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The synthesis and characterization of graphene oxide in polystyrene-ethylene-butylene-polystyrene

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Graphical Abstract

ABSTRACT

The graphene based material called graphene oxide (GO) is receiving a great deal of attention due to its outstanding properties such as low electronic conduction, but good proton conductivity because of the presence of hydroxyl, carboxylic, and epoxy groups in the hydrophilic region of GO. Furthermore, the sp^2 carbon layer present in the hydrophobic region of GO can help to increase the mechanical strength of the membrane due to its strong covalent bonding. Fabrication of graphene based polymer composite has significantly shown the improvement of membrane properties. In this study, polystyrene-ethylene-butylene-polystyrene (PSEBS) was applied in the preparation of graphene oxide (GO) polymer nanocomposite. GO was synthesized from graphite powder using Hummer's method. The dope solution of PSEBS-GO composite membrane was prepared by introducing GO solution with 7.5 wt. % PSEBS solution with ratio of 1:3. Characterization of GO and PSEBS-GO were studied by using attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy and scanning electron microscopy (SEM). The synthesized GO was also characterized using X-ray diffractometer (XRD). The GO structure was confirmed by using ATR-FTIR with the presence peaks at 3217.32, 1604.36, 1364.12, and 1050.06 cm^{-1} assigned to O-H stretching vibrations of the C-OH groups and water, C=C stretching, C-OH stretching (in COOH), and C-O stretching respectively. The XRD analysis showed GO is successfully prepared from graphite due to the presence of intense peak at $2\theta = 11.285°$. From micrograph of SEM, the images of exfoliated GO have a bulky structure due to the defect of graphite layer when oxygen groups are introduced in the graphite layers, while PSEBS-GO having smaller pores compared to the PSEBS membrane. The percentage of water uptake of PSEBS and PSEBS-GO membrane were 29.07% and 38.26%, respectively.

Keywords: graphene oxide, polystyrene-ethylene-butylene-polystyrene, polymer composite membrane

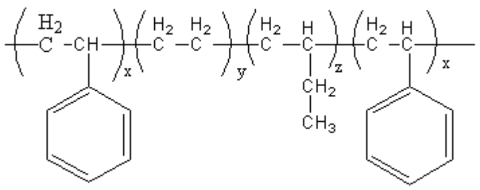
1. INTRODUCTION

Graphene oxide (GO) is the product of chemical exfoliation of graphite that has been known for more than a decade. It consist of a sheet-like graphene framework with carbonyl (C=O), hydroxyl (-OH), carboxyl (-COOH), and phenol groups, as well as oxygen epoxide groups (bridging oxygen atoms) at both sides. GO was synthesized based on Hummer's method through the oxidation of graphite powders using oxidants including concentrated sulfuric acid, nitric acid and potassium permanganate [1]. The presence of the hydrophilic oxygen groups allow GO to exfoliate into individual graphite oxide nanoplatelets in water, forming a homogeneous solution. It also has a low electronic conduction, but good proton conductivity as a result from the presence of hydroxyl, carboxylic, and epoxy groups [2]. GO has attracted a huge deal of attention in recent years for production of graphene-based materials, including in graphene-polymer composite membrane due to its large surface area, functional groups, and intrinsic mechanical and thermal stability which can effectively modify the physicochemical properties of the polymer matrix [3].

Graphene oxide have shown a great potential for various applications as it acts as the fillers for polymer matrix composites. Years ago, researchers have made successful attempts for GO and graphene-polymer composites similar to carbon nanotube (CNT) – based polymer composites [1]. The usage of GO in membrane can increase the mechanical strength of the membrane due to its strong covalent bonding of sp^2 carbon layer present in the hydrophobic region of GO. On the other hand, its large surface area, fuel barrier property and electronic insulation property make GO particularly attractive as filler in composite membrane.

The application of graphene oxide polymer composite membrane has been widely used in microbial fuel cell (MFC), a green sustainable energy source that directly transform microbial metabolic energy to electricity. MFC has been used all over the world as an alternative source of energy due to the problem of global climate change caused by greenhouse gases and environmental pollution. One of the main component in MFC is the proton exchange membrane (PEM) which, an ideal PEM should facilitate the transfer of protons from anode to cathode while at the same time it should prevent the transfer of other materials such as the fuel (substrate) and the electron acceptor (oxygen) [4]. Nafion, a perfluorosulphonic acid ionomer membrane is the commonly used PEM due to their high proton conductivity [5], but due to the problem faced by this type of membrane, researchers and manufactures started to use other material to replace Nafion.

