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Research Article

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Hybrid material based on sulfonated polystyrene and graphene

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ABSTRACT

Synthesis of hybrid materials based on sulfonated polystyrene (SPS) and graphene (G) have been done. Polystyrene has sulfonated using homogeneous method with sulfonating agent trimethylsilyl chlorosulfonic (TMSCS). Graphene has derived from coal tailings that have been carbonized 400°C and pyrolysis 800°C. Sulfonation degree were obtained 125%, FTIR spectrum showed that a symmetric vibration sulfonate groupe at region 1310-1200 cm^{-1}. Preparation of hybrid materials by mixing sulfonated polystyrene and graphene in solvent dimethyl formamide followed by step slowly evaporating the solvent at 45°C. Thermal properties have studied using TGA and DSC, electrical properties, conductivity and capacitance were measured using Impedance Analyzer at room temperature. From the measurements were obtained conductivity (σ) and capacitance (ε) maximum 13.94 mS/m and 188.32 nF/m respectively.

Keywords: Hybrid material, sulfonated, polystyrene, graphene. coal tailings.

INTRODUCTION

Hydrogen-powered fuel cells generally have a high power density and relatively efficient in their conversion of chemical energy into electrical energy that is more than 40-50%; higher than coal fired power plants or internal combustion engines [1]. Exhaust of hydrogen-powered fuel cells are free of environmentally undesirable gases such as nitrogen oxides, carbon monoxide and residual hydrocarbons are generally produced by internal combustion engines. Carbon dioxide, a greenhouse gas, is also absent from the exhaust hydrogen-powered fuel cells. Thus, using the transportation, electric vehicles especially fuel cell (FCEV), attractive and effective as a clean exhaust emissions and high energy efficiency. These features also make PEMFCs candidate most promising and attractive for a wide variety of applications ranging from portable power/micro electricity and transportation for large-scale stationary electrical systems for buildings and distributed generation [2].

Although promising achievements and prospects PEMFCs, there are three major challenges that commonly include a stable supply of high-purity hydrogen, the reduction of the cost of the system and a variety of technological problems associated with low performance and low humidity [3]. Membrane is a key-component in PEMFCs, emphasis on research aimed at reducing the cost and overcome some remaining technical problems in the PEMFC system (water management, thermal management and control of CO poisoning from the catalyst platinum) has reported. Conventional PEMFCs typically operate with a Nafion membrane. Nafion is a trademark (manufactured by DuPont) of perfluorinated material consists of a chain backbone of carbon-fluoride and perfluoro side chains with sulfonic acid ion exchange group. Favorable properties of polymers lie in the combination between hydrophobicity perfluoronated polymer backbone and high hydrophilicity branch sulfonic acid [4]. It offers good enough performance below 90 °C and have close physical characteristics that are ideal for PEMFC, high ionic conductivity, good thermal stability, sufficient mechanical strength and excellent chemical stability [5].

Graphene has attracted great interest because of the unique structure and properties. To take full advantage of its properties for the application, except for electronic devices, the integration of individual graphene in a polymer matrix to form multifunctional composites developed one of the most promising, because the polymer composites usually have a specific modulus, specific strength, and applications width in the aerospace, automobile and defense industries, etc. In addition, polymer composites can be easily processed and made into complex-shaped components with good preservation of the structure and properties of graphene using conventional processing methods [6].

It is very important to make full use of the right-outstanding bonds of graphene. Compared with the CNT, filler composites before graphene promising for isolated, graphene has a high ratio of surface-to-volume due to inaccessibility of the surface of the nanotubes in the polymer molecule.

