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Solubilization of Reduced Graphene Oxide by Grafting-On Poly(2-Methyl-2-Oxazoline)

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Abstract. Reduced graphene oxide (rGO), one of the materials regarded as the strongest material is known as insoluble in wide range of solvent. This problem limits the application of rGO on other research. The grafted polymer, poly(2-methyl-2-oxazoline) (N₃-PMeOxz) is soluble in water which could make it possible to broaden solubility of rGO in wide range of solvent. For this experimental study, N₃-PMeOxz is grafted into reduced graphene oxide (rGO) with the purpose of improving the solubility of functionalized rGO and improvement of thermal and mechanical properties of functionalized rGO. Grafted-on reaction between N₃-PMeOxz and rGO were carried out by using oxygen degassification method and heat reaction under nitrogen environment in the presence of N-methyl pyrrolidone (NMP). Characterization of the composite were analyzed by using Fourier's Transform Infrared (FT-IR) for determination of bond exist in the composite and Differential Scanning Calorimetry (DSC) for thermal transition temperature. Solubility test of the composite on few solvent confirm the attachment of PMeOxz onto rGO.

1. Introduction

In 2004, discovery by Geim and coworkers [1] attracts extensive attention to graphene worldwide. Good properties of graphene [2,3,4] leads to the material to become esteemed. Although graphene have many good properties, its great potential were limited by the limited solubility of graphene. Due to this, researcher turns to graphene-based composite to maximized the potential of graphene.

Now, some of the attention turned to reduced graphene oxide which is a form of graphene because of its ease of fabrication and bulk masss production ability [5]. Although it is easier to fabricate reduced graphene oxide, the same limitation of graphene still applied to rGO. Various soluble rGO/polymer composites were already prepared by reseachers to bypass the limitation of rGO.

Eventhough enviromental-friendly approaches like L-ascorbic acid [6] available because of the necessity to keep away from using strong chemicals [7,8,9,10,11], graphene quality from hydrazine



approach still higher compared to environmental-friendly approaches. Due to this, this work used the hydrazine approach and examined functionalization of reduced graphene oxide (rGO) with azido-terminated poly(2-methyl-2-oxazoline) (N_3 -PMeOxz) to obtain PMeOxz-grafted-rGO (Figure 1). PmeOxz is grafted onto rGO by reaction of nitrene chemistry. Reaction of nitrene chemistry were resorted to because high reactivity of the thermally generated nitrene radicals from azido group can react with double bonds in carbon materials such as fullerenes, carbon nanotubes and graphenes to form C-N covalent bonds [12,13,14].

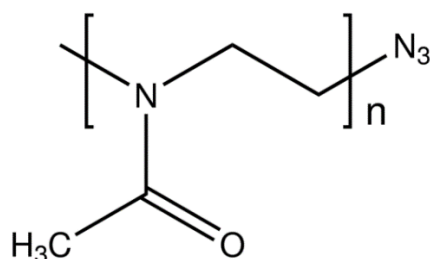


Figure 1. Molecular structure of N_3 -PMeOxz.

2. Methodology

2.1 Materials

Graphene powder (natural), sodium nitrate ($NaNO_3$), sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), hydrazine hydrate ($N_2H_4 \cdot H_2O$), poly(2-methyl-2-oxazoline) (N_3 -PMeOxz), n-methyl pyrrolidone (NMP), deionized water (DI), isopropyl ether (IPE), dichloromethane(DCM), acetone (Ac), tetrahydrofuran (THF) and Methanol (MeOH).

2.2 Preparation of reduced graphene oxide (rGO)

Preparation of graphene oxide (GO) was done using modified Hummer's method [15-17]. The mixture of 0.60 g of $NaNO_3$ and 1.20g of natural graphite were mixed inside 200 mL round bottom flask. Then, to this mixture will be added 27.6 mL of H_2SO_4 and the mixture cooled to 0 °C using an ice-water bath. The temperature of the mixture is kept to below 20 °C by adding slowly 3.6 g of $KMnO_4$ to the slurry. Temperature were kept at 35 °C in an oil bath for 30 min and stirred vigorously. Before heating the mixture to 98 °C and kept for 30 minute, droplets of 56 mL of deionized (DI) water were gradually added. The mixture is then for 10 minute were cooled by using ice-water bath. The mixture is then oxidized by adding 1.20 mL of 30% H_2O_2 and 168 mL of DI water. Centrifugation of the mixture were done at 3000 rpm for 5 minute after cooling at ambient temperature. Supernatant solution were removed and the remaining solid were washed with DI water for few times until the pH of the solid become neutral. The solid (graphite oxide) undergoes centrifugation again and dried in vacuum overnight to be collected.