As an alternative, the usage of polystyrene-ethylene-butylene-polystyrene (PSEBS) had been introduced to overcome the problems. PSEBS, as shown in Figure 1, is a thermoplastic tri-block elastomer that consist of styrene blocks (thermoplastic phase) dispersed in ethylene-butylene matrix (elastomeric phase). Hwang *et al.* [6] reported that the PSEBS membrane shows excellent mechanical stability due to the elasticity of the rubbery ethylene and butylene phase. Thus, it has excellent mechanical, chemical, and thermal stability. This type of polymer has been modified including as polymer composite membrane in order to improve its properties as the membrane in MFC [4,5,7].



x = number of styrene group

y = number of ethylene group

z = number of butylene

Figure 1 Structure of polystyrene ethylene butylene polystyrene (PSEBS)

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage was focused on the synthesized of GO using Hummer's method. The second stage was preparation of PSEBS membrane and PSEBS-GO composite membrane, while the last stage was for characterization. Graphene oxide (GO) was prepared from graphite powder by modified Hummer's method [8]. 100 mL of concentrated H_2SO_4 was cooled in ice bath to 5°C. Then, 4 g of graphite powder and 4 g of $NaNO_3$ was added carefully with constant stirring for about 15 minutes to homogenize the mixture. The temperature of the mixture was maintained below 10°C. Next, 12 g of potassium permanganate was added gradually with the temperature kept below 20°C. The mixture was stirred for another 30 minutes. Finally, the mixture was taken out from ice bath and allowed to sit in room temperature. The temperature of the mixture gradually increases up to 40°C after about 15-20 minutes. After that, 100 mL of distilled water was added while the temperature maintained about 90-98°C. The mixture was stirred for 40 minutes. The mixture was further diluted with 180 mL distilled water and 20 mL of 30% hydrogen peroxide. The color of the solution was brownish. The mixture was left overnight. Then, the mixture was washed with 100 mL of 10% hydrochloric acid and followed by several times with distilled water to remove the remaining solvent. The resulted thick mixture was then place in plastic membrane and soaked in distilled water to reduce the acidity of the solution down to pH 6-7. The water was replaced daily for at least one week. The solution resulted was next undergone sonication to allow dispersion of GO in the solution. Finally, the solution was transferred into petri dish and dried in the oven at 60°C for 24 hours.

7.5 wt.% of PSEBS solution was prepared by dissolving 7.5 g of PSEBS in 92.5 g and 72.0 g of THF for preparation of PSEBS and PSEBS-GO membranes respectively. The solution was stirred continuously at 60°C for about 3 hours to obtain a homogenous solution. On the other hand, 0.5 g of GO were added into 20.0 g of THF and sonicated for 3 hours to be used in PSEBS-GO membrane fabrication. The GO mixture was added into the PSEBS solution (7.5 g PSEBS in 72.0 g THF) and was vigorously stirred for 24 hours at 70°C to homogenize solution. The other prepared PSEBS solution was used to fabricate PSEBS membrane using a dry-wet phase inversion method. The homogenous solutions was cast onto a glass plate using a casting knife, and exposed to room temperature (~1s). After that, the glass plate covered with casting solution was horizontally immersed into deionized water for at least 1 hour to remove the solvent and solidify the membrane structure. The membrane was then peeled from the glass plate and dried in room temperature [9, 10]. The PSEBS-GO membrane was fabricated the same way as PSEBS membrane. Later, in stage three, the resulting GO, PSEBS membrane and PSEBS-GO composite membrane were characterized to study their structural and properties by using ATR-FTIR, SEM and XRD, including water uptake.

3. RESULTS AND DISCUSSION

3.1. Preparation of PSEBS and PSEBS-GO membrane

Graphene oxide was prepared by the treatment of graphite using strong mineral acid and oxidizing agent as in the Hummer's method. The solution obtained from the method was black in color indicates that GO was successfully synthesized. The color of dope PSEBS solution obtained by dissolving solid polymer PSEBS with solvent THF was colorless as presented in Figure 2 (a). As a result, the mixing of GO solution and PSEBS solution has no significant change in color, which means it stayed as black color (Figure 2 (b)). Therefore, the resulted dried PSEBS-GO membrane obtained from dry-wet phase inversion method was light black while the PSEBS membrane is colorless because the black GO solution was not added.