Due to exceptional mechanical strength and election trical/thermal conductivity properties of graphene, they show significant potential as a component of new material [7-10]. It is widely recognized that tailoring the solubility properties of graphene is very important to enable their broad application [11-14]. In particular, water-soluble graphene have attracted a lot of attention recently for a number of potential biomedical applications, including biosensing and drug delivery [15-18]. More recently, several approaches function of graphene, including coupling sidewall covalent reaction, the reaction end-groups, and non-covalent interactions exohedral, has been developed to prepare the water-soluble. Among these approaches, covalent sidewall functionalization of graphene with polymeric structures have been shown effective in increasing the solubility of the conjugate polymer-nanotube, even with a relatively low level of functionalization. Furthermore, the flexibility of polymer chemistry allows for control of the final properties of conjugated polymer-nanotube, which is determined by the chemical and physical characteristics of the grafted polymer [19]. However, current methods for the preparation of polymer-graphene conjugate is soluble in water mainly confined to the reaction with carboxylic acid groups bound to the surface-oxidized graphene [20].

In this paper has studied the synthesis of sulfonated polystyrene technique, the effect of adding graphene to bacbone polymer using FTIR and XRD, and thermal properties of hybrid materials through TGA and DSC analysis.

EXPERIMENTAL SECTION

Chemical

Commercial polystyrene and trimethylsilyl chlorosulfonate (TMSCS) were purchased from Aldrich; dimethylformamide, benzene from Merck; methanol from Sigma-Aldrich; NaOH from Merck.

Experimental procedure

Graphene was prepared as a derivative of coal tailings, coal tailing has dried in the oven at 105°C to reduce the water still contained so that when carbonization at temperatures above 400°C. Subsequently chemically activated using 30% phosphoric acid solution with a 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.

Polystyrene was dissolved in solvent at temperature of 25°C under nitrogen stream. The solvent used is benzene. The volume of solvents is required 100% of the mass of the polystyrene used. Trimethylsilyl chlorosulfonic added to the solution at room temperature; during the sulfonation reaction of nitrogen gas flow has maintained. The amount of dissolved polymer was determined base on the mole ratio between the polymer and sulfonating agent used, that is 1: 1.5 with a reaction time of 20 hours, determination of the degree of sulfonation using titration method. Preparation of hybrid materials has done by blending sulfonated polystyrene and graphene in solvent dimethyl formamide, carried out slowly evaporating the solvent at 45°C with the mass ratio between the polymer SPS-graphene 1:1, 1:1.5 and 1:2.

Characterizations techniques

The FTIR spectra were recorded on a Bruker Alpha-P with Attenuated Total Reflectance in a range of 4000-400 cm^{-1}. The thermal stabilities of materials were examined by TG analyses using Perkin Elmer STA 6000. The samples (~10 mg) heated from room temperature to 700°C under N_2 atmosphere at a scanning rate of 10°C/min. DSC measurements was carried out using a Perkin Elmer JADE DSC under nitrogen atmosphere; heating cooling curves were recorded at a 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 therange 2θ between 0° and 70°. Conductivity and capacitance were measured using Impedance Analyzer at room temperature.

RESULTS AND DISCUSSION

From Fig. 1 showed the physical differences between coal tailings before carbonization and after carbonization, where coal tailings after carbonization indicate a rather glossy black color. Furthermore, pyrolysis and activation process were carried out at temperature of 800ºC, chemical activation using 30% phosphoric acid solution with a ratio of 0.5: 1 volume per weight of phosphoric acid and carbon, activation has done for one night with stirring. The

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sequel is pyrolysis at 800°C for 3 hours. The results of pyrolysis were used for reinforcing phase material which had blending with sulfonated polymer.

