

## Article

# In Situ Processing to Achieve High-Performance Epoxy Nanocomposites with Low Graphene Oxide Loading

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**Abstract:** Modifying the polymer matrix by nanoparticles can be a promising approach to improve the performance of fiber-reinforced polymer (FRP) composites. Organic solvents are usually used for dispersing graphene oxide (GO) well in the polymer matrix. In this study, a green, facile, and efficient approach was developed to prepare epoxy/GO nanocomposites. In situ polymerization is used for synthesizing nanocomposites, eliminating the need for organic solvents and surfactants. By loading just 0.6 wt% of GO into the epoxy resin, Young's modulus, tensile strength, and toughness improved by 38%, 46%, and 143%, respectively. Fractography analysis indicates smooth fracture surfaces of pure resin that changed to highly toughened fracture surfaces in this nanocomposite. Plastic deformation, crack pinning, and deflection contributed to improving the toughness of the nanocomposites. FTIR investigations show that amide bonding was created by the reaction of the carboxylic acid groups in GO with some amine groups in the curing agent during the dispersion processes.

**Keywords:** polymer matrix; mechanical properties; microstructural analysis; plastic deformation



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## 1. Introduction

An increasing demand for the use of high-performance materials in the construction industry has spurred researchers to develop structural fiber-reinforced polymer (FRP) composites for civil engineering applications such as FRP reinforcement for concrete structures [1,2]. FRP reinforcement is successfully replacing traditional steel reinforcement due to its outstanding properties like high tensile strength, resistance to aggressive environments, and easy transport and assembly. Epoxy resin is one of the most important classes of thermosetting polymers that have many applications in the polymer and construction industries because of its outstanding properties like chemical resistance, dimensional stability, good stiffness, and specific strength [3]. The major drawback with epoxy matrixes—especially FRP composites and probably their structural applications—resides in their inherent brittleness and higher water absorption [4]. Enhancing the durability performance, mechanical properties, and toughness of epoxy resin in order to satisfy the increasing demands of FRP composites in civil engineering and other applications remains a major challenge. Inorganic nanofillers, such as nanosilica, metal oxides, nanoclays, and carbon nanomaterials, have been investigated to enhance the mechanical properties and toughness of thermoset resins [5–9].

Because of their exceptional structure and outstanding electrical and mechanical properties, graphene nanoparticles, consisting of a single layer of carbon atoms, have attracted the greatest attention as promising nanomaterials for polymer composites, electronics, and energy storage applications. Graphene and GO nanoparticles are increasingly used to improve the properties of polymer matrixes for mechanical, electrical, and barrier performance [10–13]. Carbon nanoparticles have strong forces and tend to agglomerate, interfering with nanoparticle dispersity, which, in turn, limits the load transfer from the matrix to the nanoparticles. This phenomenon limits increments in the properties of polymer

nanocomposites. Therefore, preventing the aggregation of graphene sheets in the polymer matrix is a major objective in preparing nanocomposites. In an effort to solve this problem, quite a bit of research has focused on reinforcing the polymer matrix with graphene nanoparticles through the use of organic solvents, ionic liquids, and surfactants [14–17]. Removing the residual solvents and surfactants is not easy and entails a complicated process, thereby considerably increasing expenses and seriously hindering the practical development and utilization of FRP bars. Another method of solving this problem that has been considerably investigated is the surface functionalization of graphene and graphene oxide [3,4,18]. Nevertheless, most of the methods used for modifying the surface of GO are very complicated and expensive. Moreover, they still need to use organic solvents, which are not eco-friendly. Additionally, most of these approaches require using vigorous mechanical processes and incorporating relatively high amounts of graphene oxide, which remarkably restricts industrial implementation. Therefore, finding a practical approach for the surface modification of GO remains a real challenge.

