition or if in addition ion-exchange site act as crosslinkages.

Arnold and Assink[5] claimed that the presence of the ionic groups in the sulfonated polysulfone membrane structure helps to reduce the chain mobility by virtue of their bulkiness or by their ability to act as an interchain ionic crosslink. Ironically they observed that only one Tg and not two was identified, suggesting that sulfonated polysulfone does not have a domain structure. If large domains existed, two Tgs would be noted that is one for nonpolar phase and one for an ionic phase.

Johnson et al.[6] highlighted that it is critical to use well extracted and carefully dried samples to obtain well defined Tg. It is interesting and somewhat disturbing to note that the heat capacity changes at the Tg "smeared out" with increase in sulfonation degree. This indication describes that the Tg definition by this method become increasingly vague as the concentration of ions increased. Preparations of membrane samples are extremely important as the produced membrane might contain a residual salt that is left from the synthesis of original polymer. Soxhlet extraction methods have been used for further purification process as the group found out that the membrane was not highly transparent even at higher sulfonation degree. It is possible to observe sharp glass transition behavior in the DSC provided the sample is completely dried and for reproducible data, the experiment were conducted two or three times. It was neither agreed nor denied possibilities that the effects of excessive inorganics ions or solvent are the causes to these apparent effects on Tg identification.

In contrast to the earlier work, O'gara et al.[7] reported that glass transition value for sulfonated polysulfone was found to increase nonlinearly with sodium sulfonate content. They also claimed that by performing SAXS study there was no evidence of the ionic clustering occurred in the polymer. It was postulated that below 12 mol% sodium sulfonate, mainly single ion pairs are found and the slight increase in the glass transition is related to internal chain stiffening. Meanwhile, above 12 mol% sodium sulfonate, multiplet ionic crosslinking may occur and thus account for the higher rate of increase in Tg.

Thermal effects, which are due to desulfonation in the same range of temperature, do not allow evaluating the Tg value with accuracy. The Tg value obtained by Lufrano et al.[8] is reported at about 200ºC to 220ºC and they claimed that precise determination of this value is hindered by desulfonation process occurring in the close region of temperature. They also studied the sulfonation of polysulfone with respect to its polymer chain degradation. It was proven in their study by an increase in intrinsic viscosity with increasing sulfonation degree, confirming that the sulfonation process helps to preserve the polymer chain from degradation. Thermal analysis of sulfonated polysulfone samples reveals higher glass transition temperatures and lower decomposition temperatures with respect to the unsulfonated sample. These phenomena could be explained by the introduction of bulky groups in polymer chain that produces steric hindrance to intersegmental motion, hence reducing mobility as well as flexibility of the ether groups and increasing Tg values.

Though many studies have been performed on the thermal stability of the sulfonated membrane, unfortunately no precise conclusion were made on the exact type of ion concentration occured in the sulfonated hydrocarbon membrane and how the increase in Tg really affect the membrane performance. Perhaps the reasons behind all those dissimilarity value of Tg reported for sulfonated polysulfone membrane are the variation methods for measurement, diverse sulfonating agents being used during the reaction and different techniques of sample preparation.

Therefore, in this study we synthesized and fabricated SPSU membranes with different degree of sulfonation and the effects of sulfonation process on the produced membrane were studied through thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), x-ray diffraction (XRD) and scanning electron (SEM). Detail explanation will be given in correlation with degree of sulfonation via molar ratio of the sulfonating agent to polymer unit.
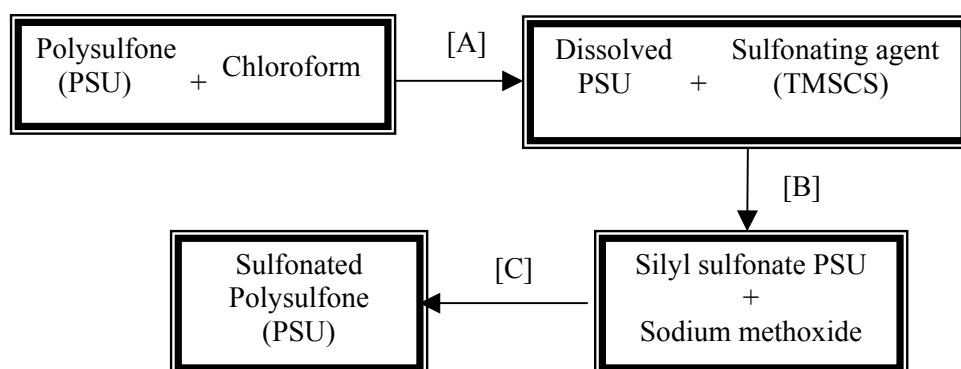
2. Experimental

2.1. Materials

A Polysulfone Udel polymer, which was used for the synthesis, was purchased from BP Amoco and dried at 100 ºC under vaccum before use. Trimethylsilyl chlorosulfonate (TMSCS) and sodium methoxide was purchased from Fluka and used as received. Chloroform, N, N-dimethylformamide (DMF) and methanol were purchased from commercial source and used in the synthesis.