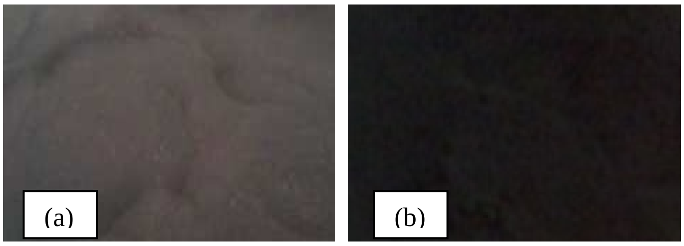

Fig. 1 Carbon before carbonization (a) and after carbonization (b)

FT-IR spectroscopy

FT-IR spectra of the SPS and SPS-G 1:1, 1:1.5 and 1:2 are represented in Fig. 2 showed a strong absorption band as shoulder at 1200 cm^{-1} attributed to asymmetric O=S=O stretching [21]. Vibration of phenyl ring attached a sulfonic –SO_3^- group leads to the peaks at 1005 cm^{-1}. the increase in intensity, the effect of adding graphene this showed in the area of wave numbers 950 -1250 cm^{-1}. From Fig. 2 the SPS-G 1: 1.5 deviation from the spectra information, this possibility has not been homogeneous. Sulfonating agent was used for sulfonation of polystyrene contrast with previous studies that have reported by several investigators. Such as acetyl sulfate, acetyl sulfate as the sulfonating agent prepared by reacting concentrated sulfuric acid and acetic acid anhydride in a solution of dichloroethane at low temperatures. On the other hand sulfonating agent such as sulfuric acid and phosphoric pentaoxide has mixed in cyclohexane solvent. The advantages of using trimethylsilyl chlorosulfonic as sulfonating agent is not spoil the primary structure of the polymer.

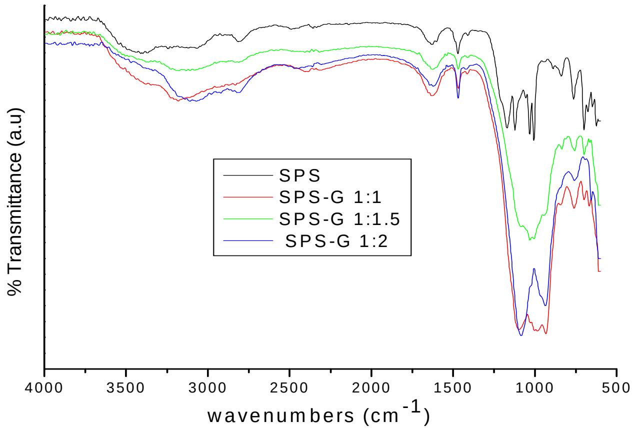

Fig. 2 FT-IR spectra of the SPS and SPS-G 1:1, 1:1.5 and 1:2

Thermal analysis

Thermal properties of SPS-graphene blend membranes were studied by TGA and DSC. In a previous study, decomposition of poly(4-styrene sulfonate) studied through TGA, It has reported that the first slight. From Fig. 3 showed that weight change that occurs from 100 to 150°C was attributed to absorbed water [22]. The second weight loss, which observed over the temperature interval 150–200°C due to degradation of the polymer [22]. In this study, a similar degradation pathway for all the SPS-graphene blend membranes was observed where the first weight change up to 150 °C was due to absorbed humidity in these hygroscopic materials, which is none other than sulfonate group. From Fig. 3 also showed the SPS-G 1: 1.5 deviation from the thermogram information, the same as in Fig. 2.

From DSC analysis has obtained by heating-cooling cycles from 25 to 200°C, and (the glass transition temperature) Tg values of the blends evaluated from the second heating curves. Tg of pristine PS is nearly 108 °C. The glass transition temperature of the blends increased after blending with graphene, which are determined as 123, 126, 128 and 130°C for SPS and SPS-G 1:1, 1:1.5 and 1:2, respectively. The increase in the glass transition temperatures could be attributed to the restriction of SPS polymer segmental motions that may result from the ionic complexation [21]. Shifting in the glass transition temperature is higher than the material originally, this is due to interaction between the sulfonated polymer backbone and graphene causes the molecular movement becomes impeded and produce material more compact so that the glass transition temperature will increase. Besides increasing the glass transition temperature can be caused by the formation of crosslingked between molecules so that complicates the movement of the polymer itself and also that it will increase the value of Tg.

