Properties of Graphene Filled Polyaniline Nanocomposite

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Abstract. Graphene, a new carbonous material with two-dimensional (2D) nanostructure, has attracted great attention both in fundamental science and applied research. Polymer nanocomposites have been the subject of fundamental scientific interest due to their immense applicational potential and could be used in differential application. Among the conducting polymers, polyaniline (PANI) is the most promising material for electronic application due to its excellent capacity for energy storage, easy synthesis, high conductivity, and low cost. Graphene were applied in PANI to produce graphene filled PANI nanocomposite. In this study, PANI was synthesized by using interfacial polymerization. Graphene filled polyaniline nanocomposites were fabricated by sonochemical method. The morphology and properties of the composites were characterized by scanning electron microscopy (SEM), high resolution transition electron microscopy (HRTEM), fourier transform infrared (FTIR) spectroscopy and electrical conductivity test. Graphene filled PANI nanocomposites has great applicability in electronic, optical and magnetic materials. From the results of four point probe resistivity measurement, graphene filled PANI nanocomposite shows better electrical conductivity, 17.2831 S/cm which increases around 17 times compared to pure PANI, 1.1617 S/cm.

1. Introduction

Graphene is essentially a single layer of graphite in the form of a hexagonal lattice of carbon atoms bonded in the sp² configuration. Due to its ultrathin, two-dimensional, sp²-bonded carbon nature and unprecedented properties, graphene have been intensively studied [1]. The combination of the nanomaterial with polymer is very attractive not only to reinforce polymer but also to introduce new electronic properties based on the morphological modification or electronic interaction between the two components. Depending on the nature of the components used and the method of preparation, significant differences in composite properties may be obtained. Conductive polymer composite have several advantages over their pure metal counterparts including lower cost, ease of manufacture, high flexibility, reduced weight, mechanical shock absorption ability, corrosion resistance and conductivity control [2].

Polyaniline is most likely chosen to be the conductive polymer backbone for graphene polymer composites because of its ease of synthesis, low cost, excellent environmental stability and many interesting chemical, electrical and optical properties [3]. Composite of graphene nanopowder (GNP) coated with PANI produced by in situ polymerization of aniline monomer was reported by Li et.al [4]. In this study, PANI was synthesized by using interfacial polymerization. The objectives of the present study are to synthesize PANI using surfactant and to investigate the properties of PANI nanocomposite produced using multilayer graphene.
2. Experimental study

2.1 Materials

The raw materials and chemical used in Polyaniline synthesis were aniline (ANI), ammonium persulfate (APS), hydrochloric acid (HCl) and sodium dodecylbenzene sulfonate (SDBS). Commercial multilayer of GNP used in graphene filled PANI nanocomposite. GNP and HCl were supplied by SkySpring Nanomaterials, Inc. and J.T. Baker and ANI, APS and SDBS were supplied by Sigma-Aldrich Sdn. Bhd.

2.2 Methodology

2.2.1 Synthesis of polyaniline. In the synthesis of PANI, 4 mmol (0.372 g) of ANI was dissolved in 20 mL HCl (1 M) and stirred with magnetic stirrer for one hour. About 4 mmol (0.913 g) of APS was dissolved in 20 mL HCl (1 M) and magnetically stirred for one hour. APS was used as an oxidant (initiator). Then, the APS solution was added into the ANI solution and was left at room temperature for 6 hours. Finally, the black green precipitate was collected and washed several times by acetone and distilled water. The pure PANI was then dried at ambient temperature for 24 hours.

Another set of PANI is prepared using the same method as above; the only difference is that surfactant with amount of 0.7 g of SDBS was added in the solution of APS and HCl. After both APS with SDBS solution and ANI solution was mixed, the colour of polymerization solution changed with polymerization step. In the initial stage, ANI/ SDBS/ APS solution was colourless with high transparency. As the polymerization proceeded, the colour of the solution changed from white through yellow, brown and finally to green, which indicates the formation of PANI emeraldine salt (ES).

2.2.2 Fabrication of Commercial multilayer graphene filled polyaniline nanocomposite. In the synthesis of commercial multilayer graphene filled PANI nanocomposite, GNP suspension was prepared by adding 0.5 g of graphene in the solution of HCl (100 mL). 2 mmol (0.7 g) of SDBS was added into 20 mL GNP suspension (5 g/L) and the mixture was ultrasonicated for 30 min. About 4 mmol (0.372 g) of ANI was rapidly poured into the above mixture and stirred for another one hour. Then, about 4 mmol (0.913 g) of APS, (the molar ratio of ANI/ APS is 1) which dissolved in 20 mL HCl (1 M) and magnetically stirred for one hour was added to the mixture drop by drop. The reaction was kept for 20 h with continuous stirring in the ice bath. Finally, the product was collected and washed repeatedly with distilled water, then dried in a vacuum oven at 80 °C for 24 h.

2.3 Characterization

In this study, PANI powder and commercial multilayer graphene (CMLG) filled PANI nanocomposite was characterized using a Perkin Elmer Spectrum One FTIR spectrometer by transmittance techniques. The surface topography, morphology of PANI, PANI nanocomposite samples were observed under FESEM model Zeiss Supra 35VP. HRTEM (Tecnai G2 20 s-twin, Fei.) was employed to monitor the multilayer graphene, surfactant-modified PANI and CMLG filled PANI composite powder morphology in terms of particle size and shape. A four point probe is a simple apparatus for measuring the resistivity of polymer samples and polymer composites sample.