Three major methodologies for the synthesis of polymer nanocomposites are based on the following: melt blending, solution mixing, and in situ polymerization [19]. Xue et al. achieved the acceptable dispersion of GO into epoxy resin by the surface modification of GO by applying wet mixing and solvent evaporation, which is not ecofriendly. At first, they directly mixed the aqueous GO dispersion with the TDE85/*N,N*-dimethylformamide (DMF) solution to prevent irreversible agglomeration [20]. In the case of thermosetting polymers, the best practical approach can be in situ polymerization, which consists of mixing nanoparticles with pre-polymers or monomers, achieving a proper dispersion, and then polymerizing them. In our previous research, we used a solution mixing process by introducing a binary solvent system for well-exfoliated graphene/vinyl ester resin nanocomposites [21]. In this study, we applied the in situ polymerization approach to synthesize epoxy nanocomposites.

Given the above issues, the incorporation of GO into a hardener can potentially improve the properties of the epoxy resin thanks to amine groups being introduced into the GO nanosheets. Some amine groups in the curing agent attach to GO sheets, increasing the crosslinking process between the GO sheets and the epoxy resin. Moreover, the attachment of GO nanoparticles to polymer chains might reduce GO agglomeration, leading to improved exfoliation, dispersion, and distribution of the GO sheets in the polymer matrix. This approach involves no organic solvents and is technically convenient for the industrial-scale production of high-performance polymer nanocomposites.

In this research, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and a scanning electron microscope (SEM) were employed to examine the structure and composition of synthesized GO. We introduced amine groups of polyetheramine onto the GO surface, which enables the graphene oxide nanosheets to covalently bond with epoxy networks. The interfacial interaction between the graphene oxide nanosheets with epoxy matrix was also assessed. Nanocomposites with different weight contents (0.2, 0.4, and 0.6 wt%) of GO were prepared, and their tensile and viscoelastic properties were investigated. Moreover, the effects of functionalization on the dispersion status of GO and the morphology of fracture surfaces were qualitatively investigated using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively.

## 2. Materials and Methods

### 2.1. Materials

Graphite powder with an average particle size of 30  $\mu\text{m}$ , purity (%) > 99.5, was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Epoxy (EP) resin EPX TFC (1000R) with a viscosity of 600–750 cps and a curing agent (D230) (polypropylene glycol (PPG)-based polyetheramine) with a viscosity of 90 cps was purchased from Resoltech (Marseille, France).  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$  (95%),  $\text{H}_3\text{PO}_4$  (85%),  $\text{H}_2\text{O}_2$  (30%),  $\text{HCl}$  (30%), and ethanol from Sigma-Aldrich (Darmstadt, Germany) were used as received.

## 2.2. Synthesis of GO Sheet

Graphite oxide powder was synthesized from graphite by the Tour method. This is safer than the Hummers method, generating no toxic gases and allowing for easy temperature control [22].

## 2.3. Freeze-Dried Graphene Oxide

A novel method was used to obtain well-exfoliated graphene oxide (GO) nanosheets. First, the as-prepared graphite oxide was suspended in deionized water and sonicated (5 s on-pulse; 2 s off-pulse) at 70% amplitude with an ultrasonic probe sonicator (Q-sonica with 5 mm microtip) for 2 h. Then, the residual graphite oxide was separated by centrifugation (4000 rpm for 30 min) from the resulting graphene oxide dispersion. After that, the graphene oxide aqueous dispersion was frozen for 24 h. Lastly, the prepared graphene oxide was vacuum-dried with a freeze-drying apparatus (VirTis SP scientific Sentry, Scientific Product, Philadelphia, PA, USA) for 48 h to remove the frozen water by sublimation under vacuum, leaving a fluffy GO powder, leading to the highly exfoliated GO becoming a very thin layer (details shown below).

