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PREPARATION OF COMPOSITE MEMBRANES BASED ON SULFONATED POLYSULFONE AND ACTIVATED CARBON

Irfan Gustian*, Asdim and Evi Maryanti
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Bengkulu, Jalan WR. Supratman Kandang Limun, Bengkulu 38371, Indonesia
*E-mail : irfan.g@unib.ac.id

ABSTRACT

Preparation of composite membranes based on sulfonated polysulfone and activated carbon have been done. Polysulfone was sulfonated through homogeneous method using sulfonating agent trimethylsilyl chlorosulfonate. Activated carbon derived from coal tailings which then carbonized at temperature of 400 °C and activated through chemical activation in 30% of phosphoric acid with ratio of 0.5: 1 volume per weight of phosphoric acid and carbon. The composite membranes was prepared by blending the sulfonated polysulfone and activated carbon with mass ratios of 1:1; 1:1.5; and 1:2. Dimethyl formamide used to dissolve the sulfonated polysulfone, with stirring for 12 hours at room temperature. The manufacture of composite membranes have been done by evaporating dimethyl formamide of each variation. The composite membranes were characterized by FT-IR, TGA, and XRD analysis. From the results of FT-IR spectra showed that interaction between sulfonated polysulfone and activated carbon. Whereas the results of TGA analysis showed a slight increase in stability over temperature range of 100 °C to 250 °C. From diffractogram pattern shows amorphous phase have reduced due to the addition of activated carbon, The maximum conductivity (σ) has been measured for the composite membranes 1: 2 as 8.8 x 10^{-4} S/cm at 40 °C .

Keywords: Composite, membranes, sulfonated polysulfone, activated carbon, conductivity.

INTRODUCTION

Proton conducting membrane is still a source of alternative energy in the future. Early generation proton conductive membranes made of perfluorinated sulfonic acid has given real hope, has been used by the project GEMINI. The commercialization of Nafion by DuPont in the late 1960s helped to demonstrate the potential interest in terrestrial applications[1-3]. In the last decade, research on PEM has focused on the developing polymer electrolyte anhydrous in order to maintain the existence of proton conductivity at high temperature. The operation of the fuel cell at high temperature can provide benefits such as improved CO tolerance of platinum catalyst, increasing the mass transport, improved reaction kinetics, and simplifying humidity[3-5].

Polysulfones (PSU) have high thermal stability, chemical resistance, has good mechanical strength and resistance to swelling. PSU can be used as polymer electrolyte membrane (PEM) after sulfonation and increasing its acid groupe. The proton conductivity of the sulfonated polysulfone (SPSU) membranes depends on the sulfonating agent ratio[6], and have lower gas permeability and liquid (water and methanol) permeability than the sulfonated perfluorinated ionomers[7]. The studies about SPSU are mostly based on humidity control[8-12], but there are little works about its usage in anhydrous proton conducting systems. In order to obtain highly sulfonated polysulfone, the polysulfone polymer has to be dissolved in a solvent, and then treated with a sulfonating agent with a given mole ratio. Sheng et al. used 1,2-dichloroethane and the TMSCS sulfonating agent with mole ratios of 1:1.43 and 1:2.86 at room temperature, which resulted in sulfonation degrees of 87% and 127%, respectively.

The mechanical properties combined with electrical, thermal, and many other properties have been extensively investigated. Some results have been compared with carbon/polymer composites. However, the properties reported are scattered and even lower than for carbon/polymer composites. Many factors, including the type of carbon used and its intrinsic properties, the dispersion state of carbon in the polymer

matrix and its interfacial interaction, the amount of wrinkling in the carbon, and its network structure in the matrix can affect the properties and application of carbon/polymer composites. Nevertheless, with the rapid development of fabrication techniques for carbon and carbon/polymer composites and ways to modify the carbon surface, these challenges are being gradually overcome[13]. Other efforts in the search for alternative energy sources in the future has been done using natural polymer membrane[14].
In this work, SPSU has synthesized using trimethylsilyl chlorosulfonate (TMSCS) as sulfonating agent in homogeneous solution 1,2-dichloroethane (DCE). Membrane composite material prepared by mixing SPSU and activated carbon (AC) in some of the mass ratio. Composite polymer membranes were evaluated in terms of the degree of sulfonation, functional groups by FT-IR, thermal stability by TGA, diffractogram patterns by XRD, and proton conductivity.

EXPERIMENITAL

Materials

Commercial polysulfone (PSU), trimethylsilyl chlorosulfonate (TMSCS) and methanol purchased from Aldrich, dimethyl formamide and 1,2-dichloroethane from Merck, and activated carbon has made from coal tailings obtained from Bengkulu.

