



## Article

# Reinforcement of Epoxy Resin by Additives of Amine-Functionalized Graphene Nanosheets

Tung-Yuan Yung <sup>1</sup>, Yu-Chun Lu <sup>2</sup>, Jeng-Shiung Chen <sup>3</sup>, Yu-Wei Cheng <sup>4</sup>, Ting-Yu Liu <sup>4,\*</sup>  and Po-Tuan Chen <sup>5,\*</sup> 

<sup>1</sup> Nuclear Fuels and Materials Division, Institute of Nuclear Energy Research, Lontang, Taoyuan 325, Taiwan; romeoyung@yahoo.com

<sup>2</sup> Zhongsun Co., Ltd., New Taipei City 220, Taiwan; cssc.sales@gamil.com

<sup>3</sup> Yottadeft Optoelectronics Technology Co., Ltd., Taipei 10460, Taiwan; jsc@yottadeft.com

<sup>4</sup> Department of Materials Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan; louischengblue@gmail.com

<sup>5</sup> Department of Vehicle Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

\* Correspondence: tyliu0322@gmail.com (T.-Y.L.); r92222019@ntu.edu.tw (P.-T.C.)

**Abstract:** In this study, graphene oxide (GO) nanosheets were modified with an amine functional group to obtain amine-functionalized graphene (AMG) nanosheets and then blended with the aniline curing agent of bisphenol-A (BPA) epoxy resin to crosslink BPA epoxy resin. The AMG-blended curing agent and BPA epoxy resin formed an intermolecular hydrogen bond that was stronger than the  $\pi$ - $\pi$  stacking force between benzene rings of graphene nanosheets. Therefore, AMG nanosheets exhibited excellent dispersion in the aniline curing agent. The amine group of AMG-blended curing agents and the epoxy functional group of BPA epoxy resin exhibited strong chemical activity and underwent crosslinking and polymerization. AMG nanosheets were mixed with BPA epoxy resin to form a crosslinked structure through the epoxy ring-opening polymerization of the resin. The mechanical properties of the epoxy resin nanocomposites were significantly improved by the added 1 wt.% AMG nanosheets. The tensile strength was enhanced by 98.1% by adding 1 wt.% AMG in epoxy. Furthermore, the impact resistance of the epoxy resin was enhanced by 124.4% after adding 2.67 wt.% of AMG nanosheets. Compared with other reinforced fillers, AMG nanosheets are very light and can therefore be used as nanocomposite materials in coating applications, the automotive industry, aerospace sheet materials, wind power generation, and other fields.

**Keywords:** amine-functionalized graphene; epoxy resin; composite material; spectral characterization



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## 1. Introduction

Graphene, a new high-profile material, is used extensively because of its excellent performance in applications such as electron transmission, supercapacitors, heat dissipation materials, and photocatalytic catalysts. However, these applications require extremely high-quality graphene. The process of producing such high-quality graphene is expensive, which is not conducive to the material's wide-spread use. The hydrothermal method can be used to produce graphene oxide (GO) at a low cost [1]. However, unlike perfect graphene, numerous oxygen functional groups exist on the basal planes and edges of GO [2,3]. A GO sheet is an electrical insulator. Despite reduction decreasing the number of oxygen functional groups, which alters the electronic structure from that of an insulator to that of a semiconductor with an energy gap of 3.39 eV (O/C ratio = 50%), and further reduction (O/C ratio = 25%) converting energy into conductivity [4,5], reduced GO still has many defect structures and residual oxygen functional groups [6]. Therefore, although many reduction methods have been proposed, obtaining a structure with a perfect graphene lattice is difficult.

Several studies have attempted to enhance the properties of graphene to improve its industrial applicability [7]. For example, graphene was added to epoxy resin to enhance its

mechanical properties [8]. Epoxy resins are widely applied thermosetting plastics. Mixing epoxy resin and a curing agent containing amine groups into graphene followed by heating is an effective and feasible method of enhancing graphene's properties. Aromatic amines are commonly used curing agents in which the amine group undergoes a proton transfer reaction with the chemically active epoxy group, causing the amine group to bond with the ring-opened epoxy group to cure epoxy resin. The aromatic group of the aromatic amine has a strong  $sp^2$  resonance structure, resulting in high hardness of the cured resin, and is widely used in industry. In recent years, studies have focused on amine-modified graphene and its application in the field of composite materials. Heterogeneous nitrogen atoms are typically incorporated into GO to form a commonly used composite. Several studies have demonstrated that graphene grafted with amine-containing molecules may crosslink and polymerize with resins, which improves its mechanical hardness [9], anti-corrosivity [10], electrochemical sensitivity [11], and heat dissipation [12]. For example, Zhou et al. [9] synthesized a functional graphite oxide with an amine-rich surface to produce epoxy composites and claimed that a strong covalent interface formed between epoxy and the functional graphite oxide, which promoted stress transfer. The addition of 0.3 wt.% functional graphite oxide increased the tensile strength, flexural strength, elongation at break, and toughness of the epoxy resins by 20%, 40%, 90%, and 145%, respectively. The mechanical properties of epoxy nanocomposites were significantly improved by the trace additives. However, due to the poor dispersion of the additives in epoxy during preparation, increasing the amount of additives was a challenge.

