

Synthesis of Sulfonated Polystyrene from Styrofoam Waste as Manufacturing Material Polymer Electrolyte

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Abstract. The synthesis of polymer electrolyte of sulfonated polystyrene (sPS) has been carried out from Styrofoam waste. The polystyrene was sulfonated using various concentrations of acetyl sulfate at 40 °C for 1 hour. The resulting sulfonated polystyrene was characterized using FTIR, thermal analysis, and cationic exchange capacity (CEC). FTIR data show the success of sulfonation with the appearance of sulfonate groups in PST. The thermal data showed that the addition of sulfonic agents decreased the thermal stability of polystyrene. The highest CEC was obtained for 25 mmol of acetyl sulfate addition, with a CEC of 6.610 meq/g. The characteristics of the resulting product show that sulfonated polystyrene from Styrofoam waste potentially is used as a material for advanced technology of polymer electrolytes such as fuel cells and Li-Battery separator.

Keywords: *acetyl sulfate; PEMFC; polystyrene; Styrofoam; sulfonated polystyrene.*

1 Introduction

Styrofoam (SF) or also called expanded polystyrene (EPS) is a type of plastic that is widely used for single-use food packaging, preventing damage to electronic goods during the shipping process and as an insulator material, causing a lot of waste to be generated. SF cannot be degraded without the help of solvents, so it can cause environmental pollution problems. Its light nature can be carried away by water currents which will cause water pollution. In fact, SF consisting of benzene and styrene can cause health problems (Baig et al in [1]). In addition to the need to overcome the problem of water pollution, SF has the potential to be applied in the field of renewable energy. The increasing demand for fuel is inversely proportional to the availability of fossil fuels which are actually getting depleted. The use of fossil fuels in various fields causes environmental problems such as the greenhouse effect.

PEMFC can efficiently produce high power density which can convert energy efficiently into a compact and robust form and can operate at low temperatures

(Garraín et al in [2]). The advantages of using fuel cells such as high energy efficiency, low emission contaminants, and being a clean energy source make its development more promising. One of the important components in PEMFC is an ion exchange membrane or polymer electrolyte membrane which can deliver protons from the anode to the cathode. This type of membrane should have high thermal resistance and good mechanical stability (Pali-Cassanova et al in [3])

Polystyrene (PS) can be used for the manufacture of cation exchange material due to good mechanical properties and high thermal stability (Pramono et al in [4]). In addition, recyclable PS is a low-cost material and can reduce the potential for environmental pollution (Al-sabagh et al in [5]). Although it has good mechanical properties and high thermal stability, hydrophobic PS needs to be modified so that it can produce charged materials and can exchange protons. One of the modifications that can be done is the sulfonation process. The sulfonating agents that are often used for the sulfonation of aromatic compounds include acetyl sulfate, sulfur trioxide, and complexes, fuming sulfuric acid, sulfuric acid, chlorosulfonic acid, and trimethylsilyl chlorosulphonate (Khoemin et al in [6]). Acetyl sulfate is used as a sulfonating agent because it is more efficient than other sulfonating agents, and can be considered more environmentally friendly because the reaction can be carried out at a relatively low temperature, in a short time with less sulfonating reagents and the formation of sulfone does not occur (Wolska & W.Kulikowska in [7]). The use of acetyl sulfate as a sulfonating agent has been applied to Chitosan (Bagaskara et al in [8]), Polystyrene – Polyethylene (PS-PE) dispersed with sulfonated graphene oxide (SGO) (Mandanipour in [9]), Poly(styrene – isobutylene – styrene) (SIBS) combined with ionic liquid (IL) (Ortiz – Negrón in [10]) and irradiated Polystyrene (PS) / Poly(ethylene vinyl acetate) (PEVA) (Ghobashy in [11]) applied in manufacture of polymer electrolyte membrane fuel cell (PEMFC). So far, there has been no reports on the use of polystyrene from Styrofoam waste and its sulfonation products as electrolyte material.

Based on these problems, in this research, SF waste as a source of polystyrene modified using acetyl sulfate. Modified polystyrene was analyzed on functional groups, thermal properties, and cation exchange capacity to determine the ability of acetyl sulfate-modified polystyrene to exchange cations.