2.2. Sulfonation of polymers

Sulfonation reactions were carried out according to procedure described by Chao and Kelsey[9]. Typically 40 ~ 80 g of polysulfone was dissolved in 450 ~ 800ml chloroform at room temperature. An inert atmosphere (nitrogen) was provided over the reaction solution to remove HCl effluents formed during the substitution reaction and to reduce the excessive water vapor as they can interfere the sulfonation reaction. The dissolved polysulfone was reacted with a drop wise of 50 ml trimethylsilyl chlorosulfonate (TMSCS) to form an intermediate medium, silyl sulfonate polysulfone. Cleavages of the silyl group was obtained by adding a base medium (sodium methoxide 15% in methanol solution), yielding the desired

sulfonated polymer products. The amount of base medium added is sufficient enough to cleave pendant silyl groups and to neutralize any acid still present in the solution. To stop the sulfonation reaction, the solutions was decanted into a nonsolvent bath of methanol to obtain a precipitate white fluffy porous product. The sulfonated particles were washed several times with water and methanol, and then dried in a vaccum oven for 24 hours at 80 ºC for complete removal of the solvent. Film of sulfonated membrane was prepared by casting on a glass plate by a pneumatically casting machine with 22 ~30 wt.% of SPSU dissolved in dimethylformamide (DMF). After being dried and complete removal of residual solvent at 60 ºC for 4 hour, the SPSU membrane was detached from the glass plate by immersing into deionized water. The membrane was converted into acid form by immersion in 1 M HCl overnight. Four SPSU membranes samples were studied accordingly to their molar ratio of sulfonating agent to polysulfone polymer. Degree of sulfonation of the membrane sample was determined by elemental analysis based on sulfur to carbon ratio using CHNOS Elemental Analyzer (Vario EL II) supplied by Elementar Germany. Figure 1 shows the sulfonation process sequence.

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┌─────────────────────────┐        [A]      ┌──────────────────────────────────┐
│ Polysulfone             │  ──────────────▶ │ Dissolved       Sulfonating agent│
│  (PSU)     +  Chloroform │                 │   PSU       +      (TMSCS)        │
└─────────────────────────┘                  └──────────────────────────────────┘
                                                              │
                                                             [B]
                                                              ▼
┌─────────────────┐        [C]      ┌──────────────────────────────────┐
│ Sulfonated      │ ◀────────────── │ Silyl sulfonate PSU              │
│ Polysulfone     │                 │          +                       │
│  (PSU)          │                 │ Sodium methoxide                 │
└─────────────────┘                 └──────────────────────────────────┘
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[A] = reaction at ambient temperature
[B] = continuous stirring for 24 h
[C] = stirr for 1 hour, then added drop wise into methanol bath
(TMSCS) = Trimethylsilyl chlorosulfonate

Note: The solution were continuously stirred under N_2 atmosphere during the process

Figure 1 : Sulfonation process sequence

2.3 Thermal gravimetric analysis (TGA)

Dynamic TGA was performed on a Perkin Elmer TGA7 instrument in nitrogen environment to assess the thermal stability of sulfonated polysulfone membrane. The samples were heated at different heating rate of 5ºC/min from 50ºC to 500ºC. Possible weight loss was measured and reported as a function of temperature. The thermal stability of the polymers was generally reported at the observed temperature of 5% weight loss.

2.4 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer DSC7 instrument. Thos analysis was used to determine the glass transition temperatures (Tg) of the synthesized membranes. Films were cut into small pieces to provide a suitable sample size about 5 mg. Programmed heating cycles were used to heat the samples at a heating rate of 5 °C/min and 10 °C/min under nitrogen atmosphere from 100ºC to 300ºC. The midpoint of the specific heat increase in the transition region during the second heating is reported at the Tg (glass transition temperature).

2.5 X-ray diffraction (XRD)

The x-ray analysis were carried out on a Siemens diffractometer D5000 using a radiation source. Through this analysis it is possible to show the evidence of structural changes caused by the sulfonation process on the polysulfone polymer.