The one-pot hydrothermal method is a simple method of doping graphene with nitrogen and amine functional groups. This method reduces the cost of production of perfect graphene for high-rigidity applications. Studies have investigated the methods of improving the properties of graphene. Nitrogen doping of graphene enhances several properties of graphene [13–15]. Thus, we extend its application, proposing that three-dimensional crosslinking of amine groups with epoxy resin forms a unique three-dimensional network structure. Such a material is promising for several applications. However, to date, few studies have demonstrated the use of amine-functionalized graphene (AMG) as an epoxy curing agent. P. Paraskar et al. reported that the use of AMG on epoxy matrix composites improved the tensile strength by 67% and impact strength by 152%. The thermal properties of the epoxy–AMG composites for glass transition and thermal stability temperatures increase from 88.4 to 97.3 °C and 351 to 358 °C, respectively. Moreover, Aso Navaee et al. reported the AMG synthesis method with Bucherer reaction in the autoclave of mixing  $NH_3$ ,  $NaHSO_3$  at 170 °C overnight [11,16,17].

To verify this concept, we prepared AMG through chemical synthesis. We used concentrated ammonia to attach GO to the amine group. This process could also exfoliate the few layers of graphite on the surface to obtain graphene. Next, we used spectral measurement to analyze the structure of the product and confirmed that the amine functional groups were grafted onto the graphite sheet. These amine functional groups reacted with epoxy resin. We performed the ASTM D256 impact resistance test to verify that the reaction enhanced the mechanical properties of the composite material. In order to evidence the amine functional groups modified on the surface of GO, we compared the spectral characteristics of AMG with those of few-layer graphite, GO, and polydiallyldimethylammonium chloride-modified graphene oxide (GO-PDDA). The enhancement of the mechanical properties and the impact resistance of the nanocomposites after AMG nanosheets addition will be discussed in this study.

## 2. Materials and Methods

### 2.1. Materials

A method of obtaining AMG that can act as an epoxy curing agent was developed, combined with a formula containing AMG (0.5–2.67 wt.%) as a curing additive into commercial aniline curing agent (CAS #135108-88-2, Henan Tianfu Chemical Co., Ltd., Zhengzhou, China). This AMG curing agent was mixed into a bisphenol-A (BPA) epoxy resin (Nanya

epoxy resin NPEL-128, Taipei, Taiwan), which then formed a cross-linked structure through ring-opening polymerization (ROP) of epoxy groups in the resin. The few-layer graphite used in this study was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). GO and AMG were synthesized using our own approach. Potassium permanganate ( $\text{KMnO}_4$ , 99%), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydrochloric acid ( $\text{HCl}$ ) and PDDA were purchased from Sigma-Aldrich.

## 2.2. Synthesis of AMG Nanosheets

The modified Hummers method [18] was used for GO preparation. First, 2.0 g of graphite was added to the mixture of  $\text{KMnO}_4$  (10 g), 72 mL of concentrated  $\text{H}_2\text{SO}_4$ , and concentrated  $\text{HNO}_3$  (65%) for the oxidation reaction and stirred for 40 min. Then, the residual ions of the reaction were washed with 12 mL of  $\text{H}_2\text{O}_2$  solution (65%) followed by washing with 400 mL of deionized (DI) water multiple times until the solution was close to neutral. Finally, GO was peeled off through ultrasonic vibration. Amine-functionalized graphene [19] was prepared by mixing the GO nanosheets (80 mg in 10 mL DI water) and ammonia water (70 mL) in an appropriate ratio, placing the solution in a hydrothermal tank, and heating it to 200 °C for 12 h. Then, the solution was repeatedly washed with 0.1 M  $\text{HCl}$ , DI water, and alcohol and centrifuged several times until the solution was close to neutral. Finally, the resultant product was dried in vacuum oven at 60 °C for 24 h. The boundary of the resultant amine-functionalized graphene contained the AMG functional group.

