Development of Conductive Graphene/Polyaniline Nanocomposites Produced by In-situ Polymerization and Solvent Blending Method

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Abstract

Polyaniline (PANI) is one of the most promising conducting polymers due to the excellent environmental stability, good electrical properties and easily prepared. Addition of graphene filler in the PANI matrix was found to increase the conductivity of PANI nanocomposites. Generally, conductive nanocomposites can be produced using three types of methods, including in-situ polymerization, solvent blending and melt blending. The present paper aims to study and compare the properties of conductive nanocomposites graphene/PANI fabricated using two methods which are in-situ polymerization and solvent blending methods. Electrical conductivity, thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM) were used to analyze the samples. It is found that in-situ polymerization method is more suitable to be used to produce graphene/PANI nanocomposites samples where better dispersion of graphene fillers and smaller diameter size of PANI fibers were produced by this method compared to that of solvent blending method. Sample produced by in-situ polymerization method showed 88 % higher electrical conductivity and better thermal stability compared to that of solvent blending method.

Keywords: graphene, polyaniline, nanocomposites, in-situ polymerization, solvent blending

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Introduction

Graphene is known as a unique two-dimensional (2D) structure of one layer carbon atoms that is packed into a honeycomb crystal where it has attracted remarkable attentions since its discovery in 2004 [1-3]. Nowadays, graphene is considered as a special and unique material due to its astonishing electrical, mechanical and thermal properties [4-6]. The reason for this interest is mostly due to the versatility of this 2D structure which combines special properties such as greater thermal conductivity (5000 W/mK) [7], high electron mobility (200,000 cm^2/V s) [8, 9], large surface area (2630 m^2/g) [10], high modulus elasticity (1 TPa) [11] and excellent electrical conductivity. These outstanding properties make it a brilliant choice as fillers in composites for diversity of applications such as electrical and energy devices, solar cells, sensors, supercapacitors, etc [12]. Moreover, according to the previous work [6], graphene nanosheet is likely more successful in improving the conductivity properties of nanocomposites than carbon nanotubes (CNT). Compared with CNT, graphene shows much higher surface-to-volume ratio because of the inaccessibility of the CNT inner tube surface to polymer molecules. For that reason, potential applications of graphene have fascinated both industrial and academic interest to include them into polymers as the reinforcing fillers to fabricate nanocomposites [5-6, 13]. The discovery and breakthrough of conducting polymers these days has generated a great interest in conductive nanocomposites.

Intrinsically conducting polymers (ICP) have been discovered in the year 1960. It was expected that ICP would discover their potential applications in many areas such as sensors, electrical, electronics, electromagnetic, electrochemical, etc [14]. Polyacetylene (PA) was the first ICP to be discovered, synthesized by Shirakawa et al. [15]. Following the research on PA, other polymers such as polyaniline (PANI), polypyrrole, poly (phenylene vinylene), polyphenylene, polythiophene and Poly (3, 4 ethylenedioxythiophene) as well as their derivatives, have been produced and stated as a new group of polymers recognized as ICP [14]. Along with all the available ICP, PANI has attracted more attention because of its better stability, ease to synthesize, tunable properties and low cost monomer compared to other ICP. However, the major problem related with the effective utilization of all ICP is inherent in their lesser level of conductivity compared to metal [9-13]. Figure 1 shows the conductivity range of the materials for insulators, semiconductors, metallic conductors and conducting polymer [13].

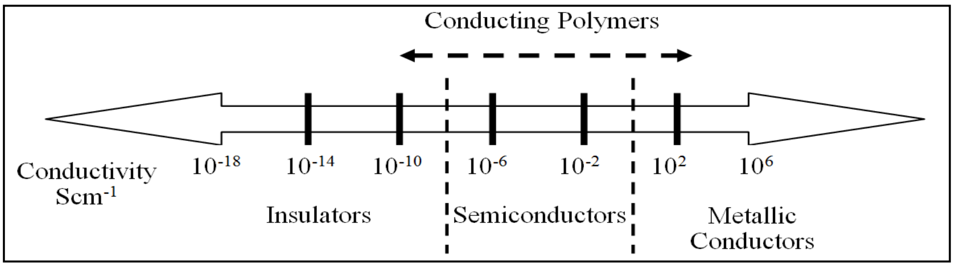

Figure 1: Conductivity range of the materials [13].