2.6 Scanning electron microscopy (SEM)

The scanning electron microscope (Philips SEM Model XL-40, Holland) was widely used to study the structure of membranes. The samples were dried and then immersed in liquid nitrogen before their breaking. The samples were recovered with a thin gold layer and placed on a support in the SEM. The SEM analysis was carried out under high vacuum on the dried membranes. The cross sections of the sulfonated polysulfone membranes and the skin layer morphology were investigated in details.

3. Results and discussion

3.1 Sulfonation process

Sulfonation process has been conducted several times by varying the molar ratio of the polymer to sulfonating agent. Suitable operating conditions of the sulfonation process have been identified by trial and error. Four respective sulfonated polysulfone membranes (SPSU1, SPSU2, SPSU3 and SPSU4) were then characterized and studied as shon in Table 1.

Table 1
Sulfonation process operating condition

Membranes	Molar ratio[a]	Reaction Temperature	% Weight	Degree of sulfonation
SPSU1	1.8	25-28 °C	25.0	27.55
SPSU2	2.1	25-28 °C	30.0	41.84
SPSU3	2.5	25-28 °C	24.5	60.20
SPSU4	3.0	25-28 °C	24.3	78.57

[a]mol sulfonating agent for mol of polysulfone

3.2 Effects of sulfonation process on thermal stability of the membranes

The thermal stability of the polymer electrolyte membranes was studied by thermal gravimetric analysis (TGA). Thermogravimetric analysis for sulfonated polysulfone membrane with different degree of sulfonation were performed in order to investigate how much the synthesized polysulfones are thermally stable and to explore which functional groups are vulnerable by heat. Data obtained form TGA also give evidence on the occurrence of sulfonation reaction of the polymer at which the degradation temperature of sulfonic group was observed. The membrane samples were heated from 50ºC to 500ºC to study the thermal history of the sulfonated membrane. As shown in Figure 2, polysulfone sample shows a weight loss of 2.77% starting at about 153ºC indicating the loss of residual solvent that was strongly bound to the polymer during the reaction. The residual solvent could only be removed well above its boiling point when the polymer is in rubbery state. However, this was not observed in the SPSU sample as the residual solvent cannot be removed completely from SPSU films by heat treatment due to decomposition of sulfonic acid group below Tg value[10].

The second weight loss of PSU sample is observed above 450ºC corresponding to the polymeric backbone degradation. The first weight loss around 100ºC for SPSU samples is related to the loss of water physically absorbed in the samples and bonded to the sulfonic group. It was observed that the decomposition of the polymer main chain decreases by increasing the degree of sulfonation. This differences could be explained by an enhanced symmetry in the polysulfone structure due to the introduction of SO_3 groups renders it less regular and therefore less stable. Meanwhile, degradation temperature starting at 250ºC was observed for all SPSU sample can be assigned to the loss of sulfonic acid group similar as reported by Gupta and Scherer[11]. Although SPSU samples show lower degradation temperature with respect to PSU samples, this temperature is significantly higher than Nafion 117 membranes reported by Lufrano et al.[8].