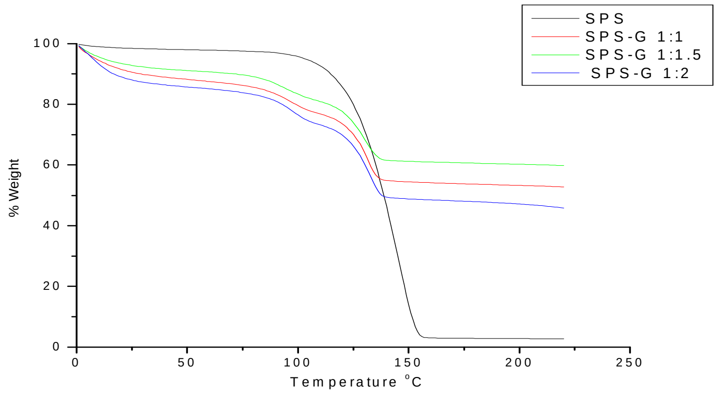

Fig. 3 Thermogram of the SPS and SPS-G 1:1, 1:1.5 and 1:2

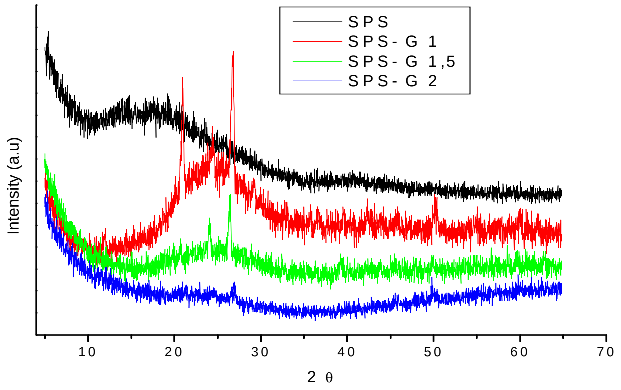

Fig. 4 Difractogram of the SPS and SPS-G 1:1, 1:1.5 and 1:2

The consequences of the addition of graphene has shown on difractogram. From Fig.4 showed that sulfonated polystyrene and SPS-G 1:1 still shows the nature of semi-crystalline, which indicated the existence of an amorphous phase in the region of 20-30° and under 10°. When graphen 1.5 was added, the amorphous phase begins to decline, but the area under the 10° still show a wider amorphous regions. For additional graphene 1: 2 ratio of amorphous phase in the region of 20-30° is not there but the area under 10° still exist.

Table 1. Electrical Properties polistriren sulfonated-Graphene

Sampel	σ mS/m	ε nF/m
SPS	55.92	89.88
SPS-G 1:1	3.81	93.67
SPS-G 1:1,5	6.30	147.96
SPS-G 1:2	13.94	188.32

From Table 1 showed electrical properties of sulfonated polistriren-Graphene. Table 1 has shown that the conductivity seen a decline in the addition of 1:1 and there was a slight increase in 1: 1.5 and 1: 2. While the properties of the capacitance increases with the addition of graphene. From this data it can be said that there is an opportunity sulfonated polystyrene used as proton conducting membranes in fuel cells, while blending sulfonated polystyrene and graphene are also a chance as capacitor material.

CONCLUSION

The results showed that the sulfonated polystyrene can be done using a sulfonating agent trimethylsilyl chlorosulfonic (TMSCS) at room temperature. Interaction between sulfonated polystyrene and graphene has proved through investigation using FTIR, TGA, DSC and XRD. The results showed that the effect of adding graphene to sulfonated polystyrene, in particular shifting the wave number, temperature degraded. and Tg after the material that has been contain graphene. The increase of Tg and reduced amorphous phase after increasing of accretion graphene.

From the electrical properties, sulfonated polystyrene can be used as proton conducting membranes in fuel cells, while blending sulfonated polystyrene and graphene are also a chance as capacitor material.

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