## 2.4. Dispersion of GO Nanofillers

We used a novel, green method without involving any solvents and surfactants, which are not environmentally friendly, to disperse the GO nanofiller. Instead, GO was dispersed into the hardener because its viscosity was much less than the epoxy matrix. The dispersion of GO nanosheets was performed as follows: In a typical reaction, 200 mg of GO sheets was added to a flask with the required amount of the curing agent and stirred at 1000 rpm for 30 min at room temperature, before 3 h sonication occurred in a bath sonicator (digital ultrasonic cleaner model, 40 kHz, 150 W). Then, the mixture was kept under magnetic stirring (1000 rpm) and heated for 12 h at 90 °C. The black mixture was degassed in a vacuum oven for 1 h at 40 °C to remove the air bubbles.

## 2.5. Fabrication of Epoxy Nanocomposites

The epoxy/GO nanocomposites were fabricated by high-shear mixing and bath sonication procedures. First, the as-prepared GO/hardener mixture was added to the required epoxy resin (resin-to-hardener weight ratio of 100:50) and mixed for 1 h with a high-speed mixer at 7000 rpm to achieve the optimum doughnut effect. Then, the mixture was sonicated for 1 h in a bath sonication. Subsequently, the mixture was degassed under vacuum at 30 °C for 1 h to remove the air bubbles and was poured into the curing mold and cured at room temperature for 24 h. Table 1 summarizes the compositions of the evaluated recipes.

**Table 1.** Specimen composition.

| Specimen   | Graphene Oxide (wt%) | Epoxy/Hardener (g) |
|------------|----------------------|--------------------|
| Pure Epoxy | 0                    | 100                |
| EP/GO 0.2  | 0.2                  | 100                |
| EP/GO 0.4  | 0.4                  | 100                |
| EP/GO 0.6  | 0.6                  | 100                |

## 2.6. Characterization

*Differential scanning calorimetry (DSC).* The DSC measurements were performed with a TA Instruments DSC (mode Q100 calorimeter, New Castle, DE, USA) under a nitrogen atmosphere from 0 °C to 100 °C at a rate of 3 °C min<sup>−1</sup>.

*X-ray diffraction (XRD).* XRD (Bragg-Brentano, X'Pert Pro PPD, Malvern Panalytical Ltd., Malvern, PA, USA) with Cu target radiation was used for characterizing the crystal structures of the graphite and GO. Wide-angle diffraction scanning was applied at 40 kV and 50 mA within the range of 5–50° and at a scanning rate of 3°/min.

*X-ray photoelectron spectra (XPS).* The XPS analyses were carried out with a Kratos Axis Ultra spectrometer (VG ESCLab 250, Manchester, UK) equipped with a hemispherical electron analyzer and a monochromatic Al K $\alpha$  source (15 mA, 14 kV).

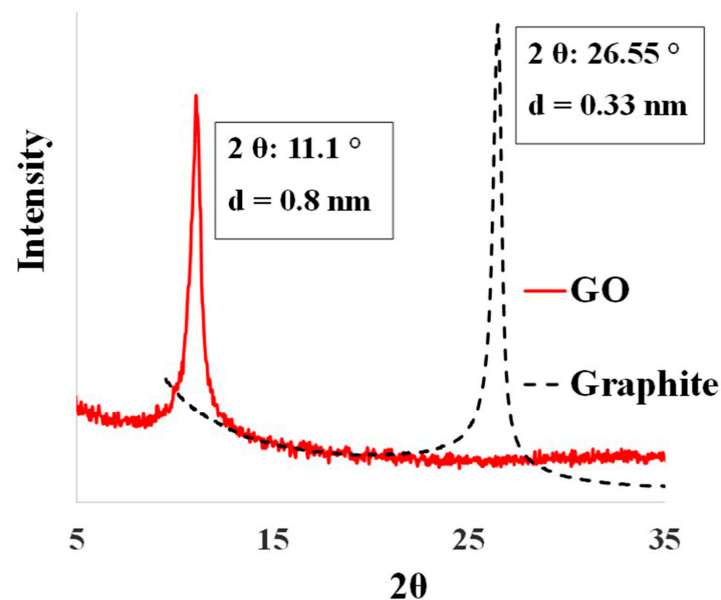
*Fourier transform infrared (FTIR).* The FT-IR spectrometer Perkin Elmer (model 4600, Boston, MA, USA) was used to obtain FTIR spectra between 500 and 4000 cm<sup>-1</sup>.