We dispersed GO powder (60 mg) in 20 mL of DI water, which was followed by sonication for 10 min. Then, we added 800  $\mu\text{L}$  of PDDA and stirred the solution for 10 min. The solution was heated to 90 °C for 12 h. The color of the solution changed from brown to black. The upper solution was removed through centrifugation several times. The resultant compound was N-containing GO-PDDA with no amine groups.

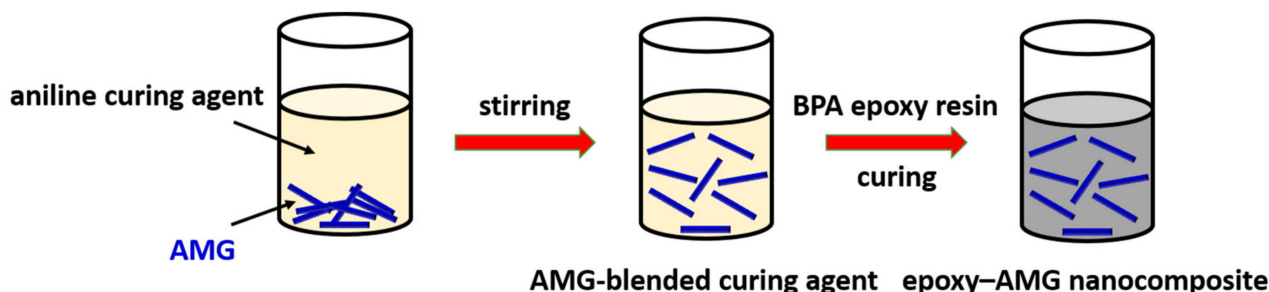
## 2.3. Preparation of Nanocomposite Cured by Epoxy Resin

Self-developed and inexpensive GO and N-containing graphene powder were processed using a high-power ultrasonic crusher to obtain graphene nanosheets, which easily dispersed in the solvent. Liquid bisphenol A (BPA) epoxy resin (Nanya Plastics Co., Ltd., Taipei, Taiwan) with an equivalent epoxy weight of 184–190 g and a viscosity of 12,000–15,000 cP was used in the experiment. The main components of the curing agent (WK113, Guangzhou Wells Electronic Material Co., Ltd., Guangzhou, China) were 4,4'-methylenedianiline, 2-hydroxybenzoic acid, benzyl alcohol, and furfuryl alcohol.

The AMG sheets were evenly dispersed in the final composite. Graphene powder has poor dispersibility in epoxy resin [20]. Multiple three-roll rolling is used in the industry for well-dispersion, but this method increases the viscosity of the graphene and epoxy resin mixture, which limits the applicability of graphene. AMG has a  $-\text{NH}$  or  $-\text{NH}_2$  functional group. By contrast, AMG in the aniline curing agent solution exhibits excellent dispersibility and exists in the liquid state. This is conducive to subsequent dispersion in epoxy resin. Although a little AMG precipitates after a long period of storage, it dissolves into a pure liquid after simple stirring or shaking. This solution-state curing agent mixes evenly with epoxy resin, which considerably improves the mechanical properties of epoxy resin after curing.

To prepare composite materials, the aniline curing agent was first stirred for 10 min and AMG was confirmed to be uniformly dispersed. Then, an appropriate weight of the BPA epoxy resin was mixed with AMG-blended curing agent in different proportions. After configuring the AMG-blended curing agent, BPA epoxy resin (mass ratio of 1:2) was added and the mixture stirred for approximately 10 min to ensure uniform mixing. The solution was poured into a suitable mold and cured at a temperature of 50 °C (Scheme 1). This method of placing the prepared AMG nanosheets in a curing agent solution and then adding epoxy resin improves the dispersion of the composite and prevents poor dispersion, which results in processing difficulties [21,22]. However, the graphite, GO, and GO-PDDA

were difficult to disperse in the epoxy resin curing agent, due to the absence of amine-like N bonding types on the surface of GO. Therefore, we did not prepare composite materials with graphite, GO, or GO-PDDA.