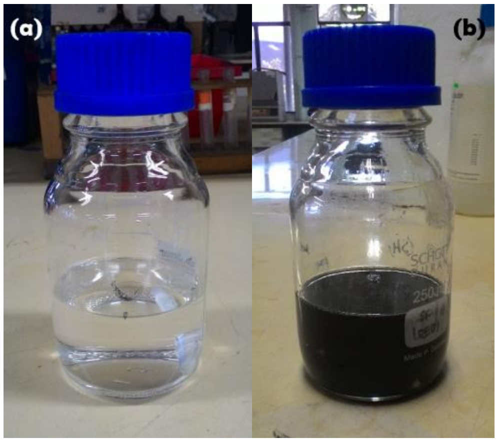


Figure 2 Color of dope polymer solution (a) dope PSEBS solution (b) dope PSEBS-GO solution

3.2. X-ray diffraction pattern of GO

Figure 3 shows the XRD pattern of GO nanosheet. Work by Cao *et al.* (2011) stated that the typical graphite particles showed a sharp diffraction peak at 2θ = 27°, while GO gave an intense peak at 2θ = 11°. In this study, an intense peak for GO was observed at 2θ = 11.285°, which indicates that the layer distance was much higher than that of graphite [11] and it can be concluded that the graphite was successfully oxidized as it was comparable to the previous study.

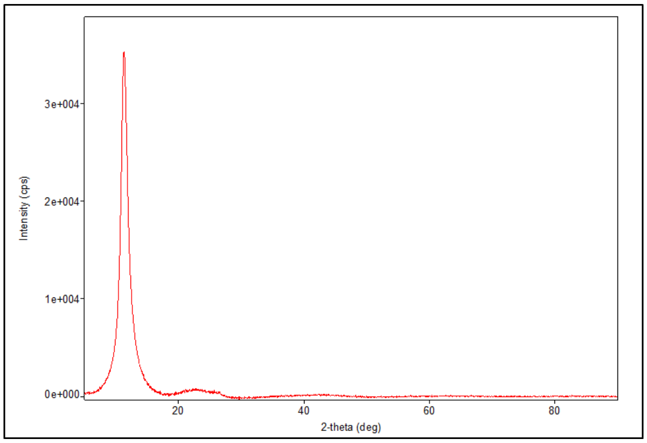


Figure 3 X-ray diffraction pattern for GO nanosheet

3.3. Molecular structure of GO and composite membrane

FTIR spectra obtained for graphite powder and GO are shown as in Figure 4. Since pure graphite does not have any functional group [2], no peak was found in the graphite spectrum while four new peaks were observed in GO spectrum as a result of graphite oxidation. From previous study, the characteristic absorption bands for GO were observed at 3401.37, 1631.72, 1224.37, and 1049.78 cm^{-1}, for O-H stretching, C=C stretching, C-OH stretching, and C-O stretching, respectively [2]. In this study, the peaks found at 3217.32, 1604.36, 1364.12, and 1050.06 cm^{-1} are assigned to O-H stretching vibrations of the C-OH groups and water [8], C=C stretching, C-OH stretching (in COOH), and C-O stretching respectively. Therefore, these peaks confirmed the structure of synthesized of graphene oxide.

The FTIR spectra for pure PSEBS membrane and PSEBS-GO composite membrane were obtained as in Figure 5. From the spectra of PSEBS and PSEBS-GO, the bands that present at 1492.11 cm^{-1}, 1459.59 cm^{-1}, 1378.12 cm^{-1} for PSEBS spectrum and at 1492.67 cm^{-1}, 1457.46 cm^{-1}, 1378.49 cm^{-1} for PSEBS-GO spectrum are attributed to the aromatic skeletal which the characteristic band of PSEBS. There are no significant difference between both spectra. The typical peaks of GO in PSEBS-GO spectrum presented in Figure 5(b) does not obviously observed might be due to overlap of these peaks with the characteristic peaks of PSEBS due to low doping amount of GO.