In this study, the prepared samples were also characterized by tensile testing machines, transmission electron microscopy (TEM), and scanning electronic microscopy (SEM). Their details were mentioned in our previous research [21].

### 3. Results and Discussion

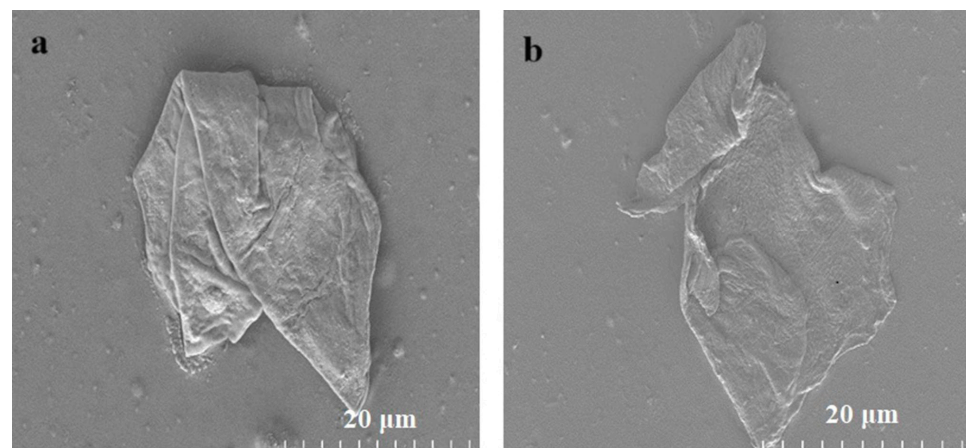
#### 3.1. Characterization of As-Synthesized GO

*XRD.* Figure 1 shows the X-ray diffraction results of graphite and as-prepared GO. The XRD spectrum of graphite and the synthesized GO exhibit sharp diffraction peaks at 26.48° and 11.10°, respectively. Graphite consists of several stacked graphene nanosheets with an internal spacing of 0.33 nm. The Tour oxidation process generates carboxyl, epoxide, and hydroxyl groups on graphite oxide nanosheets, and the d-spacing of graphite oxide was enhanced to 0.8 nm [23,24].



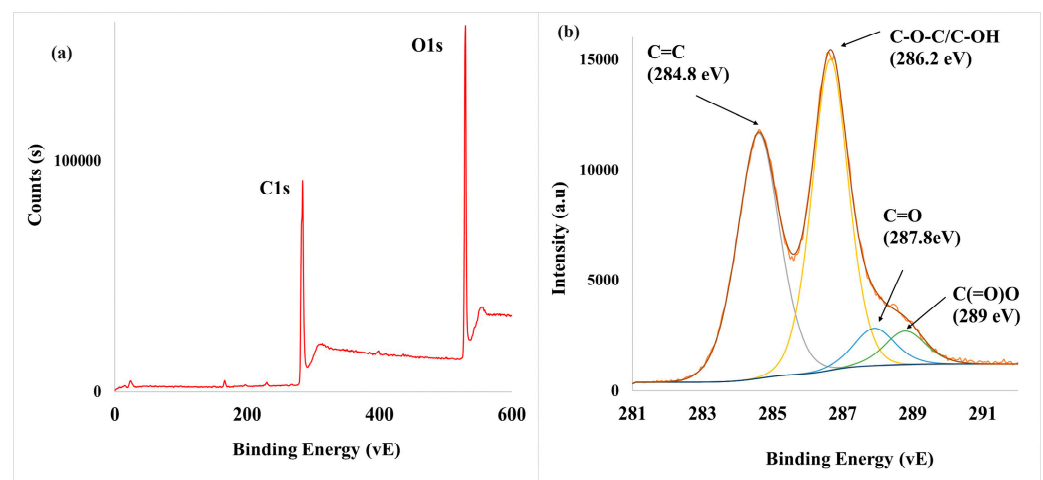
**Figure 1.** XRD of graphite and as-prepared GO.

