

# Sulfonated polystyrene and its characterization as a material of electrolyte polymer

*by* Gunawan Gunawan

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## Sulfonated polystyrene and its characterization as a material of electrolyte polymer

Ngadiwiyana<sup>1</sup>, Ismiyanto<sup>1</sup>, Gunawan<sup>1</sup>, Purbowatiningrum RS<sup>1</sup>, Prasetya, N.B.A.<sup>1</sup>, Kusworo, T.D.<sup>2</sup>, Susanto, H.<sup>2</sup>

<sup>1</sup>Chemistry Department, Faculty of Mathematics and Sciences Diponegoro University

<sup>2</sup>Chemical Engineering Department, Faculty of Engineering, Diponegoro University

[ngadiwiyana@gmail.com](mailto:ngadiwiyana@gmail.com)

**Abstract.** The research of polystyrene modification from Styrofoam waste and its application as a main material of electrolyte polymer had been done. The sulfonation reaction of polystyrene was conducted using sulfuric acid as sulfonation agent and the reactions were done with variation times of 1, 2, 3, 4 and 5 h. The characterization of the sulfonated products covered analysis of functional groups using FT-IR spectrophotometer, sulfonation degree, measurements of ion exchange capacity, conductivity and swelling degree. The sulfonated polystyrene product was white solid as confirmed by the spectra of FT-IR with the presence of wide band absorption of O=S=O at the wavenumber of 1080-1411  $\text{cm}^{-1}$  as indication. The research showed the best sulfonated polystyrene prepared in 4 h as a material of electrolyte polymer, since it had the highest degree of sulfonation, ion exchange capacity, conductivity and swelling degree with the values were 28.52 %, 1.550 meg/g,  $15,924.10^{-6} \Omega^{-1}\text{cm}^{-1}$  and 332.4 %, respectively.

### 1. Introduction

Research on new materials for electrolyte polymers continues to be developed, such as by utilizing polystyrene from styrofoam waste. Polystyrene cannot conduct protons; therefore, it must be modified into a material that can conduct proton in order to be used as an electrolyte polymer base [1]. Polystyrene is a polymer with a benzene group as main backbone. The benzene group can be modified by sulfonate addition through sulfonation reaction following aromatic electrophilic substitution mechanism. The sulfonate group is super acidic and may play a role in proton transfer, which is one of the characters of electrolyte polymer [2].

The polystyrene sulfonation reaction can be carried out using sulfuric acid as a sulfonating agent. Sulfonation degree can be calculated to determine the success of the sulfonation reaction. The sulfonation degree can be controlled by temperature, time and sulfonation agents [2]. The sulfonation degree shows the number of hydrogen atoms (H) that have been substituted with sulfonate ( $\sim\text{SO}_3\text{H}$ ) group in the polymer chain [3]. The sulfonation degree will affect the character of sulfonated polystyrene (SPS), which are cation exchange capacity (CEC) value and proton conductivity, as sulfonation process will increase hydrophilicity and proton conductivity of polymer in the presence of sulfonate groups in polymer chain [4]. Proton conductivity is very important parameter for electrolytic polymer membrane because the greater the proton conductivity the greater the membrane ability to deliver the protons [5].



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In this research, polystyrene sulfonation on styrofoam waste was carried out by using sulfuric acid as sulfonation agent with sulfonation time variation. The success of the synthesis of SPS were investigated by determining the sulfonation degree, cation exchange capacity and functional group analysis using FTIR. The increase of conductivity of SPS was measured by Inductance (L), Capacitance (C) and Resistance (R) meter (LCR meter).

## 2. Methods

### 2.1. Equipment and materials

2.1.1. *Equipments*: Analytical balance, beaker glass, conical flasks, measuring cylinder, dropping pipette, watch glass, volumetric flask, glass stirrer, glass funnel, buchner funnel, tweezer, oven, reflux apparatus, vial, burette, filter paper, pH indicator, FTIR dan LCR-Meter (HOKI 3522-50 LCR HiTESTER).

2.1.2. *Materials*: waste food wrap styrofoam, chloroform p.a (Merck), aquadest, 96% sulfuric acid p.a (Merck), sodium hydroxide (NaOH) p.a, sodium chloride (NaCl) p.a (Merck), hydrochloric acid 37% (HCl) p.a (Merck), silica gel, phenolphthalein indicator (PP).

### 2.2. Methods

2.2.1. *Synthesis of SPS with sulfuric acid*. Styrofoam (10 g) and chloroform (250 mL) in beaker glass were stirred until homogeneous. Then, 96% sulfuric acid (25 mL) was added at room temperature. The mixture was then refluxed with a variations of 1, 2, 3, 4, and 5 hours of sulfonation time at 60-65 °C. The reaction was stopped by addition of cold aquadest to form top layers followed by separation. The obtained SPS was washed with aquadest until neutral pH and dried in an oven at 60 °C.