2 Experimental

2.1 Materials

Styrofoam waste from food wrappers, aquadest, chloroform (Merck), dichloromethane (DCM) (Merck), 2-propanol (Merck), sulphuric acid (Smart-Lab, 96-98%), and acetic anhydride (Merck).

2.2 Polystyrene Insulation from Styrofoam Waste

Referring to the study of Salim et al [12], modification of PS isolation from SF waste was carried out with 13 g of SF, dissolved in 50 mL of chloroform, then stirred until dissolved. The mixture is then isolated by dripping over hot distilled water. The results of the isolation were then placed in an oven at 60 °C for 24 hours.

2.3 Sulfonated Polystyrene Synthesis

The sulfonation of PS followed previous report of Salim et al in [12], about 5 g of polystyrene was added to a three-neck flask, then 40 mL of dichloromethane was added, stirred until dissolved. The mixture was then added with acetyl sulfate with a certain variation, and refluxed at 40 °C for one hour. Variations in the addition of acetyl sulfate used were 5, 10, 15, 20 and 25 mmol. Termination was carried out by adding 10 mL of 2-propanol and stirring continuously for 10 minutes. Stirring was continued without heating for 30 minutes. The mixture is then isolated by dripping over hot distilled water. The resulting sulfonated polystyrene was then oven-dried at 60 °C for 24 hours. The acetyl sulfate used was prepared using a mixture of anhydrous acetic acid dissolved in dichloromethane, stirred until dissolved and cooled to 0 °C, then sulfuric acid was added, and stirred until a yellowish color appeared in the solution.

2.4 Characterization of Sulfonated Polystyrene

The functional group of sulfonated polystyrene were analyzed by using *Fourier Transform Infrared* (FTIR, IRPrestige-21 Shimadzu) with KBr plate in the range of 400 – 4000 cm⁻¹. Thermal analysis was performed by using *Thermogravimetric Analyzer* (TGA, Linseis PT-1600) with heat rate of 10 °C per minute.

2.5 Cation Exchange Capacity

A total of 0.1 g PS and sPS were immersed in 25 mL of 1 M HCl for 24 hours. Then dried in the oven for 1 hour at 60°C. After that, the sample was immersed in 25 mL of 0.5M NaCl for 24 hours. The solution was then taken and titrated using 0.02 M NaOH using phenolphthalein as an indicator. The value of the cation exchange capacity is determined using the formula (1).

$$CEC = \frac{V_{NaOH} \times M_{NaOH}}{W_{sample}} \quad (1)$$

Where V is the volume of NaOH required (mL), M is the concentration of NaOH (mol/L), and W is the weight of the sample (g).

3 Result and Discussion

3.1 Characterization of Sulfonated Polystyrene

Acetyl sulfate as a sulfonating agent is prepared by reacting acetic anhydride with a certain amount of sulfuric acid resulting in a side reaction of acetic acid. The use of acetic anhydrous aims to remove excess water in the reaction mixture. Acetyl sulfate is used because the polymer degradation effect is negligible and the sulfone is not formed. (Wolska & Walkowiak-Kulikowska in [7]). Sulfonation reaction of acetyl sulfate with polystyrene at 40°C was presented at Figure 1.

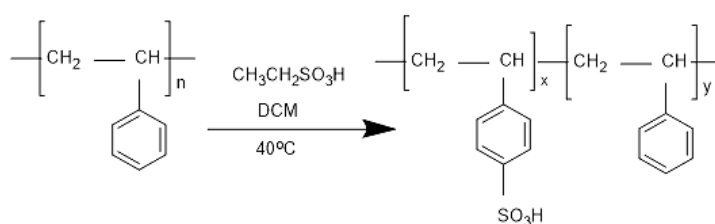


Figure 1. Schematic illustration of the sulfonation reaction (Wolska & Walkowiak-Kulikowska in [7]).