Conductivity of the ICP can be increased by adding the conductive fillers in the polymer systems [6, 16]. Recently, nano-sized conductive graphene filler have been explored widely for the development of polymer based conductive composites [15]. Dispersion of the nanofillers is really important in the polymer nanocomposites. Excellent dispersion of filler enhances and improved the maximized reinforced surface area in the polymer matrix, which affect the neighboring polymer chains and subsequently the properties of the whole matrix. For that reason, great efforts have been focused on achieving well-dispersed and homogeneous filler [17]. So far, three main methods including the in-situ polymerization, solvent blending and melt blending, have been engaged to prepare polymer nanocomposites. It was reported that melt blending method resulted in poorer dispersion due to high viscosity of the polymer than those in-situ polymerization and solvent blending methods [18]. In addition, melt blending method is not possible for the PANI application because PANI easily decomposes at temperature below its melting point [19]. Table 1 shows the comparison between in-situ polymerization and solvent blending methods.

Table 1: Comparison between in-situ polymerization and solvent blending methods [12, 17-20].

	In-situ polymerization	Solvent blending
Method	Filler are mixed with monomers and the polymerization process that is performed after that leads to the production of the composites.	Mixing of filler with a polymer that is already dissolved in a solvent by ultrasonication or shear mixing.
Advantages	Provides good interaction between the filler and polymer matrix, facilitating stress transfer and enables homogeneous and outstanding dispersion of filler.	Facile and fast procedure, this method also really versatile, since a number of different solvents can be used to dissolve the matrix and disperse the filler.
Disadvantages	Some difficulties are associated with the increase of viscosity during the polymerization process, that limits the filler loading and the processing of the composites. This method also not commonly applicable to all the polymer types.	Some of the problems involve the use of toxic solvents, the total removal of solvents in the final product and the possible re-aggregation of the filler during one of the preparation steps.

The present paper aims to fabricate and compare the properties of graphene/PANI conductive nanocomposites produced by using in-situ polymerization and solvent blending methods. Electrical conductivity, thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM) were used to analyze the sample. Comparison on the electrical properties, thermal stability and morphology of these two nanocomposites were made.

Materials and Methods

Materials

Raw materials and chemicals that used in synthesize of PANI are aniline, ammonium persulfate (APS), hydrochloric acid (HCl), chloroform ($CHCl_3$) and acetone. Dimethylformamide (DMF), used as a solvent in solvent blending method. These raw materials and chemicals were purchased from chemical company (Sigma-Aldrich, Merck and J.T. Baker) and they were used as received without further purification process. Nanofiller that used are commercial graphene with the size of 11-15 nanometers, supplied by SkySpring Nanomaterials, Inc.

Sample preparation

In-situ polymerization method

2 types of solutions were prepared, 20 mL chloroform which included 4 mmol aniline and 5 wt% graphene filler and the second solution 20 mL hydrochloric acid (1 M) which included 4 mmol ammonium persulfate. Each solution was stirred with magnetic stirrer for 1 hour. Then the oxidant based solution was transferred to aniline based solution. After a short time, the reactions occur and the polyaniline was formed at the interface of the solutions. After 24 hours, the black green graphene/PANI nanocomposites were filtered and washed several times with acetone followed by distilled water. The sample was dried at room temperature for 24 hours. Figure 2 shows the schematic diagram of in-situ polymerization method.