*Microstructure of as-prepared GO.* More realistic insight into GO nanosheets can be achieved by SEM micrographs, although determining the precise particle size is practically impossible due to the large surface area and strong attractive van der Waals forces. Consequently, GO nanosheets are always susceptible to wrinkling, overlapping, and folding [23]. A novel method was used to obtain good images of the as-prepared graphene oxide. At first, 100 mg of GO—prepared by freeze-drying (Section 2.3)—was dispersed in water and exfoliated by bath sonication. Then, a drop of suspension was put on a thin film of alginate and air-dried at room temperature for 24 h. Figure 2a,b show the SEM images of as-synthesized GO that had been sonicated in water for 30 min and 60 min, respectively. Figure 2a shows that the GO nanosheets were well exfoliated; the flakes had just a few folds and were tens of micrometers in diameter. Figure 2b shows individual unfolded GO nanosheets. Increasing the sonication time to 60 min practically removed the folds; an individual very thin layer of GO, with some small overlaps, was obtained.



**Figure 2.** SEM micrographs of sonicated as-prepared GO (a) after 30 min of sonication and (b) after 60 min of sonication.

**XPS.** The XPS spectra were investigated to further identify the surface chemical compositions of the as-prepared GO. Figure 3a indicates that the GO comprised two peaks, including C1s (286 eV) and O1s (533 eV). Figure 3b represents the C1s core level spectra of GO compared by deconvoluting each spectrum into four peaks corresponding to these functional groups:  $\text{sp}^2$  C=C (284.8 eV), C-O-C/C-OH (epoxy/hydroxyls) (286.2 eV), C=O (carbonyl) (287.8 eV), and O-C=O (carboxylates) (289.0 eV) [22]. The combination of all the percentages of the oxidized materials shows that graphite oxide had almost 58% oxidized carbon and 42% graphitic carbon.