Functional groups of PS sulfonation from styrofoam waste were analyzed using FTIR which is shown in Figure 2. An absorption of 698 cm^{-1} appeared in the PS FTIR spectra which indicated the presence of bonding characteristics in aromatic C-C, where this value was not much different from Baig et al in [1] which showed the characteristic of aromatic C-C bond at 695 cm^{-1} . In addition, absorption of 1600 cm^{-1} appears which indicates an aromatic in PS. The success of the sulfonation process was indicated by the appearance of an absorption of 835 cm^{-1} which indicated the presence of para substitution on the benzene ring. Absorption of 1033, 1127, and 1149 cm^{-1} indicates of the $-\text{SO}_3$ group and absorption of 3443 cm^{-1} which is the absorption of $-\text{OH}$ on $-\text{SO}_3\text{H}$ group. The resulting FTIR absorption is not far from the reference. According to Andreade et al in [13], the success of the sulfonation process was indicated by the absorption of 1040 and 1180 cm^{-1} which was the $-\text{SO}_3$ absorption which indicated the presence of a bound $-\text{SO}_3\text{H}$ group, and the absorption of 840 cm^{-1} which indicated the presence of benzene substitution at the para position. The effect of sulfonation causes the intensity of $-\text{OH}$ absorption in the sPS FTIR spectra to be more intense and prominent (Rath et al in [14]).

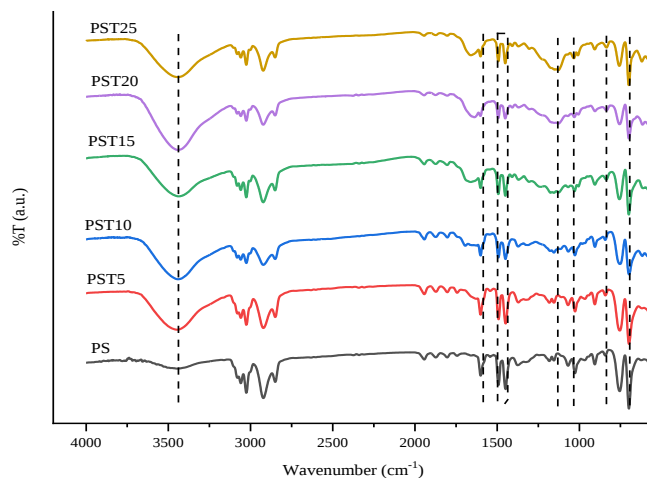


Figure 2. FTIR spectra of polystyrene and sulfonated polystyrene.

Thermal stability of PS and sPS were analyzed using TGA. Figure 3 and Table 1 show the thermogram and the degradation temperature ranges of PS and sPS. PS degradation occurs through one stage of the degradation process, while in sPS occurs three stages of the degradation process. In addition, it can be seen on the thermogram that, sPS5 and sPS10, have a similar degradation appearance to PS. However, there was an increase in thermal stability in sPs 5 and sPS 10 which was indicated by the increase in thermal stability after the addition of sulfonic agents to PS. The presence of intra and intermolecular interaction hydrogen bond in the sulfonate group causes an increases thermal stability (Luo et al in [15]).

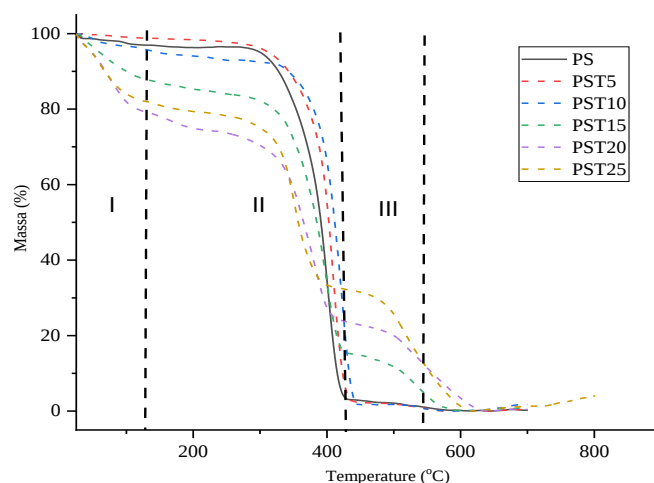


Figure 3. TGA curve of PS and sPS.