3.3 Effects of sulfonation process on Tg value

The glass transition temperature (Tg) of the sulfonated membranes was measured by DSC. Theoretically the Tg value would increase as the degree of sulfonation increased. The glass transition temperature of SPSU membrane was detected in the range of 192ºC and 325 ºC and the precise determination of this value is hindered by desulfonation process occurring in the close region of temperature[12]. The introduction of sulfonate groups has two effects on glass transition temperature: firstly, increase in molecular interaction by pendant ions, i.e. ionomer effect; and secondly, increase in molecular bulkiness. Both effects hindering the internal rotation of polymer molecule and lead to the increased glass transition temperatures for sulfonated polymers. It is believed that this Tg behavior for sulfonated polymer may reflect a significant change in microstructure of the polymer [13].
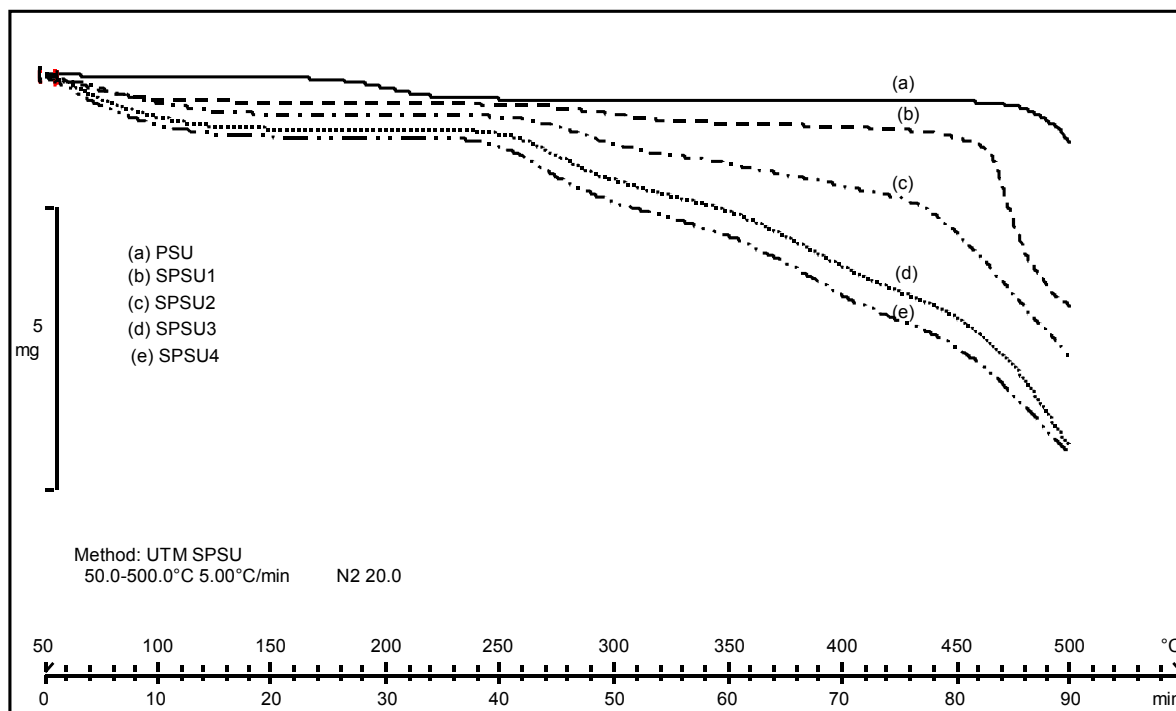
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gure 2 : TGA spectrum for polysulfone and sulfonated polysulfone sample

The Tg values detected by DSC at two different heating rates of 5 ºC/ min and 10 ºC/ min were presented in Table 2. At heating rate of 5ºC/ min, the Tg value seems to increase accordingly except for SPSU1 membrane. Meanwhile the Tg value of PSU at 10ºC/ min heating rate were found much lower than the Tg value achieved at 5ºC/ min. This slight decrease in Tg value might be due to a trace amount of organic solvent remaining in the membrane sample during casting which shift Tg to lower temperatures. Similar observation might be seen at slow heating rate of 10ºC/ min, where the Tg values of SPSU samples were found to increase by 50% but surprisingly, sudden decline of Tg value for SPSU4 samples were being observed. This rapid drop off Tg value might be due to the abovementioned similar effects. One of the plausible cause that also contribute to this drop off temperature for SPSU4 was that polymers having the hydrophilic components such as hydroxyl or amide groups form intermolecular bonds in the presence of water which strongly affect the characteristic of the glass transition. Introducing a small amount of water to a hydrophilic polymer may disrupt the intermolecular bonds, thereby enhancing the main-chain motion. In this case Tg shifts to lower temperatures in presence of water [14]. The water content studies conducted using DSC at similar heating rate supported this phenomenon.

Water content behavior for PSU and SPSU samples were also can be visualized in DSC spectrum. From Figure 3 (a) and Figure 3 (b), it was observed that at different heating rate performed (5ºC/min and 10ºC/min), the spectrum curvature turn out to be slight narrow for higher degree of heating rate especially for SPSU4 membrane representing the higher water content in the membrane samples. This was supported by the swelling effects where SPSU4 membrane significantly swells more than other membranes and these narrow curve associated to the loss of water in the membrane microstructure.

Table 2
Glass transition (Tg) value of sulfonated polysulfone membrane at different heating rate.