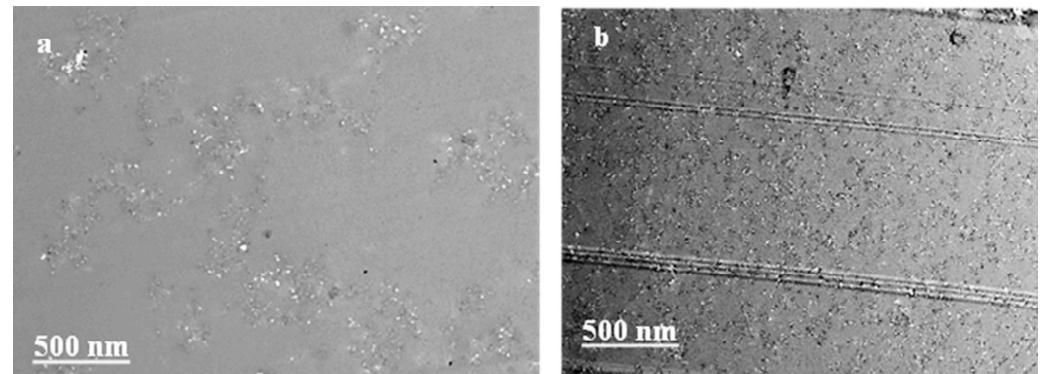


**Figure 3.** (a) XPS survey spectra of GO; (b) deconvoluted peaks of C1s XPS spectrum.

### 3.2. Microstructure of Nanocomposites

The dispersion and exfoliation levels of GO nanosheets in a polymer matrix play vital roles in determining the performance of nanocomposites. Transmission electron microscopy (TEM) was used as a straightforward technique to visualize the dispersion quality of GO nanosheets within epoxy. Figure 4 shows TEM images of nanocomposite EP/GO 0.2 and EP/GO 0.6, as manufactured by ultrasonic dispersion techniques in a curing agent. A homogeneous distribution of GO nanosheets is visible, interestingly even without any small agglomerates in the epoxy matrix. In addition, the surface-to-surface inter-particle distances between the GO nanosheets decreased by increasing the nanoparticle content from 0.2 to 0.6 wt%. This good dispersion of graphene in polymers has been rarely reported [25–27]. He et al. [16] and Guimont et al. [28] found relatively well-dispersed GO sheets just after the surface modification of GO and dispersion in organic solvents.

This high-quality dispersion of GO in an epoxy matrix can be explained by the chemical interaction, hydrogen bond, or even covalent bond between epoxy functional groups on GO nanoparticles and amine groups in the curing agent [29–32]. This high-quality dispersion of exfoliated nanoparticles leads to a more uniform stress distribution and minimizes stress-concentration centers, which considerably deteriorates the performance of nanocomposite.