**Scheme 1.** Preparation of epoxy-AMG nanocomposite.

#### 2.4. Characterizations

AMG was characterized using a Raman spectrometer (633-nm He–Ne laser of 100 mW, Horiba iHR550 spectrometer, AST, Ltd., Bensheim, Germany) and Fourier-transform infrared spectroscopy (FTIR, Perkin-Elmer One with ATR, PerkinElmer Inc., Waltham, MA, USA) to identify amine functional groups. Furthermore, X-ray diffractometry (XRD PANalytic X'Pert, PANalytical GmbH, Almelo, Niederlande) with Cu-K $\alpha$  of 1.5406 Å and High Score analytic software was used. Using the experimental measurements, the d-spacing distance could be calculated to confirm whether AMG was exfoliated and synthesized. Transmission electron microscopy (TEM, JOEL 2100F TEM, JEOL Ltd., Tokyo, Japan) was performed to compare GO, GO-PDDA, and AMG. Dynamic light scattering (zeta potential) was measured to determine the physical and chemical properties of the graphene nanocomposite coatings. After curing of the composite material, scanning electron microscopy (SEM, Olympus LEXT OLS 4000 laser confocal microscopy, Olympus Corporation, Tokyo, Japan) and XRD were performed. Tensile, bending, and compression tests of the epoxy-AMG nanocomposites were performed according to the ASTM D3039, D7264, D3410, respectively. The impact resistance test was performed by ASTM D256.

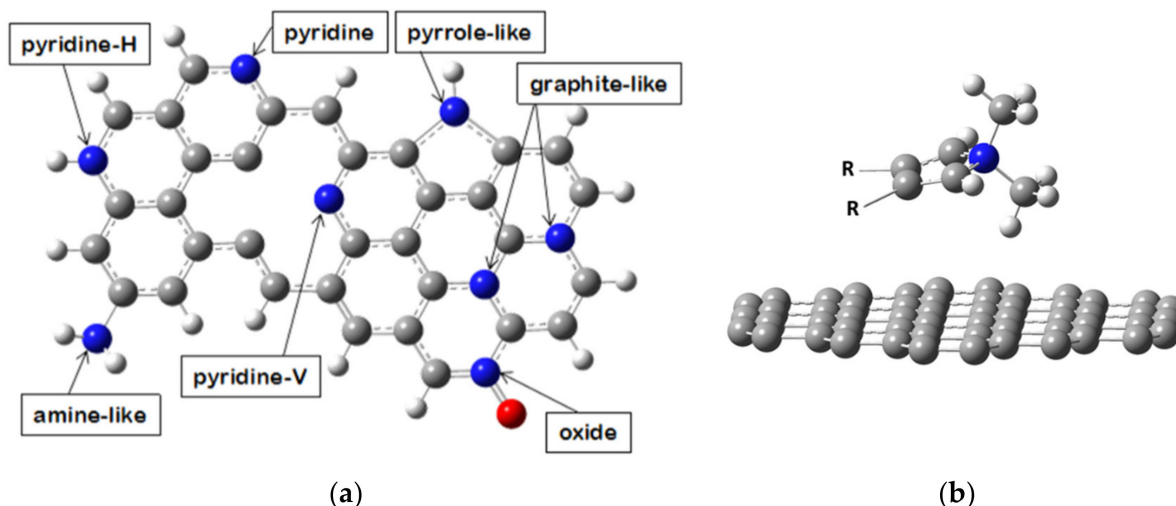
### 3. Results

#### 3.1. Structural Categorization

Unlike graphene, which has a perfect structure, GO has numerous oxygen functional groups on basal planes and edges. Spectroscopic analysis [23] revealed that epoxys (C–O–C) and hydroxyls (C–OH) formed on the surface of graphene, whereas carboxyls (–COOH) and carbonyls (C=O) were distributed at the boundary. Because of the bonding of oxygen functional groups, the thickness of GO was approximately 1 nm, which was slightly greater than the ideal value of graphene (~0.34 nm) [24]. Studies have investigated methods of improving the properties of graphene.

Nitrogen doping into graphene using chemical methods results in pyridinic N, pyrrolic N, graphitic N, nitrogen oxide, and amine-like N bonding types on the lattice of carbon atoms (Figure 1a). Pyridinic N refers to the nitrogen atom being connected to the two carbons on the edge of the graphite surface. In addition to providing an electron to the conjugated  $\pi$  bond system, the nitrogen atom also has two lone pairs of electrons that can adsorb oxygen molecules and intermediate compounds. Pyrrolic N refers to a nitrogen atom with two p-electrons and conjugated with a bond system. Graphitic N is nitrogen connected to three carbon atoms on the graphite base. Studies have revealed that greater pyridinic N content of carbon nanomaterials results in higher catalytic activity for oxygen reduction. In addition to these three common types of nitrogen doping, N–O compounds of pyridinic N are found in nitrogen-doped graphene and carbon nanotubes. In such compounds, a nitrogen atom bonds with two carbon atoms and an oxygen atom.

If concentrated ammonia is used to heat GO, then N–O and amine-like N may form in the compound. In this study, we confirmed that amine-like N was synthesized and aimed to obtain epoxy-based composite materials.