Preparation

Polysulfone has dissolved in solvent at temperature 25 °C under nitrogen gas flow, the solvent is 1,2-dichloroethane. The volume of solvent required is 100% of the mass of the polymer. TMSCS as sulfonating agent was added to the solution at room temperature; during the sulfonation, nitrogen gas flow is maintained. The amount of dissolved polymer is determined by the mole ratio between the polymer and sulfonating agent, that is 1:1.5 with a reaction time of 20 hours.
Coal tailings have been taken from the coal mining PT. Bukit Sunur Central Bengkulu district, after sorted from impurities and then dried through drying, subsequently treated with in the oven at 105 °C, carbonization of coal tailings has done at a temperature of 400 ºC. Chemical activation in 30% of phosphoric acid with ratio of 0.5:1 volume per weight of phosphoric acid and carbon. Activation has done for one night with stirring. Then the pyrolysis at 800 °C for 3 hours. The results of this pyrolysis used to reinforce materials in the blending phase with sulfonated polysulfone.

Characterization

FT-IR spectra were recorded on a Bruker Alpha-P (Wismar, Germany) in attenuated total reflectance (ATR) in range of 4000–400 cm^{-1}. Thermal stabilities of the polymer electrolytes were examined by thermogravimetric analyses with a Perkin Elmer STA 6000 (Waltham, MA). The samples (10 mg) were heated from room temperature to 700 °C under N atmosphere at a scanning rate of 10 °C/min. The X-ray powder diffraction (XRD) analysis were performed using X-ray diffractometer (Rigaku D-MAX2200, Japan) with Cu Ka (λ = 1.5406 A) radiation over the range 2θ between 0° and 70°. Conductivity of membrane was measured by IM 3590 Chemical Impedancy Analyzer HIOKI.

RESULTS AND DISCUSSION

Figure-1 showed the FTIR spectrum of polysulfone before sulfonation, when compared with the FTIR spectrum of sulfonated polysulfone obvious the difference. This difference is clearly visible at wave number 3700 cm^{-1} to 2900 cm^{-1}. At this area showed stretching vibration OH group contained in the sulfonate group -SO_3H.
Figure-2. showed the FTIR spectra of SPSU and the composite membranes. The pattern of the spectrum produced almost close similarity in blending AC 1:1 with SPSU, but after blending with AC 1:1.5 and AC 1:2 the spectrum becomes more complex. This is shown in the wave number region of 800 cm^{-1} to 1200 cm^{-1}.
From the results of the degree of sulfonation, the sulfonated polysulfone has 156% degree of sulfonation. This means that 100% sulfonate groups have replaced atom of hydrogen on the 2nd ring shown in Figure-3

and 56% were replacing atom of hydrogen on the side symmetric. Orientation of sulfonate groups will be more to occur in 2nd ring and the first ring followed, while in the 3rd ring and 4th ring are very difficult to happen that due to steric hindrance -SO_2- group contained in the main chain of polysulfone.

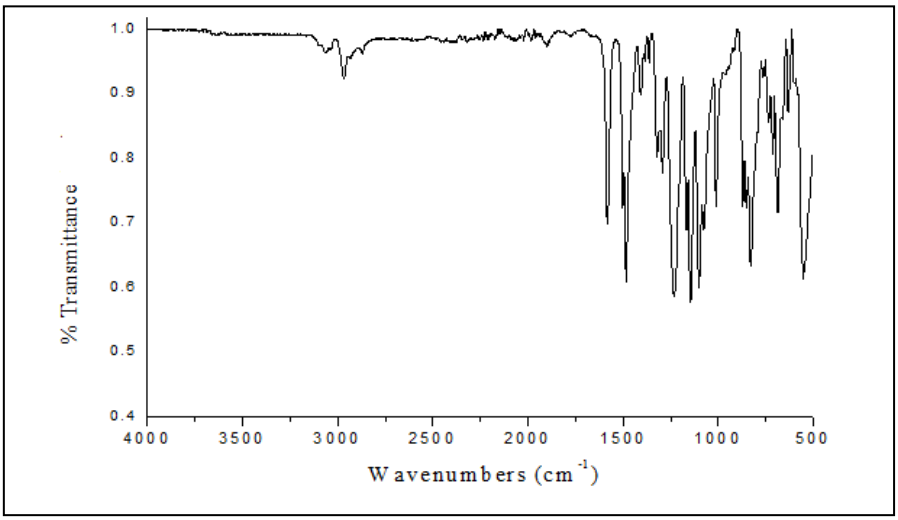

Fig.-1: Spectrum of polysulfone.