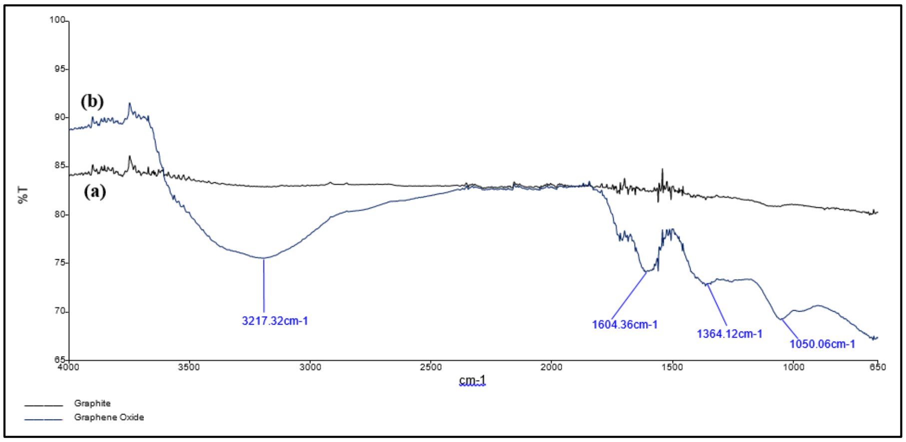


Figure 4 FTIR spectrum of (a) pure graphite powder (b) synthesized GO

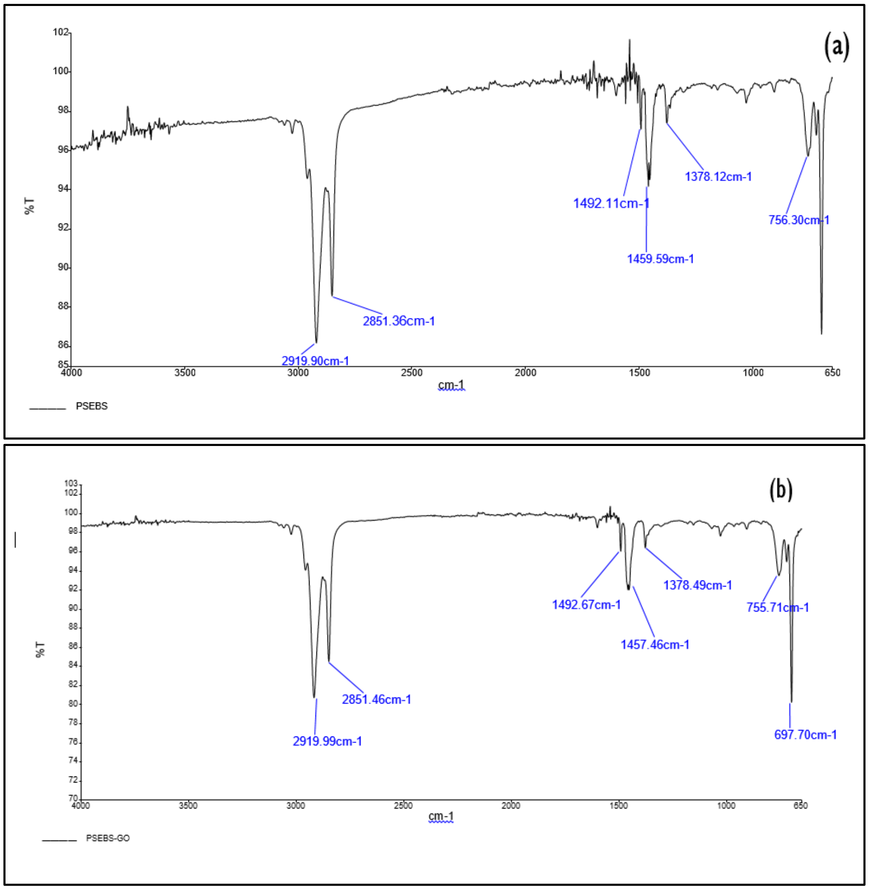


Figure 5 FTIR spectra for (a) PSEBS membrane (b) PSEBS-GO composite membrane

3.4. Surface morphology of GO and composite membrane

A scanning electron microscope (SEM, COXEM) at an operating voltage of 30.0 kV was used to investigate the morphology of the obtained materials. Morphological structure of GO synthesized from graphite powder using Hummer's method was observed in SEM under magnification of 3.0k as shown in Figure 6. The bulky structure observed was due to the introduction of oxygen functional group in between graphite layer caused the expansion of the interlayer spacing [8], while the exfoliated layered structure resulted from thermal exfoliation [12].

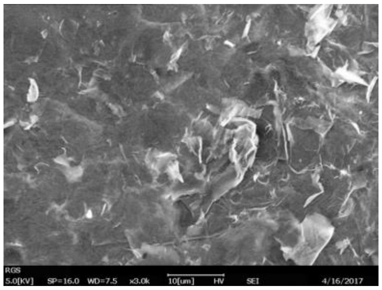


Figure 6 SEM image of GO

The surface morphology of PSEBS membrane and PSEBS-GO composite membrane was analyzed from scanning electron microscope (Figure 7) with 100 magnification. From the observation, the pore structure in PSEBS-GO are smaller than in PSEBS membrane indicates that GO particles was dispersed into the polymer matrix and it blocked the big size of pores in PSEBS membrane. The surface of PSEBS-GO slightly rough might be due to agglomeration of GO on the surface. The dispersion of GO inside the PSEBS particle cannot be observed due to the lack of information on the micrograph as it only revealed the surface morphology. However, GO particle is predicted to be presented inside the PSEBS structure as a result of the intercalation method.