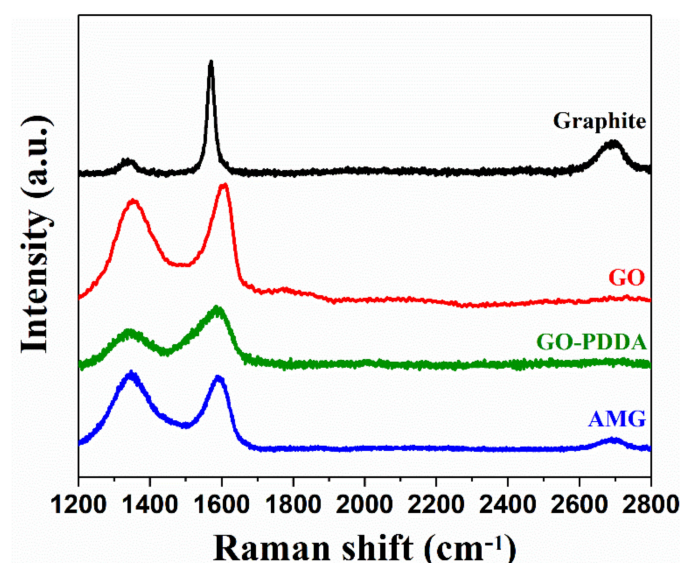
**Figure 1.** The schemes of the atomic structures for AMG and polydiallyldimethylammonium chloride–modified graphene oxide (GO-PDDA) (a) Nitrogen-containing functional group of amine-functionalized graphene synthesized using a chemical method. (b) Schematic of GO-PDDA nanosheets. (Blue is for nitrogen, gray is for carbon, red is for oxygen and the white is for hydrogen).

To examine the spectral characteristics of graphene, we synthesized graphene nitride GO-PDDA without amine groups. We previously investigated the spectral characteristics of PDDA-modified graphene [25]. PDDA is an ionic polymer that dissociates in solutions and generates  $\pi$ – $\pi$  stacks that attach to graphene (Figure 1b). Such composite materials can improve the performance of electrical catalysts.

### 3.2. Characterization of AMG

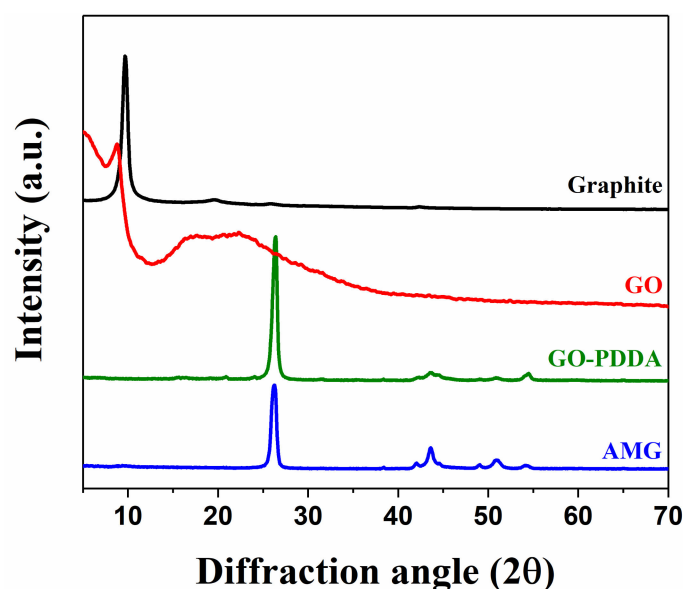
In this study, a 633-nm red laser was used for Raman analysis of GO, GO-PDDA, and AMG. Figure 2 depicts the Raman analysis spectra. Raman peak of D-band and the G-band appeared at approximately 1350 and 1583  $\text{cm}^{-1}$ , respectively. The Raman spectrum of graphite revealed that the intensity of the D-band was lower than that of the G-band ( $I_D/I_G$ : 0.09), which indicates that the benzene ring structure of graphite is closer to perfect, and there are fewer surface defects. For GO, the intensity of the D-band was considerably higher than that of graphite, and the intensity of the G-band was slightly lower. The ratio of  $I_D/I_G$  of GO was increased from 0.09 to 0.83, indicating that the formation of GO oxidation was guided by oxidation and exfoliation of pristine graphite. GO-PDDA and AMG exhibited the same D-band and G-band positions, which indicated that after modification, the structure of the GO benzene ring had not changed. However, the GO-PDDA exhibited relatively low intensity and lower ratio of  $I_D/I_G$  (0.53), indicating that the incorporation and reduction of PDDA reacted to reduce the ratio of  $I_D/I_G$  at room temperature. When amine functional groups are modified on the surface of GO, the surface damage structure leads to increased intensity of the D-band. In addition, the ratio of  $I_D/I_G$  of AMG increased to 1.13 after amino-phenyl functionalization [26]. On the other hand, a 2D peak (2680  $\text{cm}^{-1}$ ) appeared in the AMG spectrum because the oxygen functional groups on the surface of GO were reduced by the amine groups in the solution. The results indicate that the amine-functionalized modification of GO leads to the morphology formation of stacked multilayer graphene.