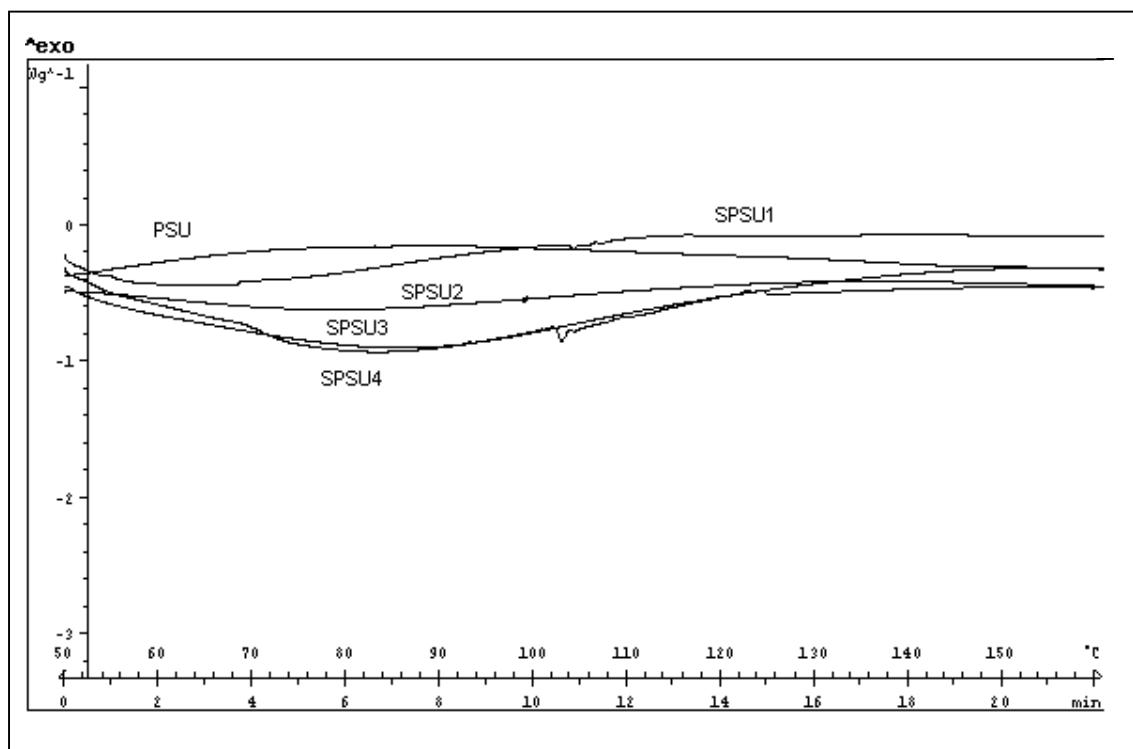| Membranes	Tg at 5ºC /min (ºC)	Tg at 10ºC /min (ºC)
PSU	180.03	140.56
SPSU1	165.39	232.00
SPSU2	192.42	318.66
SPSU3	204.34	325.73
SPSU4	212.55	224.07

Figure 3 (a) : DSC spectrum of PSU and SPSU membranes at heating rate 5ºC/min

3.4 Effects of sulfonation process on membrane microstructure

The microstructure of base polysulfone and sulfonated polysulfone membrane were studied by x-ray diffraction and scanning electron microscopy. The X-ray analyses were carried out on a Siemens diffractometer D5000 using a radiation source. Through this analysis it was possible to detect the structural modification caused by the sulfonation on polysulfone polymer. The x-ray diffraction patterns of various SPSU membranes with wide range of 2θ degrees were illustrated in Figure 4. A slight shift of the amorphous peak to higher angles was observed for highly sulfonated samples, corresponding to small change in intersegmental spacing. The spectrum shows typical broad band of amorphous polymer with slight peak of crystallinity were found for PSU and SPSU1 membrane. Though SPSU3 and SPSU4 samples