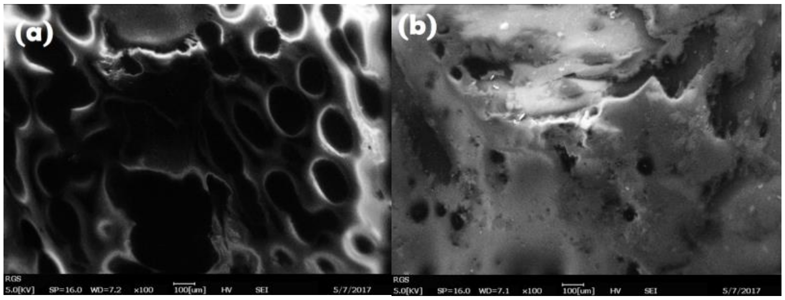


Figure 7 SEM images of (a) PSEBS membrane (b) PSEBS-GO membrane

3.5 Water uptake

The result of water uptake of the membranes were plotted as in Figure 8 with the percentage of water uptake were 29.07% and 38.26% for PSEBS and PSEBS-GO membranes respectively. The values shows that membrane with filler took up higher amount of water uptake as compared to the one without it when they were immersed in liquid water. These indicates that GO membrane filler could helped the membrane to take up more water for ion conductivity when it is being applied in MFC. Even though water uptake is an important criteria for the application of PSEBS membrane in MFC because of the direct dependence of proton conductivity on water uptake, too high water uptake could cause the membrane to lose its shape and to form wrinkles when dry even at room temperature [2]. Therefore, this aspect of GO composite membrane need to be controlled.

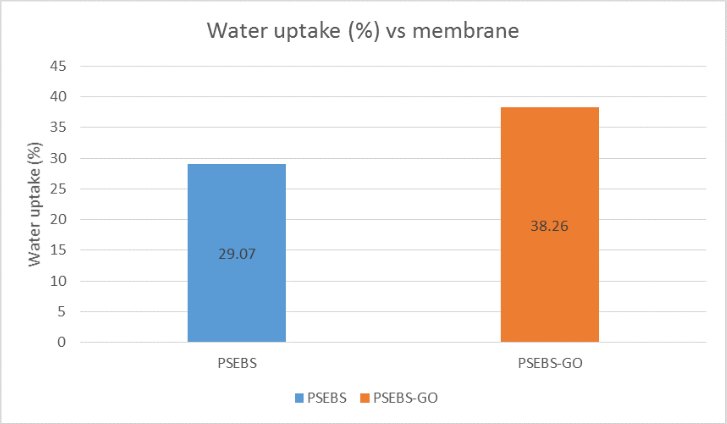


Figure 8 Graph of water uptake (%) versus membrane

4. CONCLUSION

Graphene Oxide, GO was successfully prepared through Hummer's method with back in color and being characterized using ATR-FTIR, XRD and SEM. ATR-FTIR shows the presence of GO peaks at 3217.32, 1604.36, 1364.12, and 1050.06 cm^{-1}, which are assigned to O-H stretching vibrations of the C-OH groups and water [4], C=C stretching, C-OH stretching (in COOH), and C-O stretching respectively. The XRD value are also confirmed that GO successfully synthesized from graphite as the graphite diffraction peak at $2\theta = 11.285°$ was observed. The surface morphology of GO was obtained from SEM under magnification of 3.0k, where the bulky structure was observed to the introduction of oxygen functional group in between graphite layer.

PSEBS and PSEBS-GO membrane were successfully prepared and characterized using ATR-FTIR and SEM. Spectrum of PSEBS-GO did not show much different from pure PSEBS due to low amount of GO doping. For the PSEBS-GO membrane, the GO was dispersed into the polymer matrix as the pores presented are smaller than that in PSEBS membrane and the surface of the PSEBS-GO was slightly rough due to agglomeration of GO on the surface observed in SEM image under magnification of 100. From the data obtained, the water uptake percentage was higher for PSEBS-GO membrane compared to PSEBS membrane due to the presence of GO filler that gives hydrophilic properties to the membrane and allowed it to adsorb more water molecule.

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