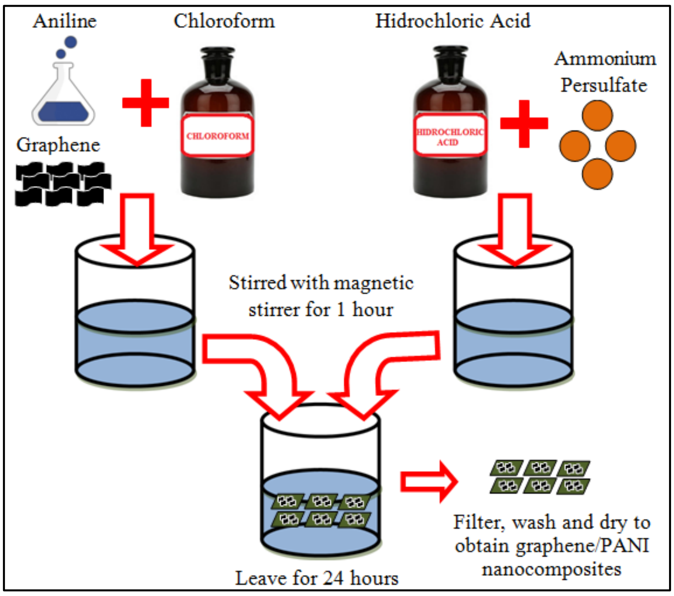

Figure 2: The schematic diagram of in-situ polymerization method.

Solvent blending method

Firstly, PANI was dissolved using dimethylformamide (DMF) solvent. Then, 5 wt% of graphene filler was mixed with the PANI solution using sonicator. The solution was sonicated for 10 min to facilitate filler dispersion. Finally, the solution was kept in the oven for 48 hours at 100°C to remove the solvent. Figure 3 shows the schematic diagram of solvent blending method.

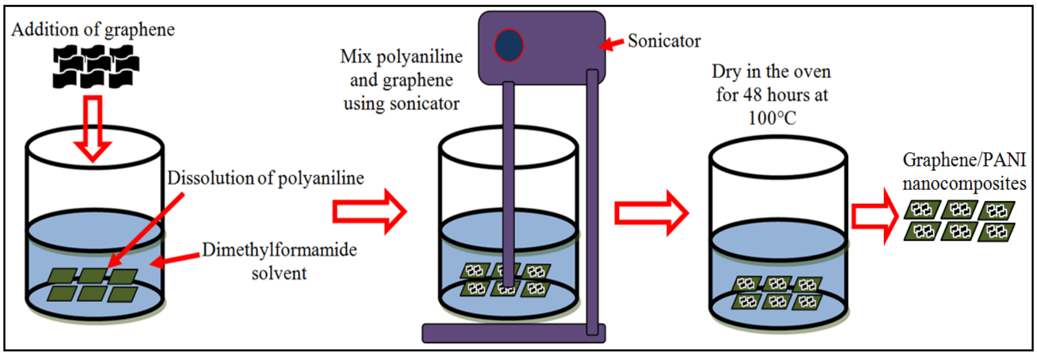

Figure 3: The schematic diagram of solvent blending method.

Characterization

Electrical conductivity (σ) of PANI, graphene and graphene/PANI nanocomposites was measured using PROSTAT PRS-812 Resistance Meter at room temperature. The sample was pressed in the form of disc pellet using 6 tons of force for 5 minutes with a hydraulic press. The measurement was done by placing the pellet on the insulated test bed (Model PTB-920) connected to a probe (PRF-912 probe). The test was mainly used to measure the surface resistance. The conductivity (σ) of the sample was the reciprocal of resistivity (ρ) according to Equation 1.

$$\sigma = \frac{1}{\rho} \qquad (Equation\ 1)$$

σ is the conductivity of the material (Siemens per metre, Sm^{-1}),
ρ is the resistivity of the material (ohm-metre, Ω.m).

Thermal stability and weight residue of PANI and graphene/PANI nanocomposites was determined using Perkin-Elmer instrument with the model Pyris^{TM} 6 thermogravimetric analysis (TGA). Samples were in powder forms, with a total weight of 10 – 30 mg. The analysis was carried out from room temperature up to 600 °C with a heating rate of 10 °C/min in nitrogen atmosphere. The morphology of the sample was characterized using field emission scanning electron microscopy (FESEM, Zeiss SUPRA 35 VP).

Results and Discussions

Electrical conductivity

Figure 4 shows the micrographs of graphene and neat PANI taken at 1000x and 10000x magnification. FESEM results show the morphology of nano layered graphene sheet and PANI nanofibers used in the research.