also show slight peak at the crystalline region, no crystalline peak were detected for SPSU2 samples. These variants may attribute to the tendency of the solvent used in the study to react with the sulfonating agent to form hydrogen bridge bonding.
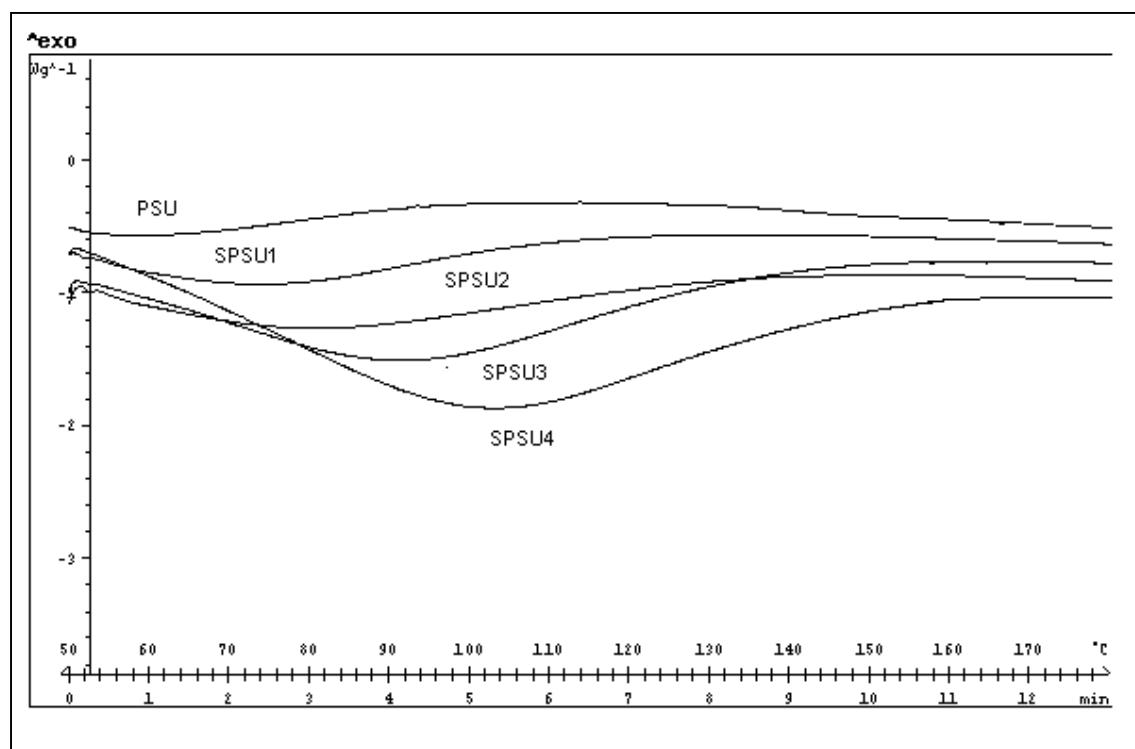

Figure 3 (b): DSC spectrum of PSU and SPSU membranes at heating rate 10ºC/min

The base polysulfone polymer is known to be an amorphous polymer with rigid polymer structure. According to Staiti et al.[15] a study on the polymer structure of the same amorphous material (polybenzimidazole) was conducted by XRD and it was found that the introduction along the chain of groups able to form inter-chain and intra-chain hydrogen bridge bondings that allows formation of a more regular structure which gives an incipient crystalline character to the material. Kopitze et al.[16] described the tendency of the sulfonic acid group to decompose the dimethylformamide solvent during the solvent evaporation process at high temperature, forming dimethylammonium sulfonated salt. Meanwhile, Bouchet and Siebert[17] also give evidence in the FTIR studies; as for the formation of hydrogen bonds in no-symmetric polymer was the cause of an increase of crystalline character. Kaliaguinie et al.[18] claimed that the introduction of dimethylformamide solvent in the sulfonated polymer structure might also contributed to the crystalline behavior in the PEEK membrane. It was believed that dimethylformamide molecules were prone to form hydrogen bonding with sulfonic groups. All of the possible factors were believed to correlate with the presence of crystalline peak in the spectrum. However, no studies on the crystalline behavior originate by dimethylformamide solvent in the sulfonated polysulfone were reported so far. The detected crystalline behavior in the membrane samples however does not modify the swelling characteristics of the polymer, as the membrane possesses good water uptake at higher degree of sulfonation.

The cross section and surface area structure of the polysulfone and sulfonated polysulfone were studied by scanning electron microscopy (SEM). The SEM photos show that the