Graphite oxide were grounded gently using mortar and pestle. 0.02 g of the ground graphite oxide and 5 mL of DI water were charged to a propylene tube. The tube were ultra-sonicated for 30 minute and small amount of solution must be drawn for UV-Vis characterization. This cycle of ultrasonication and UV-Vis were repeated for 5 times for the accumulation time of 3 hour. Exfoliated graphene oxide were isolated by centrifugation (1000rpm, 10minutes). Heat the graphene oxide (GO) to 60 °C for 24 hour to completely dry the GO. The synthesized GO were confirmed from the increasing of absorbance of UV-Vis that occur due to the exfoliation of graphite oxide into GO.

Dried GO weighed 80 mg were added into 24 mL of DI water. Hydrazine hydrate (40 μ L) were dropped into the mixture to perform reduction at 95 °C for 24 h. Upon completion, rGO were isolated

via centrifugation for 10 min at 2500 rpm, washed few times using water. The sediment is then filtered using vacuum pump and dried under vacuum oven.

2.3 Preparation of PMeOxz-g-rGO

Nitrogen bubbling method were utilized for grafting reaction of PMeOxz and rGO. Under nitrogen atmosphere, the mixture of 20 mg rGO, 20 mg N₃-PMeOxz and 10 mL NMP were stirred thoroughly for 15 minute by bubbling nitrogen into the mixture. Then, the mixture were heated at 160 °C under nitrogen atmosphere for 24 hour. The resulting mixture containing PMeOxz-g-rGO and unreacted rGO. After the mixture were cooled, it is then centrifuged at 1000 rpm for 30 minute and filtered with TEFLON filter (0.45µm) to remove unreacted rGO. To precipitate PmeOxz-g-rGO, IPE were used. Freeze-dry were utilized. The resulting sample is then analysed by using FT-IR to ensure no traces of azide compound still remains.

3. Results and Discussion

To determine the extent of exfoliation of graphite oxide into graphene oxide, an aliquot of the supernatant solution were taken at every 30 ultrasonication for 3 hour for characterization by using UV-vis spectroscopy. From the results obtained (Figure 2), the absorbance for peaks at 230 nm and 300 nm increases for each consecutive 30 minute of ultrasonication. This is in agreement with previous research done by Ogino et al [18]. From the research by Paredes et al [19], the increasing peak at 230 nm ($\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds) and 300 nm ($n \rightarrow \pi^*$ transitions of C=O bonds) are indication of an increased concentration of dispersed GO.

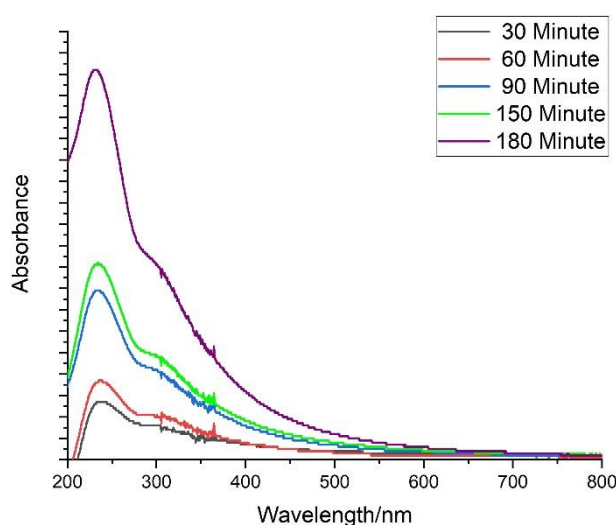


Figure 2. UV-vis of exfoliation of graphite oxide into graphene oxide

IR spectra pattern of N₃-PMeOxz, rGO, PMeOxz-g-rGO are shown in Figure 3. For IR spectra of N₃-PMeOxz, peak at 2100 cm⁻¹ is observed due to azide groups. It is the characteristic peak of azide groups. After reaction of rGO and N₃-PMeOxz, characteristic peaks exhibited by N₃-PMeOxz also were observed at 1500 cm⁻¹, 1400 cm⁻¹, 1200 cm⁻¹. Contrastly, azide groups's characteristic peak at 2100 cm⁻¹ disappear completely from PMeOxz-g-rGO thus confirming the successful complete conversion of azide precursor into nitrene which also conform to previous research [20].