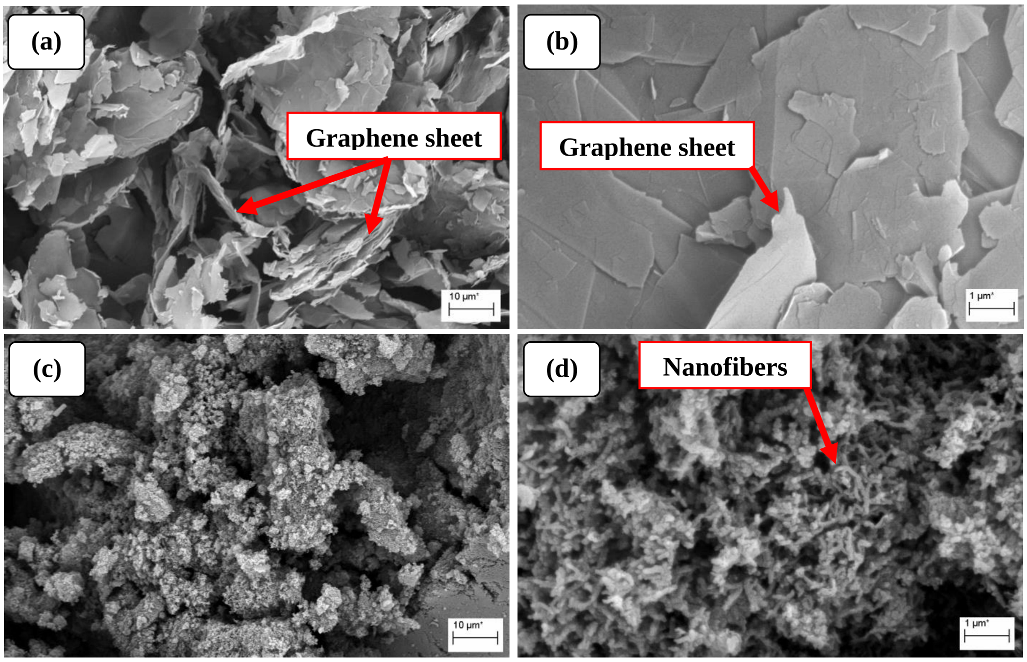

Figure 4: Micrographs of (a, b) graphene and (c, d) neat PANI at the magnification of (a, c) 1000x and (b, d) 10000x.

The electrical conductivity of PANI and graphene/PANI nanocomposites produced by in-situ polymerization and solvent blending method is presented in Figure 5. Electrical conductivity of PANI without presence of graphene filler is relatively low, with a value of 1.7 x 10^{-2} S/m when compared to in-situ polymerization method (7.2 x10^{-2} S/m). Addition of 5 wt% of graphene in PANI improved the electrical conductivity of the nanocomposites by 76% if compared to the neat PANI. According to Li et al. [21], the increase in electrical conductivity was caused by the π-π stacking between the PANI and graphene layers, where the electron mobility within the nanocomposites system increased. However, the electrical conductivity of graphene/PANI nanocomposites produced by solvent blending method with a value of 8.62 x 10^{-3} S/m, showed lower electrical conductivity compared to in-situ polymerization and neat PANI itself.