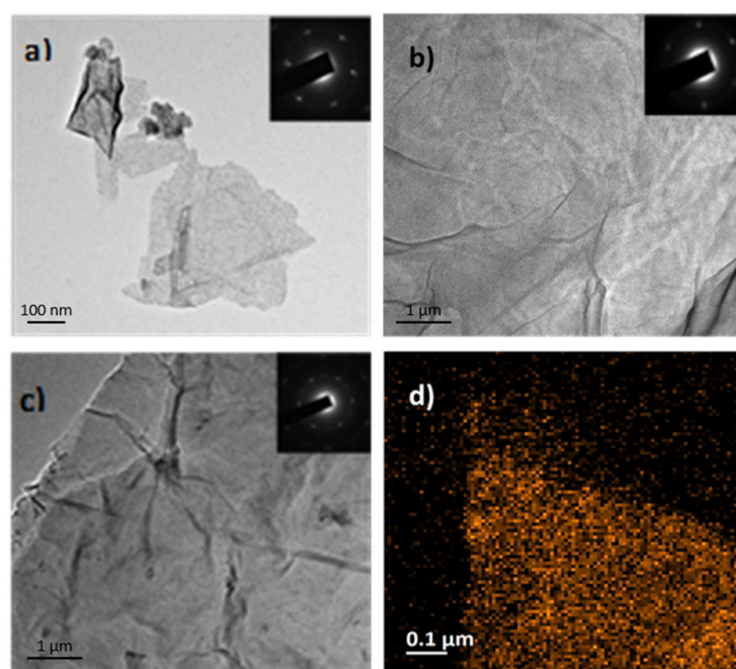
**Figure 2.** Raman spectroscopy analysis of graphite, GO, GO-PDDA, and AMG.

Figure 3 depicts the results of the XRD diffraction patterns. The XRD peak of graphite is located at  $26.35^\circ$ , whereas the peak of GO is at approximately  $8.35^\circ$ . A sharp shift was thus clear in the peak of the wave, which indicated that the graphite layer spacing was stretched or the material even delaminated. Physical stirring resulted in PDDA reacting with GO, which shifted the main peak of GO-PDDA a few degrees to the right of that of GO. The peak of AMG at  $26.01^\circ$  was attributed to the addition of the ammonia solution to reduce oxygen functional groups on the surface of GO or between the layers. The layer of the GO sheet that was originally stretched out became small again.



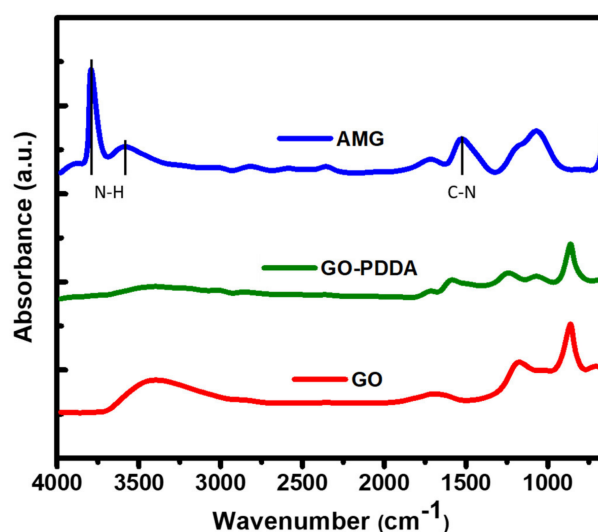
**Figure 3.** XRD analysis of graphite, GO, GO-PDDA, and AMG.

The TEM image presented in Figure 4 indicates that GO, GO-PDDA, and AMG comprised thin nanosheets and exhibited distinct diffraction points, which is typical of the angular structure of graphene. In addition, GO (obtained through oxidation) and GO-PDDA and AMG (obtained through indirect modification) retained the benzene ring structure of graphene. When amine functional groups were modified on the surface of GO, the homogenous distribution of element N was as displayed in Figure 4d.