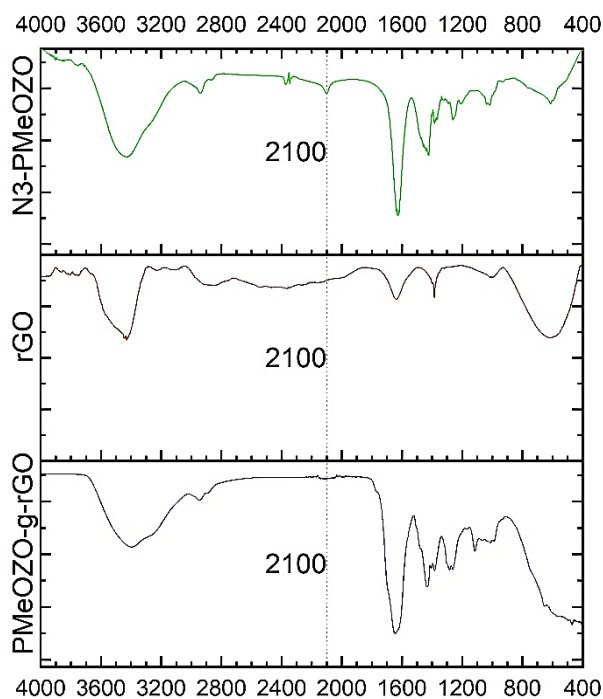


Figure 3. IR spectra of N_3 -PMeOxz, rGO, PMeOxz-g-rGO

Figure 4 shows the DSC curve of rGO, N_3 -PMeOxz and PMeOxz-g-rGO. The melting point of N_3 -PMeOxz is observed at 180°C while no obvious range of melting temperature is observed on DSC curve of rGO. After functionalization of PMeOxz onto rGO, it is observed the exothermic heat flow is better in comparison with rGO which confirm the attachment of PMeOxz onto rGO due to high exothermic heat flow of N_3 -PMeOxz. This is in agreement with the IR spectra of PMeOxz-g-rGO showing the removal azido group while retaining peak that exists on IR spectra of rGO.

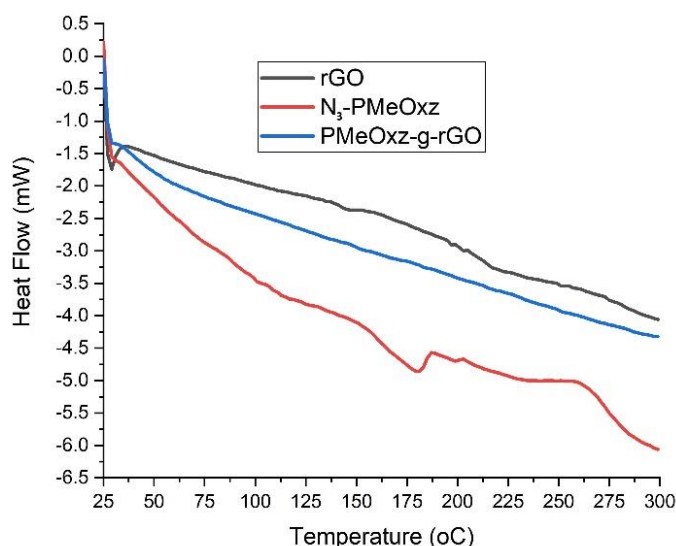


Figure 4. DSC curve of rGO, N_3 -PMeOxz and PMeOxz-g-rGO with heating rate of $10^\circ\text{C}/\text{min}$. Downward indicates exothermic heat flow.

Digital pictures were taken to display the solubility and dispersion quality of rGO, N₃-PMeOxz and PMeOxz-g-rGO in different solvents, immediately after dissolve in solvent (Figure 5, 6 and 7). The rGO were confirmed from the fast settling down of the sample compared to graphene oxide in distilled water that take more time to settle down. To identify the stability of the dispersibility and solubility of the sample with solvent pictures were again taken after 3 hour and 24 hour. Digital pictures for PMeOxz-g-rGO shows that after 3 hour and 24 hour, dispersibility still the same with digital pictures of the sample after immediately dissolve in various solvent. The suspensions was left for two weeks (Figure 8) to determine the stability of each suspension for long term storage. The results obtained as shown by the figures and table shows that PMeOxz-g-rGO have good dispersion and exhibit excellent stability in NMP, acetone and DCM.