The addition of 15 – 25 mmol sulfonic agents showed a significant effect on polymer degradation. Table 1 shows the degradation temperature ranges of sPS 15, sPS 20, and sPS 25. The first stage of degradation occurs in the temperature range up to 100 °C due to the evaporation of water bonded to the sulfonate group (Barrios – Tarzona & Suleiman in [16]). The second stage of degradation shows the degradation of the sulfonate groups in the polymer chain, while the third stage of degradation shows the degradation of the PS main chain. The thermal degradation of cationic sulfonates occurs in several stages, namely dehydration, functional group destruction with loss of SO₂ and oxidative degradation of the polymer matrix (Singare et al in [17]). The degradation temperature ranges of sPS 15, sPS 20 and sPS 25 that occur at temperatures above 100 °C indicate that this material can be used for the manufacture of polymer electrolyte. This shows that the addition of a sulfonic agent can reduce the degradability of the material. The presence of sulfonate groups in the polymer matrix provides characteristics such as increasing hydrophilicity and increasing proton exchange performance so that it can be used as a material for making polymer electrolyte (Jalal et al in [18]).

Table 1 Degradation temperature of PS and PST.

Sample	Degradation Step					
	I		II		III	
	Onset – offset (°C)	Weights loss (%)	Onset – offset (°C)	Weight loss (%)	Onset – offset (°C)	Weight loss (%)
PS			295 – 430	92.28		
PST5			292 – 438	94.27		
PST10			325 – 445	90.24		
PST15	30 – 130	11.72	183 – 426	70.25	426 – 570	14.11
PST20	30 – 125	18.62	195 – 423	51.14	423 – 632	23.99
PST25	30 – 123	16.02	173 – 411	47.23	411 – 606	32.30

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3.2 Cation Exchange Capacity

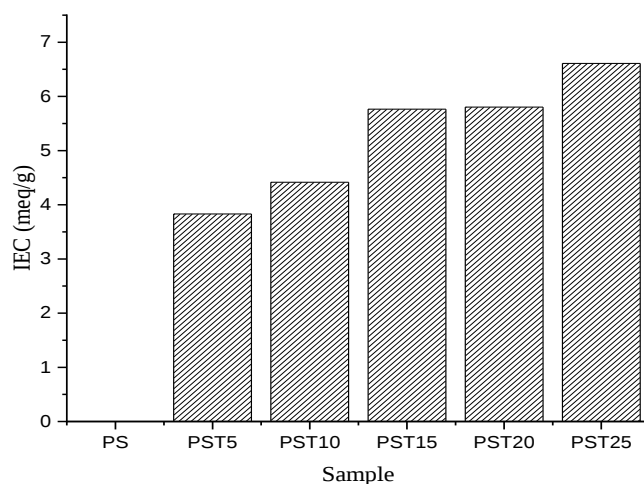


Figure 4. Effect of acetyl sulphate concentration to the cation exchange capacity.

The determination of cation exchange capacity of sulfonated polystyrene was determined using the titration method. This test aims to determine the ability of sulfonated polystyrene to exchange cations bound to the functional group with other cations (Ngadiwiyan et al in [19]). The value of the cation exchange capacity is shown in Figure 4. It can be seen in the figure that the more sulfonating agents are added, the value of the cation exchange capacity is increasing with a maximum value of 6.610 meq/g at sPS 25 with a minimum value of 3.830 meq/g at sPS 5. The increasing CEC indicates an increase in the number of sulfonate groups and the cation-exchange ability of the polymer and that this is better in the application of material polymer electrolyte (Holder et al 2017 in [20]).

4 Conclusion

The synthesis of sulfonated polystyrene was carried out using styrofoam waste using acetyl sulfate as a sulfonating agent. The appearance of the $\text{-SO}_3\text{H}$ group spectra on FTIR indicates the success of the sulfonation process. Polystyrene

undergoes one stage of degradation, while the addition of acetyl sulfate reduces the thermal stability of the material, with thermal resistance still above 100 °C. The value of CEC sPS is proportional to the amount of sulfonic agent added. The highest CEC value is 6.610 meq/g at sPS 25. On a final note, sPS from styrofoam waste can be used as a material for making polymer electrolyte.

Acknowledgments

Author(s) would like to acknowledge Sebelas Maret University for provide facilities in conducting research and testing.

Nomenclatures

CEC	=	Cationic Exchange Capacity
PS	=	Polystyrene
sPS	=	Sulfonated polystyrene

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