**Figure 4.** Mapping TEM image analysis of (a) GO, (b) GO-PDDA, (c) AMG, and (d) nitrogen-mapped AMG.

The FTIR analysis in Figure 5 reveals peaks that corresponding to the stretching of functional groups such as O–H, N–H, C–C, and C=O. The surface of the AMG prepared using the modified Hummers method could be grafted with oxygen-related functional groups characterized at  $1100\text{ cm}^{-1}$ . Furthermore, AMG exhibited one prominent peak corresponding to C–N of functional groups at approximately  $1550\text{ cm}^{-1}$ . This was attributed to the nitrogen atom in the AMG, which bonded with carbon atoms. The energy of the O–H functional group, corresponded to the peak at  $3400\text{ cm}^{-1}$ . Peaks corresponding to N–H stretching with asymmetric and symmetric forms were present at around  $3500\text{ cm}^{-1}$ . Peaks were present at approximately  $3750\text{ cm}^{-1}$ , which was attributed to pyrrolic N–H or pyridinic N–H stretching modes. Because GO-PDDA is obtained by physical modification of GO and PDDA, the oxygen functional groups are main features in the spectrum. The spectra of GO-PDDA and GO mainly display O–H, C=O, and C–O–C signals.



**Figure 5.** FTIR analysis of GO, GO-PDDA, and AMG.

Figure 6 presents the cross-sectional SEM image and XRD spectrum of the AMG blended-curing agents added to the BPA epoxy resin and mixed using an ultrasonic mill. The SEM image (left) revealed that the AMG blended-curing agents was dispersed uniformly in epoxy resin, and no clear aggregation of AMG nanosheets occurred. In addition, the XRD graph reveals the signal of carbon material (XRD peak:  $2\theta = 26^\circ$ ), which indicates that the AMG nanosheets did not aggregate at the bottom due to precipitation and were uniformly dispersed.

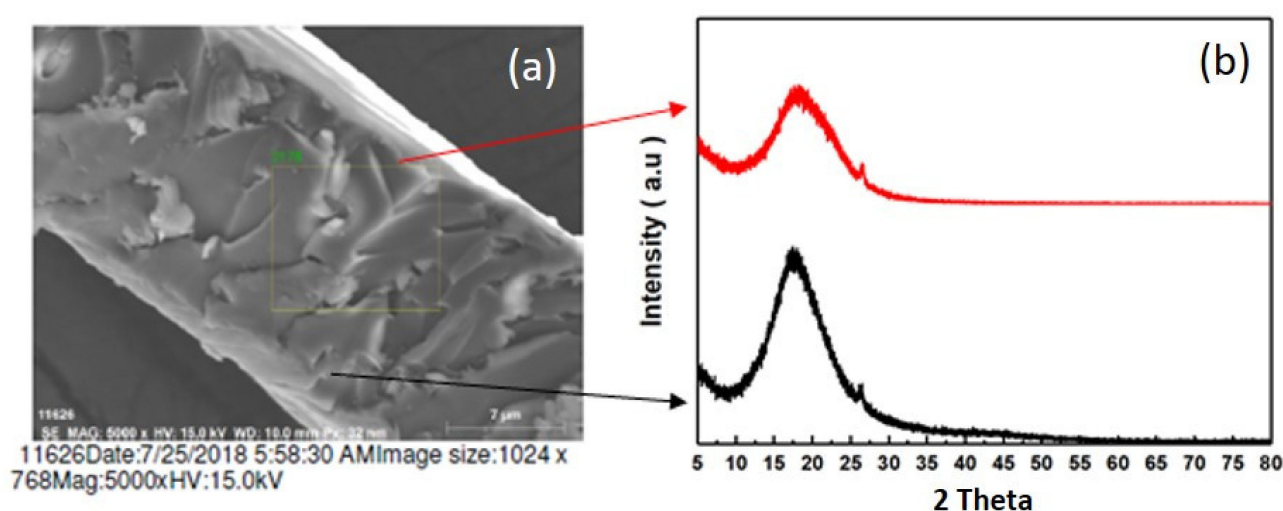


Figure 6. (a) SEM image and (b) XRD spectroscopy of the epoxy-AMG nanocomposite.