**Figure 4.** TEM images of nanocomposites (a) EP/GO 0.2 and (b) EP/GO 0.6.

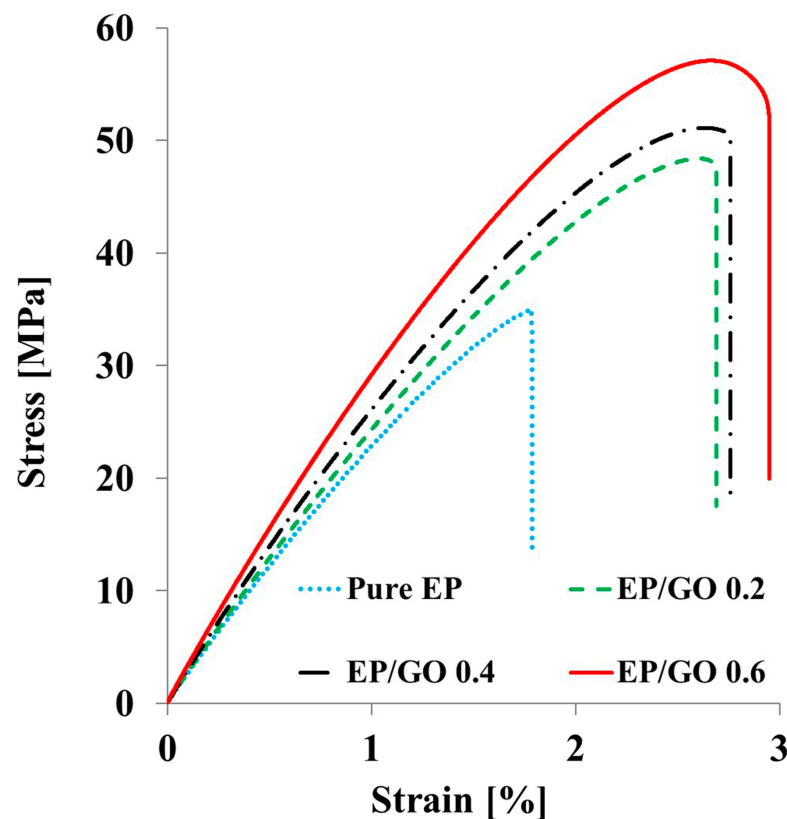
### 3.3. Tensile Properties

Figure 5 provides representative stress–strain curves of pure epoxy and the prepared nanocomposites. The results of tensile testing at room temperature—including ultimate tensile strength, Young’s modulus, strain at break, and toughness (area under the stress–strain curve)—are provided in Figure 5 and Table 2. Clearly, incorporating the GO and increasing its content considerably increased the tensile strength and toughness of the nanocomposites. Young’s modulus, strength, and toughness of the neat epoxy were 2.1 GPa, 37 MPa, and  $0.66 \text{ MJ m}^{-3}$ , respectively. Compared to the nanocomposite EP/GO 0.6 with 0.6 wt% of GO, the values were 2.9 GPa, 54 MPa, and  $1.62 \text{ MJ m}^{-3}$ , respectively, corresponding to increases of 38%, 46%, and 143%, respectively. This can be attributed to the reinforcing effects of GO nanosheets and improved interfacial interaction between the epoxy resin and GO nanosheets. In our study, we obtained this considerable improvement in the mechanical properties of epoxy by dispersing just 0.6 wt% of pristine GO into the curing agent. In the case of other epoxy nanocomposites containing more than 0.6 wt% of pristine and functionalized GO nanoparticles, however, the increase in tensile strength was relatively moderate (around 22%) [29–33]. The result of tensile testing clearly illustrates that dispersing GO nanoparticles into the curing agent can be a promising approach for achieving high-performance epoxy/graphene oxide nanocomposites with attractive mechanical properties.

**Table 2.** Tensile properties of pure PE and nanocomposites.

| Sample                                        | Pure PE         | PE/GO 0.2       | PE/GO 0.4       | PE/GO 0.6       |
|-----------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Tensile strength (MPa)                        | $37 \pm 3$      | $46 \pm 2$      | $49 \pm 1$      | $54 \pm 2$      |
| Young’s modulus (GPa)                         | $2.1 \pm 0.2$   | $2.7 \pm 0.1$   | $2.8 \pm 0.1$   | $2.9 \pm 0.1$   |
| Elongation at break (%)                       | $1.8 \pm 0.2$   | $2.73 \pm 0.2$  | $2.85 \pm 0.1$  | $3.0 \pm 0.1$   |
| Toughness <sup>a</sup> ( $\text{MJ m}^{-3}$ ) | $0.66 \pm 0.05$ | $1.24 \pm 0.04$ | $1.37 \pm 0.06$ | $1.62 \pm 0.03$ |

<sup>a</sup> Calculated by integrating stress–strain curves.