membrane, which have been sulfonated illustrated different micrograph from the unsulfonated polysulfone membrane. All of the sulfonated polysulfone membranes show basic dense structure with varying in thickness. It was observed that the variation in microstructure of these sulfonated membranes might be due to different weight percent of sulfonated polymer applied and various molar ratio used during the process. As observed in SPSU4 membrane, some small pores were visible but these pores were not visible in other sulfonated membranes. It is assumed that this might be due to the effect of excess nitrogen supply during conducting the sulfonation reaction for SPSU membrane. Meanwhile, the microstructure of Nafion 117 in this study was found similar as other microstructure being studied by other researcher in the area. In addition, the surface texture is characterized by the presence of imperfections and defects on the surface, probably due to the presence of aggregates of sulfonic groups at the film surface. SEM micrographs were illustrated in Figure 5, Figure 6 and Figure 7.
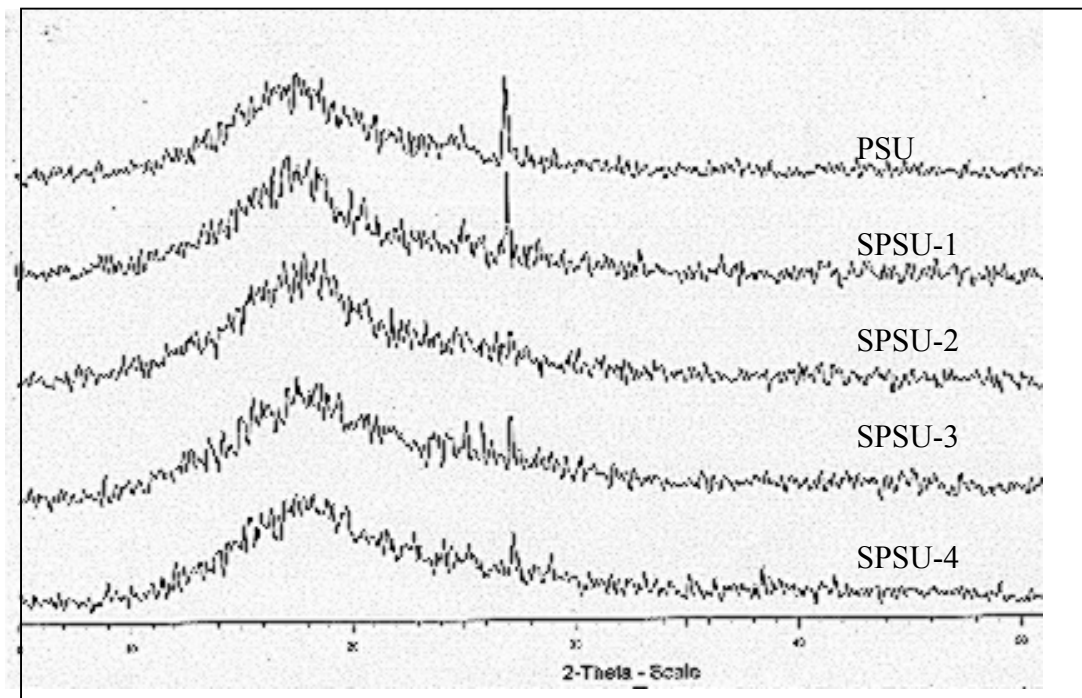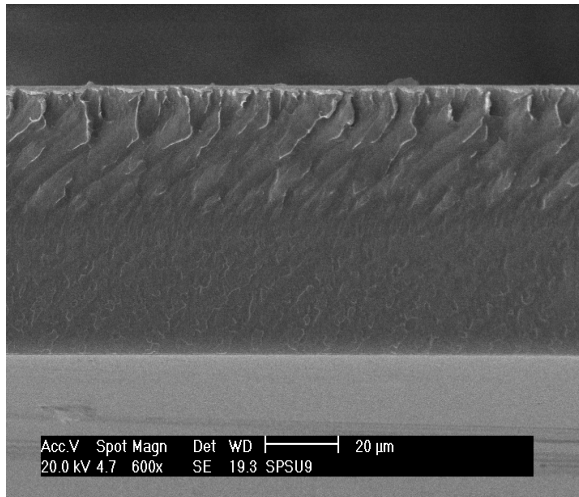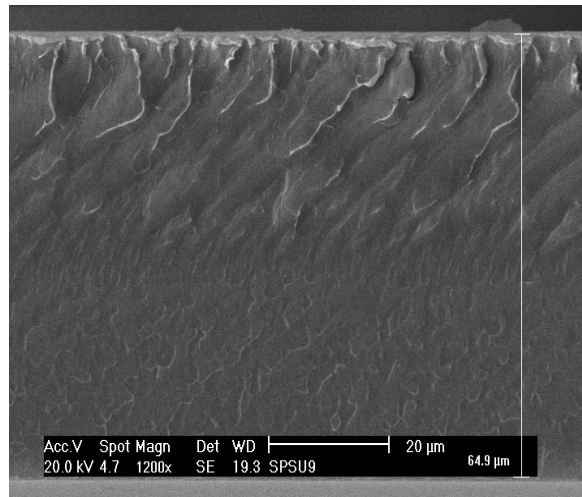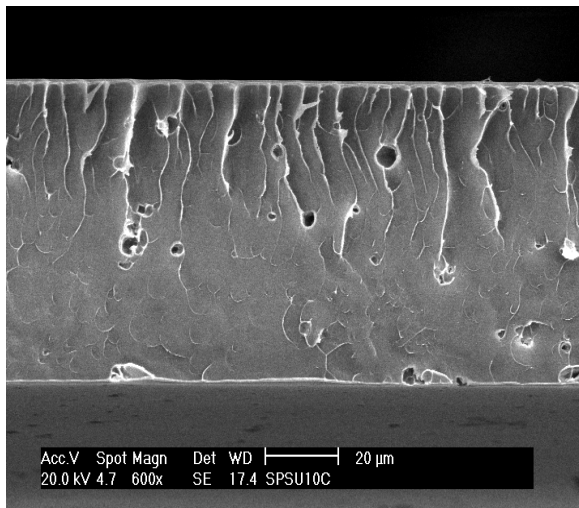