3. Results and discussion

PANI was added with surfactant and CMLG filled PANI nanocomposites. Figure 1 shows the combination FTIR spectrum of PANI and PANI with SDBS nanocomposite. The vibrational bands of 850, 1150, 1300, 1500 and 1600 cm\(^{-1}\) are referred to formation of PANI while vibrational bands of 1000, 2900 and 3200 cm\(^{-1}\) are referred to incorporating of SDBS into PANI\(^{[6]}\). The peak at 850 cm\(^{-1}\) is
attributed to the out-of-plane bending of C-H. The peak at 1150 cm$^{-1}$ is due to quinonoid unit of doped PANI \cite{7}. The peak at 1300 cm$^{-1}$ is attributed to the C-N stretching mode. The main peaks at 1500 and 1600 cm$^{-1}$ can be associated with C=N and C=C stretching vibrations of quinone and benzene rings, respectively \cite{8}. The vibrational band at 1000 cm$^{-1}$ is attributed to S=O bond, 2900 cm$^{-1}$ which is asymmetric $-CH$ stretching and 3200 cm$^{-1}$ which is symmetric $-CH_2-$ bond \cite{9}. The presence of the above bands suggested the PANI was coated successfully on the surface of graphene.

![FTIR spectrum](image)

**Figure 1.** FTIR spectrum of the combination of (a) PANI with graphene, (b) PANI and (c) PANI with SDBS surfactant

The SEM images of PANI and PANI with SDBS surfactant show in Figure 2 and 3 respectively. In Figure 2, surfactant-free PANI shows a thicker and more aggregated structure compared to the surfactant-modified PANI (Figure 3). The particle size and surface morphology were dependent on surfactant because the surfactant was adsorbed physically to the growing polymer. SDBS surfactant consists of hydrophilic sulfonic acid and long hydrophobic alkyl chain \cite{10}. The surfactant-modified PANI with hexagonal shaped is believed to have better performance compared to thicker, globular shaped surfactant free PANI, due to the high surface area and small diameter of hexagonal shaped PANI \cite{11}.

![SEM images](image)

**Figure 2.** SEM images of PANI at magnifications of a) 5 KX, b) 10 KX and c) 30 KX
Figure 3. SEM images of PANI added with surfactant at magnifications of a) 5 KX, b) 10 KX and c) 30 KX

Figure 4 shows the SEM images of multilayer graphene filled PANI nanocomposite with different magnifications. It shows that PANI have been grown on graphene sheet’s surface. There have some sharp corner and semi-transparent of graphene sheet between PANI. In some places embedded flakes of graphene in PANI matrix are seen, suggesting graphene interconnection with the polymer network and forming a highly conducting network.

Figure 4. SEM images of CMLG filled PANI nanocomposite at magnifications of a) 5 KX, b) 10 KX and c) 30 KX

The morphology and structure of surfactant-modified PANI and CMLG filled PANI nanocomposite can be characterized by using HRTEM. Figure 5 shows HRTEM images of PANI added with surfactant, at 10 K and 50 K magnifications. PANI appears irregular, globular shaped in Figure 5. There is some agglomeration also observed in the images. Figure 6 shows HRTEM images of CMLG filled PANI nanocomposite. It shows that graphene sheets appear thin and semi-transparent while PANI appear globular shape in the surface. It is observed that graphene exists not only on the surface but also embedded in the PANI particles. These results confirm that the interaction between graphene and PANI produced a PANI coated graphene sheet. This suggests that the graphene sheets which has high specific surface area which could makes a strong connection with PANI when they are formed. Graphene participate directly in the polymerization of the monomer. Therefore, the properties of the resulting composite particles are strongly dependent on the surface area and thickness of the graphene [12].

Figure 5. HRTEM images of PANI added with surfactant at magnifications of a) 10 K and b) 50K
The electrical conductivities of PANI and CMLG filled PANI nanocomposites are determined using a four point probe resistivity measurement system. Figure 7 shows the comparative bar diagram of PANI and CMLG filled PANI nanocomposites. Doping is the process by which PANI are exposed to charge transfer agent, SDBS through electrochemical oxidation or reduction. Doping of PANI creates new states (donor or acceptor states), which exist within the band gap and are energetically accessible to the pi electrons. This process will increase the conductivity of the PANI because of the increased concentration of charge carriers. In this figure, CMLG filled PANI nanocomposite has higher electrical conductivity than PANI. The increasing in conductivity is due to the high surface area of graphene sheets which could serve as effective percolative conducting bridges. Besides that, the PANI conjugated chains offer lots of conductive paths on the surface of graphene layer, which activates more electrons to participate in the directional movement. The PANI coated graphene layers may cause some interaction between PANI chains and graphene. The synergistic effect of these two parts leads to increase of the conductivity of the composites.

Figure 7. Electrical conductivities of PANI and CMLG filled PANI nanocomposites

4. Conclusion

Incorporation of SDBS which was used in polymerization modifies the structure of PANI. The HRTEM, SEM morphology and presence of the bands at 500, 850, 1000, 1150, 1300, 1500, 1600, 2900 and 3200 cm\(^{-1}\) in FTIR spectrum suggested that the PANI was coated successfully on the surface of graphene. From the results of four point probe resistivity measurement, CMLG filled PANI nanocomposite shows a better electrical conductivity compared to pure PANI. The electrical conductivity of surfactant-modified PANI shows a higher value which is 1.1617 S/cm compared to
pure PANI which is 0.8319 S/cm. The incorporating of multilayer graphene into PANI increases the electrical conductivity of PANI.

Acknowledgements

The authors would like to express appreciation for the financial support from Fundamental Research Grant from Ministry of Education (account no. 6071284) and AUN/SEED-Net, as well as support from the School of Materials and Mineral Resources Engineering Campus, Universiti Sains Malaysia.

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