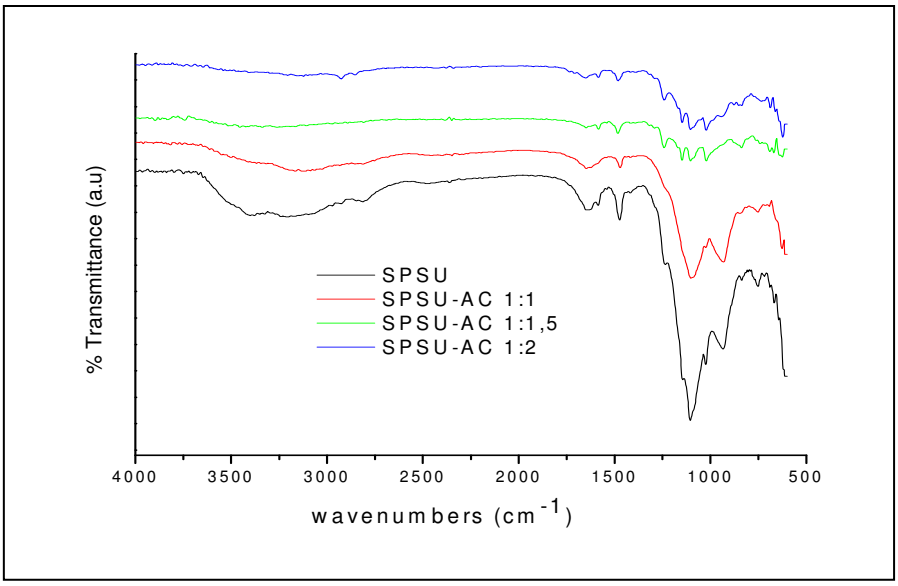

Fig.-2: Spectra of sulfonated polysulfone and the composite membranes.

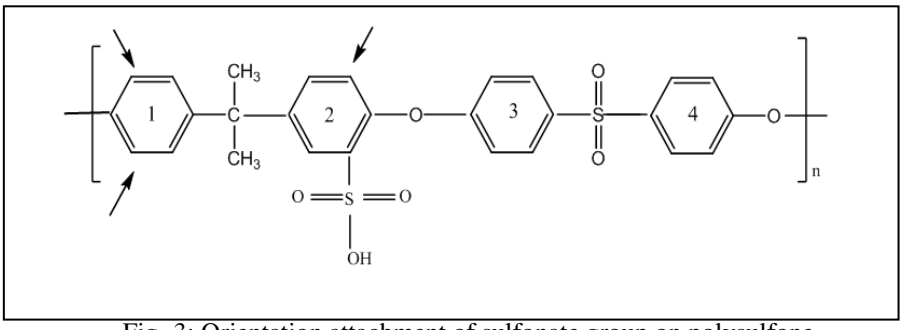

Fig.-3: Orientation attachment of sulfonate group on polysulfone.

Figure-4 showed that at temperature of 100 °C the degradation pattern of sulfonated polysulfone membrane and composite membranes is almost the same. At temperature of 100 °C, all membrane nearly as experienced weight loss of about 10%. Furthermore, at temperature of 150 °C begins there is a difference, SPSU membranes and composite membranes material at a ratio of 1:1 and 1:1.5 suffered weight loss a bit more than the membrane ratio of 1:2. The effect the addition of carbon is evident already at temperature 250 °C.