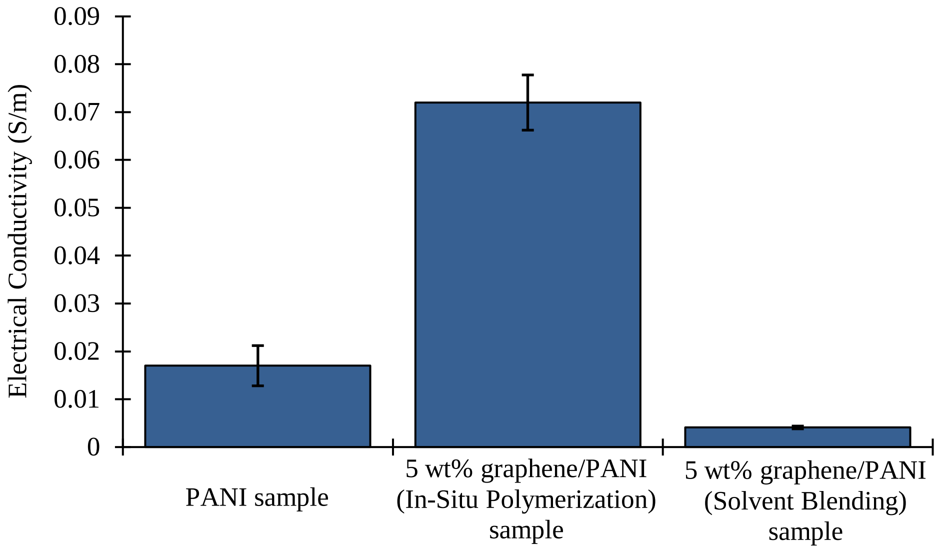

Figure 5: Electrical conductivity of PANI and graphene/PANI nanocomposites using in-situ polymerization and solvent blending method (Electrical conductivity of graphene measured by PROSTAT PRS-812 Resistance Meter is 0.59 S/m).

According to Papageorgiou et al. [12], solvent blending method caused re-aggregation of the filler and reduced the properties of the nanocomposites. Although ultrasonication procedure generally used to disperse the filler in the polymers matrix, but agglomeration and aggregation of filler happen immediately after the mixing process stopped. These problems are generally resulted from the strong van der Waals interaction force between the graphene filler, which will increase the agglomeration of the graphene. Figure 6 shows the micrograph of graphene/PANI nanocomposites produced by in-situ polymerization and solvent blending method. It is found that solvent blending method in Figure 6 (d, e) produced agglomeration of graphene fillers where the fillers are stacked together. In contrast with in-situ polymerization in Figure 6 (a, b), better dispersion of graphene filler in PANI is observed. The uniform dispersion of graphene filler enhances the electrical conductivity of the PANI nanocomposites [16]. It is generally accepted that when conductive filler is dispersed in an insulating polymer, electrical conductivity can be achieved only when the conductive filler concentration is high enough to form a conductive network.