2.2.2. *Determination of sulfonation degree (SD)*. SPS (0.1 g) was soaked in 0.1 M NaCl solution (10 mL) for 2 days. The mixture was filtered and the filtrate obtained was titrated with 0.02 M NaOH using the PP indicator. The degree of sulfonation is determined using equation (1).

$$SD = \frac{V_{NaOH} \times M_{NaOH} \times MR \text{ Monomer SPS}}{\text{Sample weight}} \times 100\% \quad (1)$$

where :  $V_{NaOH}$  = volume of NaOH (mL)  
 $M_{NaOH}$  = concentration of NaOH (M)

2.2.3. *Determination of cation exchange capacity (CEC)*. Determination of CEC of SPS was carried out by acid-base titration method. The sample was weighed as much as 0.1 gram and soaked in NaCl solution (10 mL) for 2 days. The immersion filtrate was titrated with NaOH. The value of CEC can be determined by equation (2).

$$CEC = \frac{V_{NaOH} \times M_{NaOH}}{\text{Sample weight}} \quad (2)$$

where :  $V_{NaOH}$  = volume of NaOH (mL)  
 $M_{NaOH}$  = concentration of NaOH (M)

2.2.4. *Analysis of functional groups*. Analysis of polystyrene and SPS functional groups were measured using FTIR spectrophotometer. The sample was placed into the sample container and measured the absorbance in the range of 600-4000  $\text{cm}^{-1}$  wavenumber.

2.2.5. *Determination of swelling degree (SD)*. Samples of material with a certain weight were weighed in dry conditions. Then, the sample was immersed in water for 24 hours and weighed to get wet weight. The calculation of SD follows equation (3).

$$SD = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \% \quad (3)$$

where :  $W_{wet}$  = wet weight  
 $W_{dry}$  = dry weight

2.2.6. *Determination of proton conductivity*. Proton conductivity of SPS was measured using LCR meter (impedance, capacitance, resistance) (HOKI 3522-50 LCR HiTESTER) at Pusat Sains dan Teknologi Bahan Maju (PSTBM) Batan Serpong, Tangerang, Banten. LCR meter is a tool used to measure material properties, which include inductance, capacitance and conductance to frequency function. SPS was firstly formed into pellet to check its thickness with enerpac machine with pressure of 300 Psi and diameter of 10 mm. The frequency used in this study was 100 kHz with a voltage of 20 mV. SPS was clamped between 2 electrodes which were connected with positive and negative poles on LCR meter device to measure impedance value. The proton conductivity value were determined by equation (4).

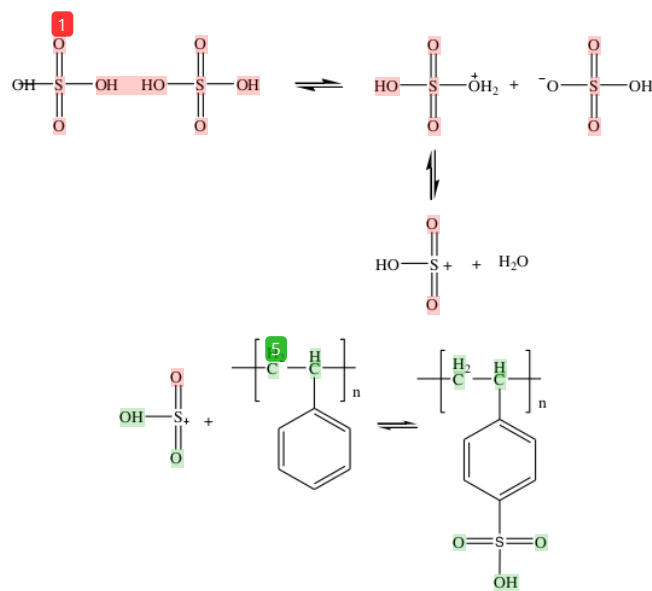
$$\rho = \frac{RA}{l}; \quad \sigma = \frac{1}{\rho} \quad (4)$$

where :  $\rho$  = resistivity ( $\Omega\text{cm}$ )  
 $R$  = resistance ( $\Omega$ )  
 $A$  = cross-sectional area of the sample ( $\text{cm}^2$ )  
 $l$  = sample thickness (cm)  
 $\sigma$  = conductivity (S/cm or  $\Omega^{-1}\text{cm}^{-1}$ )