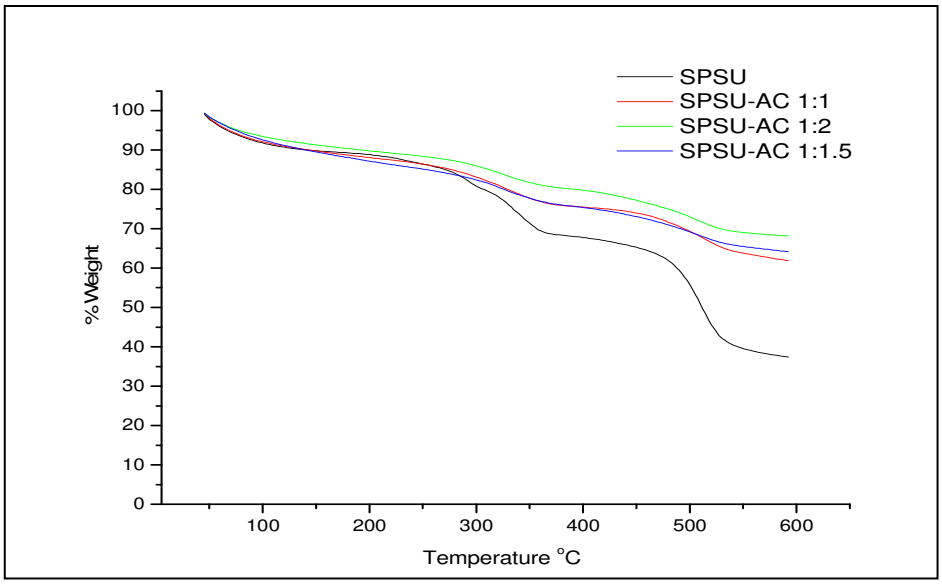

Fig.-4: Thermogram sulfonated polysulfone and composite membranes.

For SPSU at temperatures above 300 °C drastically degraded, Insertion sulfonate groups will cause chain conformation to become more softly, decomposition will commence from the pendant group of the main chain of sulfonated polysulfone and for composite material membranes at ratio of 1: 2 still indicates the weight loss that is less than the ratio of 1: 1 and 1: 1.5. Previous study has reported that degradation of sulfonated polysulfone was followed by the release of molecules SO in the area between 200-300 °C. Further degradation is the release of SO_2 molecule in the area between 300-400 °C, while at a temperature of 400-500 °C is the initial degradation of the main chain by removing the benzyl alcohol and the area between 600-700 °C benzene molecule release stage.[11-12]

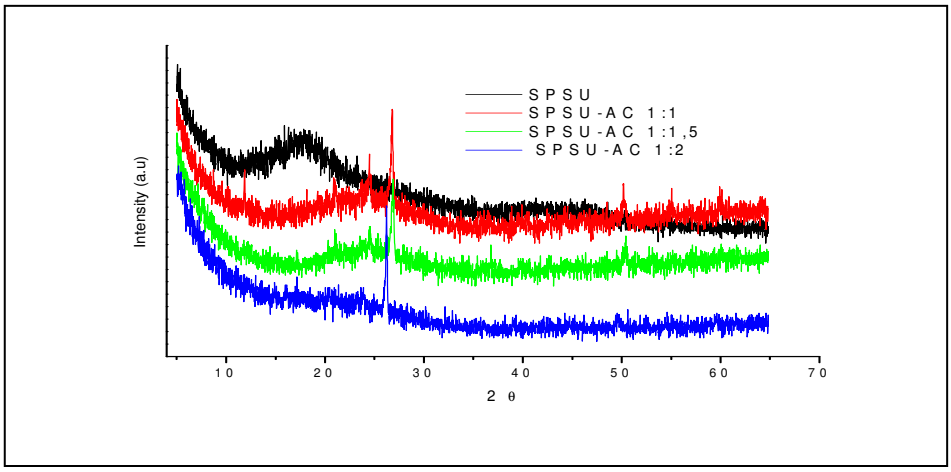

Fig.- 5: Diffractogram sulfonated polysulfone and composite membranes

Figure-5 showed diffractogram pattern sulfonated polysulfone and composite membranes (SPSU+ AC) with variation of the mass of 1: 1, 1: 1.5 and 1: 2. Diffractogram pattern for sulfonated polysulfone after mixing and sulfonated polysulfone before mixing active carbon are produces different pattern. Diffractogram showed increased crystallinity, which resulted in the addition of activated carbon will affect the crystallinity of the membrane. Properties such as this will hinder the movement of molecules and produce materials that are more compact. Diffractogram sulfonated polysulfone at 2θ between 10-20˚ clear that there are an amorphous phase. After the addition of activated carbon, the more amorphous phase disappears and is replaced by 25.5˚ peak at 2θ. Figure-6 showed proton conductivity of the composite membranes at temperature of 80-30 °C. SPSU membranes have higher proton conductivity at temperature of 80-50 °C, but at 30-40 °C composite membrane have proton conductivity greater than SPSU membranes. The maximum conductivity (σ) has been measured for the composite material membranes 1: 2 as 8.8 x 10^{-4} S/cm at 40 °C. This conductivity in terms of order equal to the results of previous research, acid-base complex pair polymer electrolyte membranes on sulfonated polysulfone with 1H-benzotriazole was found to be 3.34 x 10^{-4} S/cm at 150°C[12].