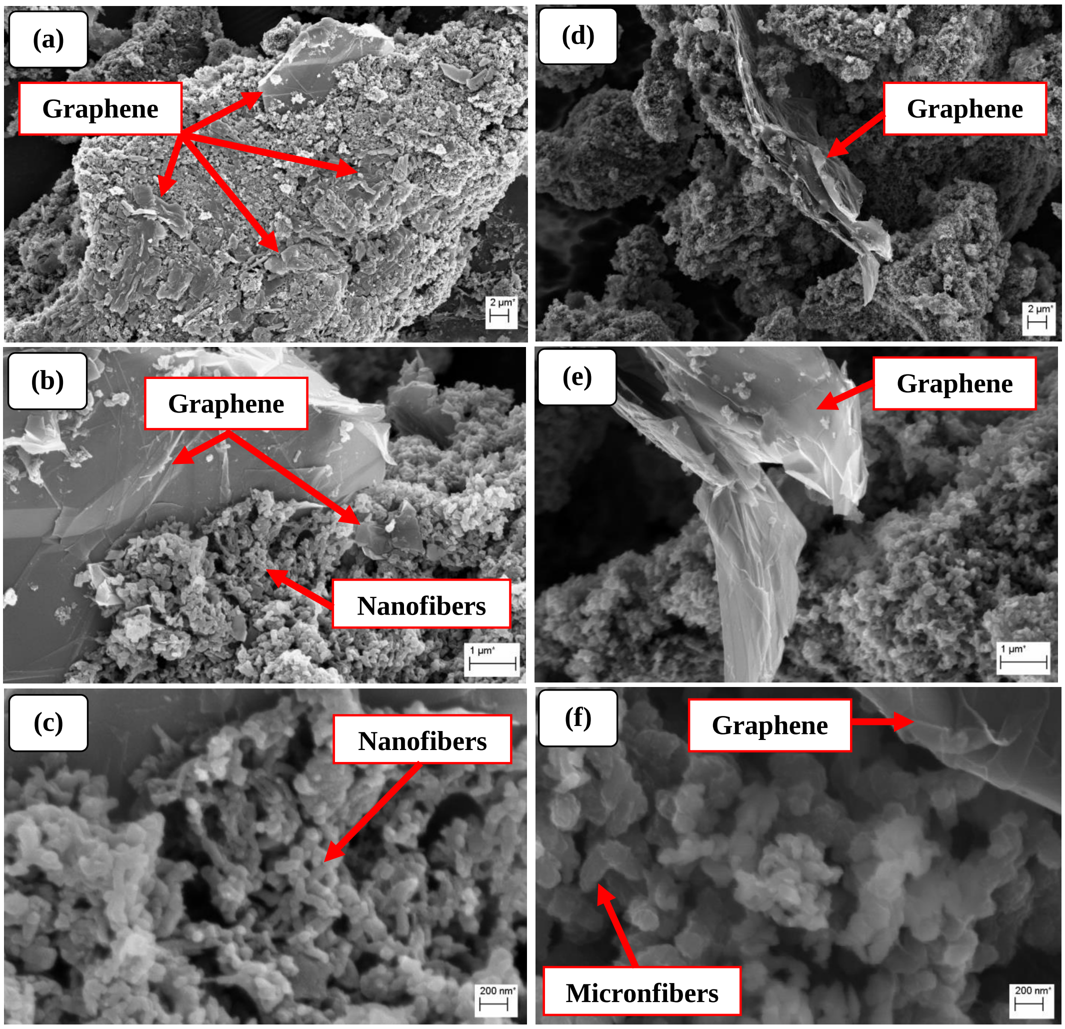

Figure 6: Micrograph of graphene/PANI nanocomposites using (a-c) in-situ polymerization and (d-f) solvent blending method at the magnification of (a, d) 2000x, (b, e) 10000x and (c, f) 30000x.

Moreover, as shown in Figure 6 (c) sample for the in-situ polymerization method showed nano-size of PANI fibers, unlike solvent blending method in Figure 6 (f) where the PANI structure is in micron-size. Verdejo et al. [17] in their research found that solvents used in their study penetrated and modified the graphitic layers of graphite oxide. It is believed that the solvent has influenced and modified the PANI structure to micron-size as shown in Figure 6 (f). Same finding also reported by Liang et al. [22], where they found that, for the sample without solvent, the average length of PANI nanofibers is 400-500 nm and smaller diameter of 30-40 nm with high dispersibility. However, in the presence of solvent, PANI fibers showed relatively bigger diameter and wide size distribution. The result signifies that the introduction of solvent apparently affected the formation of PANI nanofibers [22]. According to Abdolahi et al. [23], smaller and uniform PANI nanofibers have excellent performance compared to bigger and non-uniform PANI micronfibers. Huang [24] also reported on the same finding, where smaller diameter size of PANI nanofibers significantly increases the performance and processibility of PANI. Furthermore, Melad et al. [25] also mentioned that the addition of solvents to the PANI solution lead to decrease in the electrical conductivity. They concluded that solvents resulted in worst dispersity of the PANI in water and in the same time reduce its properties.

Thermal stability

Figure 7 shows TGA and derivative thermal gravimetric (DTG) weight loss curves of neat PANI, in-situ polymerization and solvent blending samples from room temperature up to 600 °C. Apparently, the weight loss percentage of the neat PANI and graphene/PANI nanocomposites samples increased as the temperature increased. As shown in Figure 7, the first stage of weight loss occurred at ~45 to 150 °C is caused by the evaporation of water from the polymer. The second stage of weight loss occurred at ~150 to 280 °C is caused by the elimination of the oligomers and dopant ions [26]. However, for the solvent blending sample, two times of weight loss was observed at this temperature range. DTG curve for the solvent blending method showed significant weight loss at the 180 °C. Dimethylformamide solvent has 153 °C boiling temperature. It is believed that the remaining solvent on the sample has evaporated at this temperature. The third stage of weight loss occurred at ~280 to 370 °C is caused by the decomposition of the aniline monomer in the polymer matrix. Neat PANI showed more weight loss compared to in-situ polymerization and solvent blending sample. Weight loss at the temperature of ~450 to 600 °C can be attributed to the degradation of PANI chains.