Figure 4 : X-ray diffraction spectrums of PSU and SPSUmembranes.
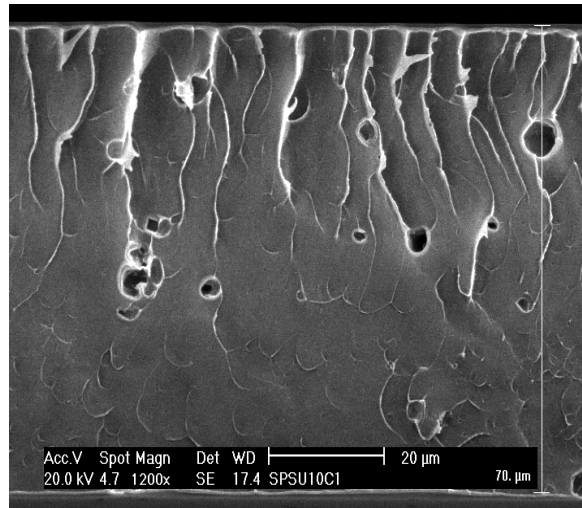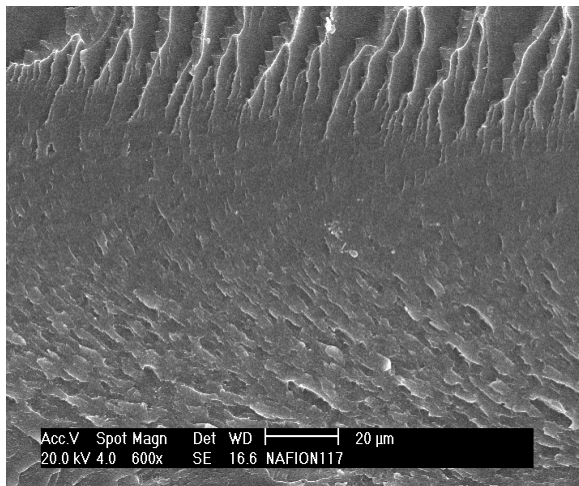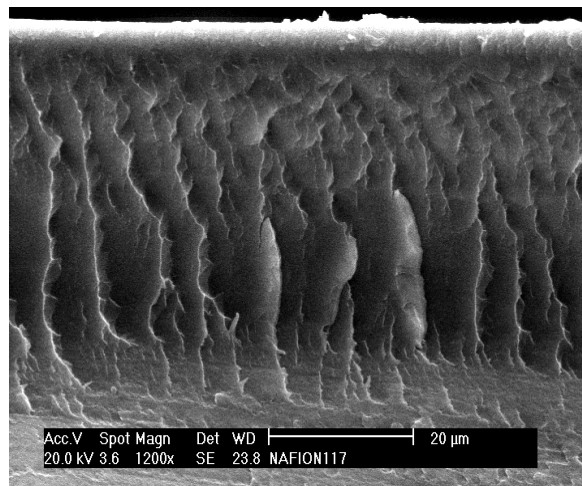
(a) SPSU3 (b) SPSU3

(a) SPSU4 (b) SPSU4

(a) Nafion 117 (b) Nafion 117

Figure 7: Scanning electron microscopy pictures of cross section of SPSU3, SPSU4 and Nafion 117 membranes at different magnification level (a) 600 and (b) 1200

4. Conclusions

The effects of sulfonation process on polysulfone polymer were successfully detected by TGA and DSC measurement. It was observed that the decomposition of the polymer main chain decreases by increasing the degree of sulfonation. Meanwhile, the decomposition temperature of sulfonic acid group was observed starting at 250 º C. The Tg value detected in this study was increased with increasing the degree of sulfonation. However, due to some hindrance such as trace amount of organic solvent left during solvent evaporation and high hydrophilicity of the produced sulfonated membranes resulted in decreasing values of Tg. XRD analysis showed that dimethylformamide solvent was prone to form hydrogen bonding with sulfonic groups hence allows formation of a more regular structure which gives an incipient crystalline character to the material structure. This however does not affect the swelling behavior of the sulfonated membranes as shown by water content in DSC spectrum. SEM micrographs also exhibited a clear altered microstructure of polysulfone polymer after the sulfonation process.

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