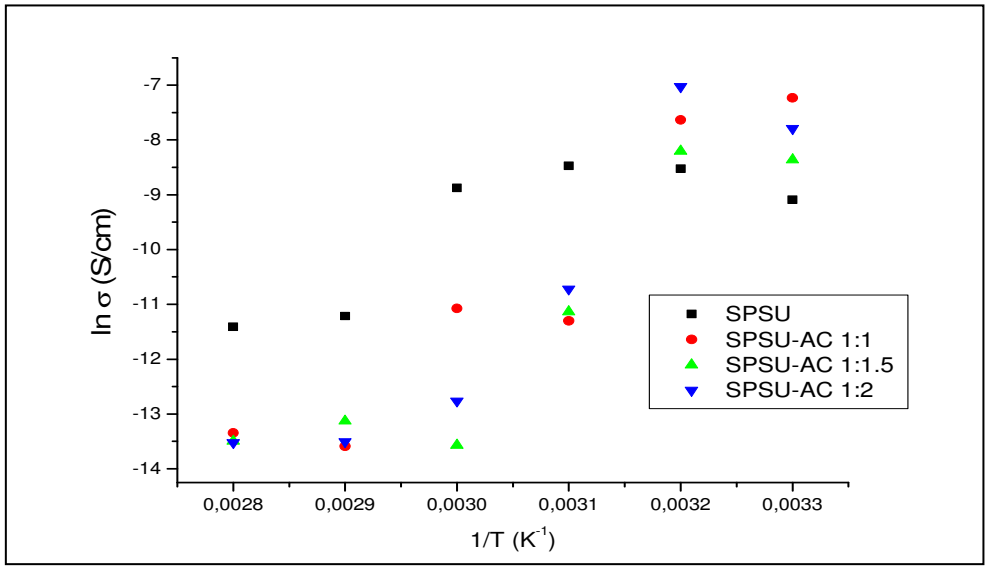

Fig.-6: DC Conductivities of sulfonated polysulfone and composite membranes as a function of reciprocal temperature.

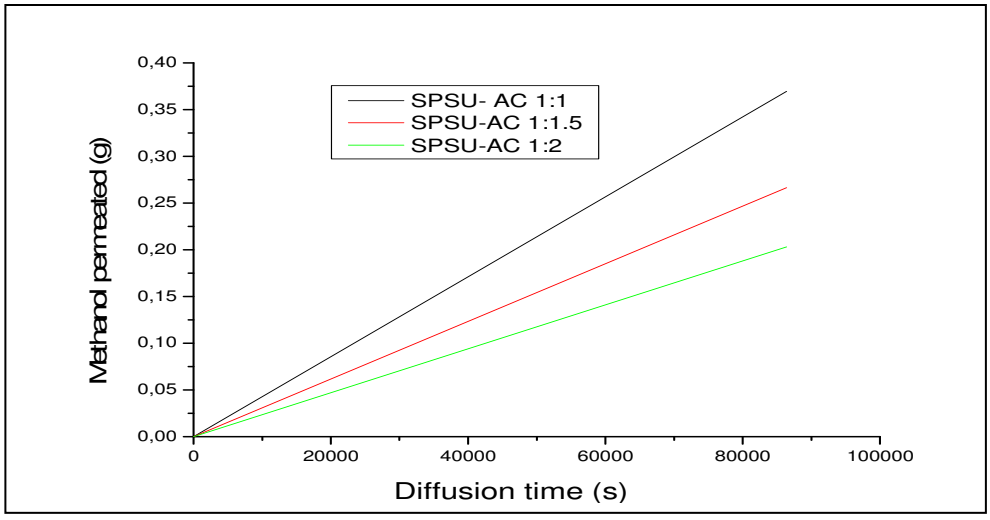

Fig.-7: Methanol mass flow of composite membranes.

Figure-7 showed that the effect of adding active carbon will hamper methanol transport across the membrane. Methanol vapor will experience along the equilibrium with the liquid concentration gradient through the membrane. Mass loss was recorded as a function of time, measuring mass flow of methanol has followed previous study[15]. The effect of adding active carbon is increasing, it is getting a little methanol passes through the membrane.

CONCLUSION

From the FTIR spectra showed that the sulfonation has been able to be produced, which is evident from the numbers specific wavelength sulfonated polysulfone. For composite membranes, FTIR spectra showed a similar pattern with the sulfonated polysulfone as the continuous phase. Different occur in the intensity of the spectrum of each of the composite membranes. From determination of degree sulfonation, sulfonate groups on sulfonated polysulfone has been obtained 156%. TGA analysis results indicate that the SPSU decreased stability after the addition of activated carbon. Whereas the results of TGA analysis showed a slight increase in stability over a temperature range of 100 °C to 250 °C. The maximum conductivity (σ) has been measured for the composite membranes 1: 2 as 8.8 x 10^{-4} S/cm at 40 °C.

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