As shown in Figure 7, the thermal stability of the nanocomposites slightly improved with addition of graphene into PANI. The incorporation of graphene produced the char barrier effect, performing as a physical protective wall to block the transfer of heat and mass, thus reducing the burning rate and increasing the thermal stability [27]. By comparing neat PANI, in-situ polymerization and solvent blending sample, it can be observed that the thermal stability and weight residue of in-situ polymerization sample is higher than neat PANI and solvent blending sample. This is due to the good dispersion of graphene filler in the PANI nanocomposites, as well as more uniform and smaller diameter size of PANI nanofibers as shown in Figure 6 (a-c) [22-25]. For that reason, high temperature and energy is needed to break down or degrade the polymer chain. This contributed to increase thermal stability of the nanocomposites.

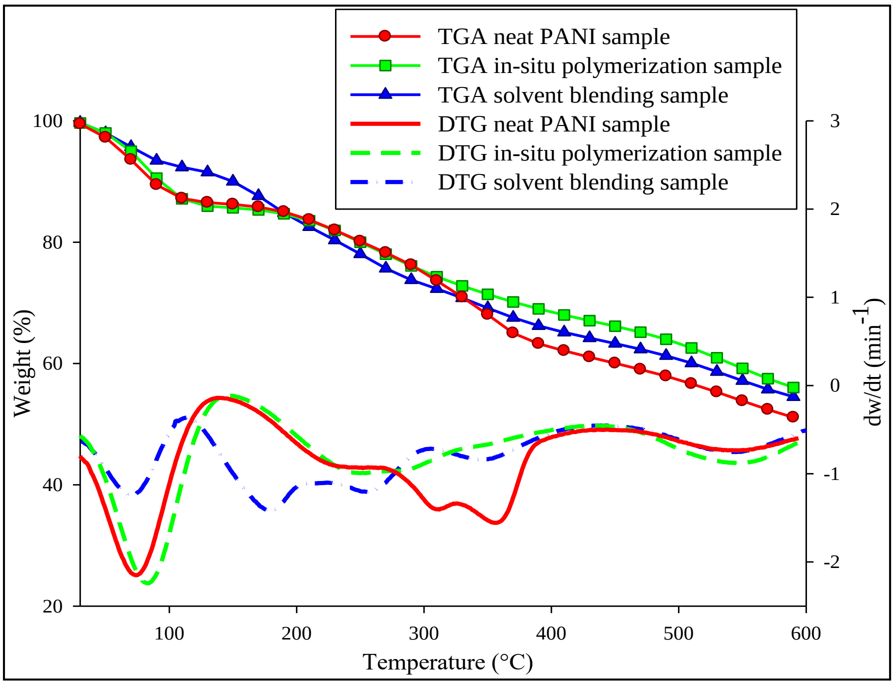

Figure 7: TGA and DTG weight loss curves of neat PANI, in-situ polymerization and solvent blending samples.

Conclusion

The in-situ polymerization method is more suitable to be used to produce graphene/PANI nanocomposites samples due to the ability to produce less agglomeration of graphene fillers compared to that of solvent blending method. In addition, sample produced by in-situ polymerization method showed nano-size of PANI fibers, unlike solvent blending method where the PANI structure is in micron-size. The results were supported by FESEM images where better dispersion of graphene fillers and smaller diameter size of PANI fibers is produced by in-situ polymerization method. These factors basically influence the properties of the nanocomposites where sample produced by in-situ polymerization method showed 88 % higher electrical conductivity and thermal stability if compared to that of solvent blending method. Graphene/PANI nanocomposites sample showed 76 % improvement in conductivity compared to the neat PANI itself. Graphene filler with extraordinary of electrical and thermal properties increased the thermal stability of the nanocomposites.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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