### 3.3. Mechanical Tests of the Composite

The contrast experiment for the epoxy-AMG nanocomposite tensile tests was performed according to the ASTM D3039 test criteria. Figure 7 displays photographs of the test samples taken during the mechanical properties and impact resistance tests. Here, 1 and 2 wt.% concentrations of AMG were added to BPA epoxy resin and the mixture centrifuged at 500 rpm for 15–30 min. Curing was then performed at 50 °C. The tensile, bending, and compression tests were performed according to the ASTM D3039, D7264, and D3410 standards. The results are displayed in Table 1. The best tensile, bending, and compression results were obtained for the 1 wt.% epoxy-AMG nanocomposite; this material had tensile strength and bending values which were almost twice those of the epoxy with added AMG. Furthermore, the compression strength was six times higher. However, elongation increased with the addition of AMG.



Figure 7. The test samples for the mechanical properties and impact resistance tests. Photographs from left to right are 0, 0.5, 1, 2, and 2.67 wt.% of AMG nanosheets addition.



**Table 1.** The mechanical properties for epoxy-AMG nanocomposites.

Mechanical Test, Unit	Epoxy	1 wt.% AMG	2 wt.% AMG
Tensile Strength, MPa	26.32	52.15	33.57
Tensile Modulus, MPa	1210	3124	2206
Elongation, %	2.34	3.51	5.72
Bend Strength, MPa	50.32	99.24	48.3
Bend Modulus, MPa	2952	3556	2252
Compression Strength, MPa	14.83	87.14	49.9
Compression Modulus, MPa	450.4	2148	1614

Studies have revealed that AMG can increase the viscoelasticity [27] of composites. We obtained nanocomposites that exhibited excellent mechanical hardness. The impact resistance test data of the cured piece revealed that an AMG content of 2% improved performance by 20%, and an AMG content of 2.67% further improved performance (Table 2).

**Table 2.** Impact resistance test performed according to ASTM D256.

AMG Addition	Test 1	Test 2	Test 3	AVG	Improved %
0.00 wt. %	1.167	1.167	1.275	1.203	0
0.50 wt. %	1.329	1.329	1.275	1.311	9.0
1.00 wt. %	1.329	1.384	1.384	1.366	13.5
2.00 wt. %	1.547	1.438	1.438	1.474	22.5
2.67 wt. %	2.6	2.638	2.862	2.700	124.4

(unit: kg·cm/cm; Izod impact test machine).

The epoxy functional group of BPA epoxy resin exhibited strong chemical activity and underwent crosslinking and polymerization. AMG nanosheets can be well-dispersed in the aniline curing agent of epoxy resin and further crosslink with BPA epoxy resin homogeneously. The mechanical properties and impact resistance of BPA epoxy resin would be significantly enhanced after graphene derivative addition. As long as 2.67% AMG is added, the impact resistance can be increased by 124%. Additionally, other tests according to the ASTM D3039, D7264, and D3410 standards also display comparable improvements, which are not presented in this paper. Compared to the report by Prashant Khobragade et al., the AMG–epoxy impact strengths obtained here are one order higher than their results [28]. Furthermore, Manuel George et al. reported that adding 0.75 wt.% graphene quantum dot could improve the impact strength by 102% [29]. Fulfilling the roles of curing agent and mechanical enhancer for AMG, the 2D materials improved the mechanical properties and were geometrically beneficial also. The results of the impact resistance and compression tests revealed considerable improvements in performance after the addition of AMG to epoxy resins.

#### 4. Conclusions

This study proposed a novel and facile method to synthesize amine-functionalized graphene (AMG) nanosheets blended with a curing agent. The AMG nanosheets were successfully prepared by amine functional groups modified on the surface of GO. The AMG nanosheets can be well-dispersed in the aniline curing agent of epoxy resin and further crosslink with BPA epoxy resin homogeneously. The mechanical properties and impact resistance of BPA epoxy resin would be significantly enhanced after graphene derivative addition. For the impact resistance test following ASTM D256, the resistance performance was increased to 124.4% when an AMG percentage of 2.67 wt.% was used. Reinforcement with the AMG nanosheet yielded satisfactory improvements compared to the previous literature [9,28,29]. In addition, we have improved the dispersion; thus, a higher amount of AMG can be used in the composites. Due to the advantages of the light weight, great heat conductivity, and strong mechanical properties of AMG nanosheets, they would be promising to apply as fillers for epoxy resins in the development of advanced nanocomposites.

**Author Contributions:** T.-Y.Y., T.-Y.L., and P.-T.C. conceived and designed the project. T.-Y.Y., J.-S.C., Y.-W.C., and Y.-C.L. performed all measurements. T.-Y.Y., T.-Y.L., and P.-T.C. prepared the manuscript draft. P.-T.C. edited the language and completed the final article. P.-T.C., Y.-W.C., and T.-Y.L. supervised the project. All authors have read and agreed to the published version of the manuscript.

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