### 3. Results and discussion

#### 3.1. Synthesis of SPS

SPS was synthesized by reacting 96% sulfuric acid with polystyrene in chloroform solvent. The sulfonation reaction was carried out by reflux method at 60-65 °C with variation of sulfonation time for 1-5 hours. Sulfonation reaction which categorized as aromatic eletrolifilic substitution reactions aims to substitute H atoms with  $\sim\text{SO}_3\text{H}$  group by chemical bonds on their carbon atoms, as shown in Figure 1. The presence of the sulfonate group causes the polystyrene to have a charged group that can deliver protons [6]. The sulfonation reaction in the polystyrene can occur in *ortho* and *para* position to the alkyl chain. However, the substitution reaction is easier to occur in the *para* position due to a steric hindrance of the *ortho* position [4]. The sulfonation reaction at the *para* position can be seen in Figure 1. In this study, SPS was obtained as a white powder polymer, similar with that of the polystyrene.



**Figure 1.** Polystyrene sulfonation reaction

### 3.2. Determination of Sulfonation Degree (SD)

The success of the sulfonation process can be indicated from sulfonation degree (SD). The magnitude of the SD value signifies the number of sulfonate groups ( $\sim\text{SO}_3\text{H}$ ) substituting H atoms in aromatic groups. The value of SD is influenced by temperature, time and number of sulfonation agents [2]. SD value indicates the ability to absorb water on the membrane that serves as a proton displacement medium. The SD values can be seen in Table 1.

**Table 1:** SD values of SPS

No	Sample variation	Sulfonation time (hour)	Sulfonation degree (%)
1	SPS 1	1	5.77
2	SPS 2	2	23.80
3	SPS 3	3	26.53
4	SPS 4	4	28.52
5	SPS 5	5	13.25

Table 1 shows that SPS 4 has the highest SD of 28.52%. This value indicates that 28% of the total polystyrene chain has been substituted by the  $\sim\text{SO}_3\text{H}$  group. The longer the sulfonation time the greater the SD value. However, SPS 5 shows a dramatical decrease. This possibly be due to the fact that the more sulfonate group of the SPS the more soluble SPS in water resulted in a higher possibility for side reactions to occur.

### 3.3. Determination of Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) shows the number of milli equivalents per gram of polymer weight. The purpose of this analysis is to determine the ability of SPS to exchange the cations attached to their functional group with other cations given to the system. The value of CEC is shown in Table 2.

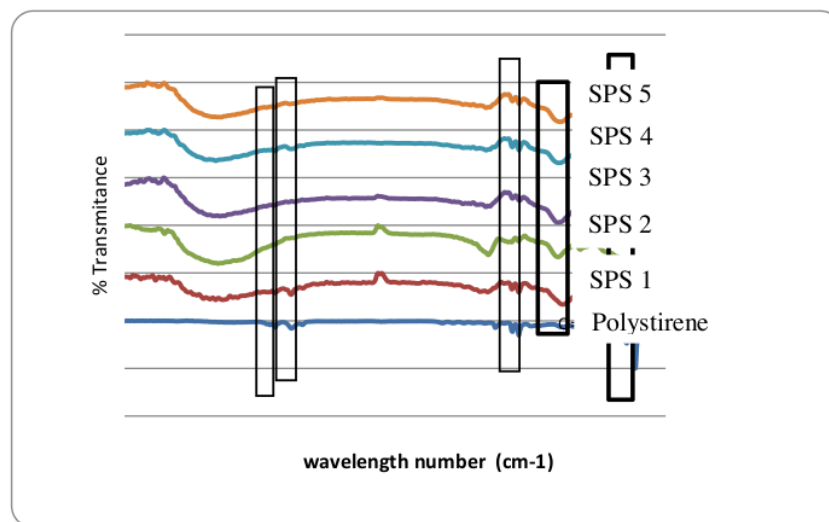
**Table 2** : CEC values of SPS

Sulfonation time (hour)	CEC (meq/g)
1	0.314
2	1.294
3	1.442
4	1.550
5	0.720

The value of CEC is directly proportional to the SD value. The greater the SD value the greater the CEC value. The longer the sulfonation reaction time the more the sulfonate group so that the more  $H^+$  ions can be exchanged. SPS 4 displayed the highest CEC value of 1.55 meq/g.

#### 3.4. Analysis of functional groups

The success of the sulfonation reaction is shown by functional group analysis using FTIR spectrophotometer. The addition of sulfonate group to the polystyrene leads to a new absorption of  $1080-1411\text{ cm}^{-1}$ . The absorption shows symmetric stretching vibration of  $O=S=O$  [7]. FTIR spectra of polystyrene and SPS are shown in Figure 2.