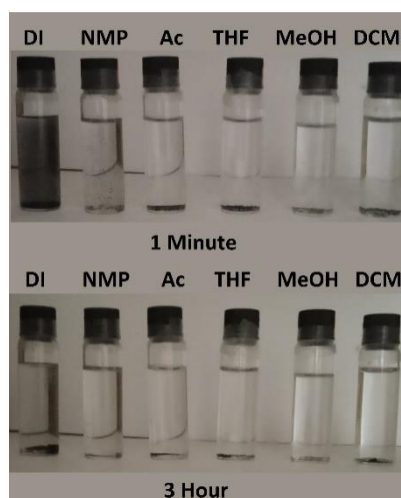


Figure 5. Digital picture of rGO dispersion in solvent. Top: After 1 min. Bottom: After 3 h.



Figure 6. Digital picture of N₃-PMeOxz solubility in solvent. Top: After 1 min. Middle: After 3 h. Bottom: After 24 h.

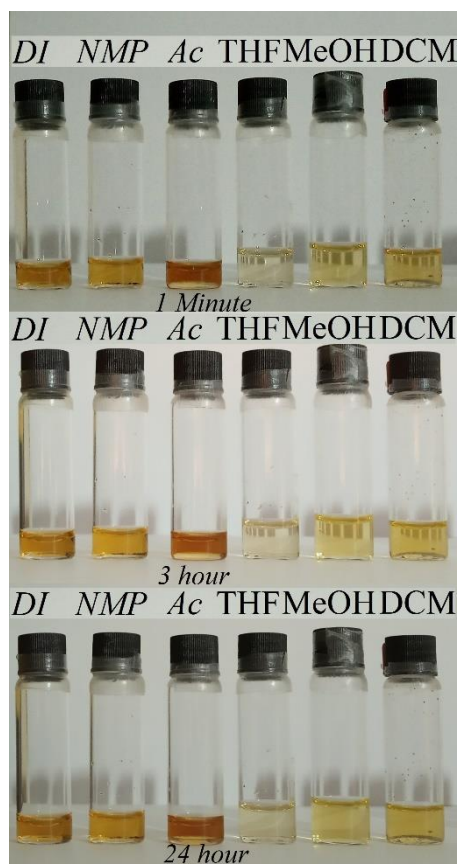


Figure 7. Digital picture of PMeOxz-g-rGO dispersibility in solvents. Top: After 1 min. Middle: After 3 h. Bottom: After 24 h.

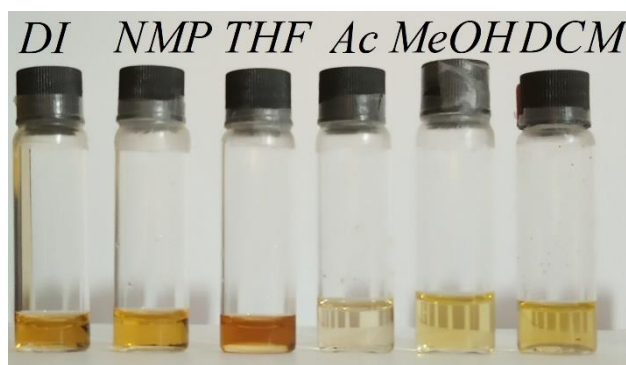


Figure 8. Digital picture of PMeOxz-g-rGO dispersion stability after 2 weeks.

Solubility of N_3 -PMeOxz explained the dispersibility of PMeOxz-g-rGO and also confirm that the grafting of N_3 -PMeOxz onto rGO was successful as shown in Table 1. For reference, dispersibility of rGO [21] also included in Table 1 to shows the dispersibility of rGO before been grafted.

Table 1. Dispersibility of PMeOxz-g-rGO and solubility of N₃-PMeOxz.

Solvent	Dispersibility PMeOxz-g-rGO	Solubility N ₃ -PMeOxz	Dispersibility rGO
DI water	Good	Good	Poor
Methanol	Good	Good	Poor
Acetone	Good	Good	Poor
DCM	Good	Good	Poor
THF	Poor	Poor	Poor
NMP	Good	Good	Poor

4. Conclusion

Functionalization of rGO with azido-terminated PMeOxz were successfully synthesized with the purpose of obtaining PMeOxz-g-rGO which has good dispersibility in various organic solvents. One-step nitrene chemistry were employed for synthesis of PMeOxz-g-rGO. IR analysis indicated that PMeOxz chains were introduced onto the surface of rGO through covalent bond formation. Changes in DSC curve from attachment of polymer into rGO also been observed which confirm the grafting of PMeOxz onto rGO. Solution-based fabrication procedures that utilized graphene can take advantage of the soluble rGO composite.

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