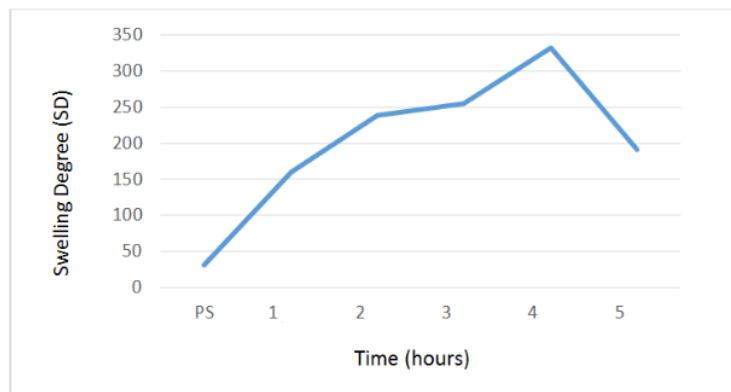
**Figure 2.** FTIR spectra of polystyrene and SPS

Figure 2 also shows other absorption bands, in regions of  $640-717\text{ cm}^{-1}$  and  $717-794\text{ cm}^{-1}$  which indicate the vibration of C-H bonds in benzene monosubstitution. Vibration of C=C bonds in aromatic ring is shown in the absorption of  $1419-1697\text{ cm}^{-1}$ . The absorbing band in the range of  $2854-2962\text{ cm}^{-1}$  exhibits vibrational bonds of aliphatic ring, while C-H vibration on the aromatic ring is indicated by absorption of  $3032-3142\text{ cm}^{-1}$ .

#### 3.5. Determination of Swelling Degree (SD)

The ability of a material to absorb water is essential in its application as an electrolyte polymer material. High water content in the material will facilitate proton transport [8]. The SD test was carried

out by immersing the sample in water for 24 hours and it was calculated by subtracting the weight of the wet sample by the weight of the dried sample and then divided by the weight of the dry sample. Graph of the SD determination is presented in figure 3.



**Figure 3.** Graph of the Swelling Degree (SD) determination.

Figure 3 shows that there is an increase in the SD from polystyrene to SPS with 4 hours of synthesis time. However, a SD decrease is observed for SPS with 5 hours of synthesis time. The presence of sulfonate ( $-\text{SO}_3\text{H}$ ) group of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) substituting  $\text{H}^+$  group causes the polymer to be hydrophilic. This results in a dramatic increase of water absorption capacity of the polymer. Therefore, the SD of SPS is greater than polystyrene. The better a material absorbs water (swelling), the easier it is to perform proton transfer [9].

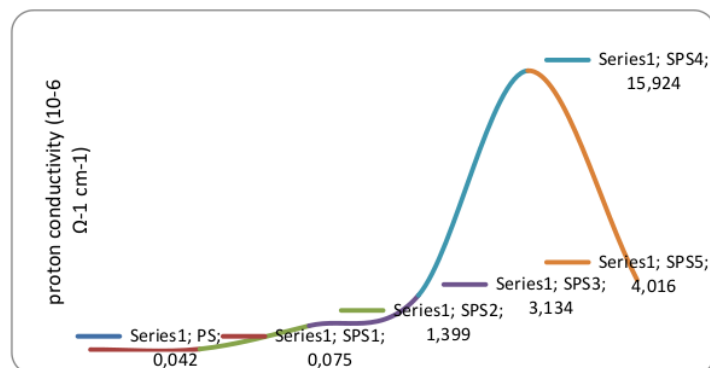
The SD of SPS 5 is decrease because there are not many sulfonic groups in the substituted polystyrene. This is probably due to the long synthesis time of SPS which made the solution becomes saturated resulting in the unoptimization of the sulfonation substitution.

### 3.6. Determination of Proton Conductivity

Conductivity shows the ability of a SPS to deliver protons. The greater the conductivity the better the SPS as the base material for electrolyte polymer membrane application. The proton conductivity graph can be seen in Figure 4.

Polystyrene has the smallest proton conductivity value of  $0.0423 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . This is because polystyrene cannot deliver protons well. After sulfonation, the conductivity increases with the duration of sulfonation. The highest conductivity value is obtained by SPS 4 which is  $15.924 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . However, the conductivity of SPS 5 decreases, which may occur due to side reactions so that the sulfonate group is not substituted properly.





**Figure 4.** Proton conductivity graph

#### 4. Conclusion

The research showed the best sulfonated polystyrene prepared in 4 h as a material of electrolyte polymer, since it had the highest degree of sulfonation, ion exchange capacity, conductivity and swelling degree with the values were 28.52 %, 1.550 meq/g,  $15,924 \cdot 10^{-6} \Omega^{-1} \text{cm}^{-1}$  and 332.4 %, respectively.

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