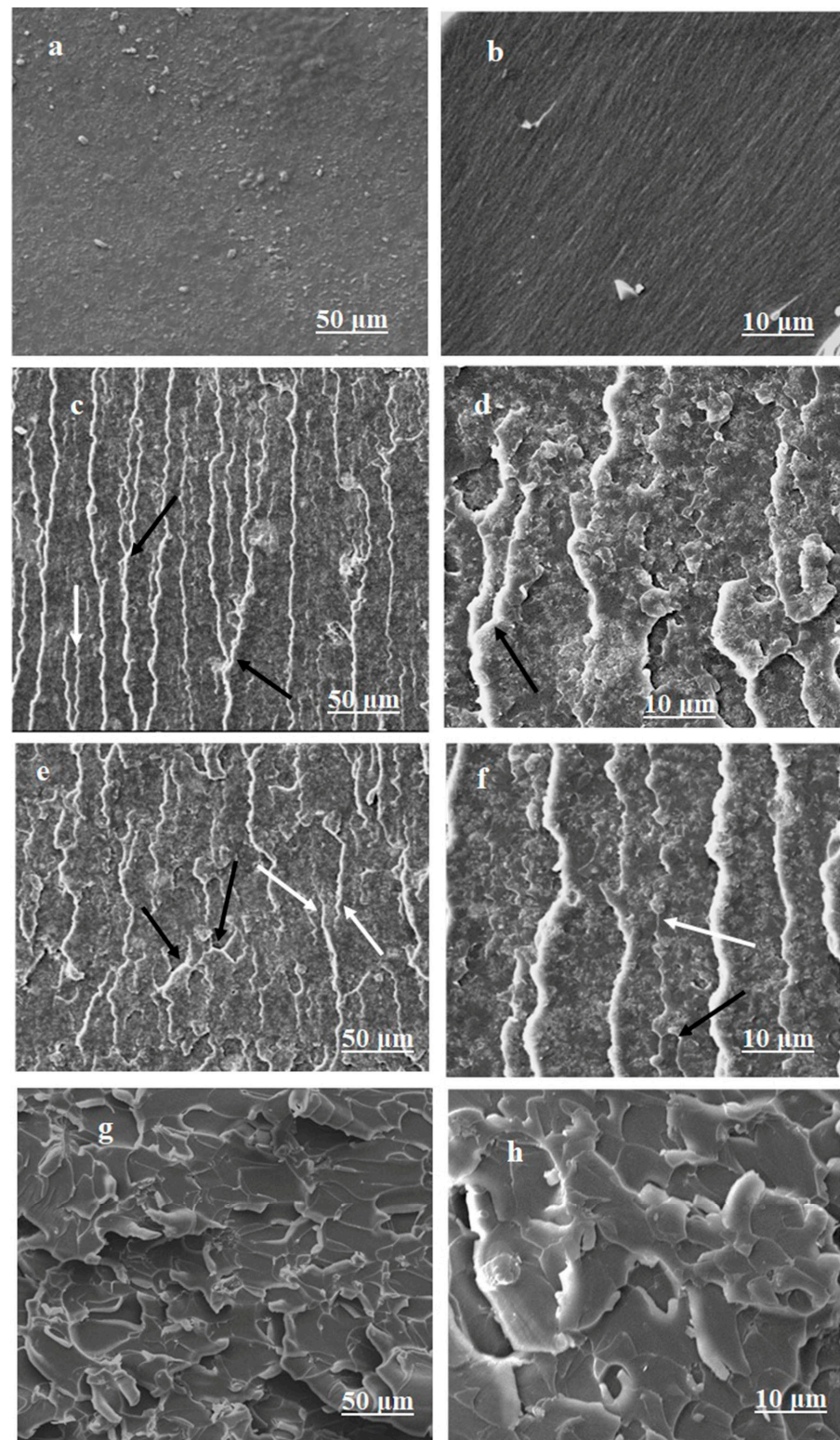


**Figure 5.** Representative stress–strain curves of pure PE and nanocomposites.

### 3.4. Fractography and Microstructure Analysis

After tensile testing, the epoxy composites were studied under SEM to further evaluate the influence of the dispersion of GO particles on the mechanical properties and the possible toughening mechanisms of the fracture surface (Figure 6). The incorporation of rigid nanoparticles like graphene and GO can induce a few toughening mechanisms in polymer matrices, such as the creation of dimple-like structures, plastic deformation, crack deflection, and crack pinning [34,35]. Upon encountering a rigid particle, a crack by twisting might be deflected (crack deflection), needing more energy, improving remarkably the characteristics of the polymer matrix. On the other hand, crack pinning explains that as the propagating crack confronts nanoparticles, it might twist between the rigid nanosheets and remain pinned at the particles [6,36].

The fracture surface of neat epoxy displays smooth surfaces, representing brittle fracture (Figure 6a,b). Generally, the SEM images of nanocomposites indicate a uniform distribution and dispersion of GO nanosheets in the epoxy without noticeable nanoparticle agglomerations. Moreover, crack deflection, crack branching, and crack blunting or bowing are responsible for higher fracture toughness in the GO/epoxy nanocomposites. Figure 6c,d show the fractured surfaces of the 0.2 wt% GO/epoxy nanocomposite specimen, including crack branching (white arrows) and crack pinning (black arrows) that enhance the fracture toughness and mechanical properties of the nanocomposite. The fracture surface morphology of the nanocomposite with 0.4 wt% of GO indicates crack-deflection (black arrows) and crack pinning phenomena (Figure 6e,f).



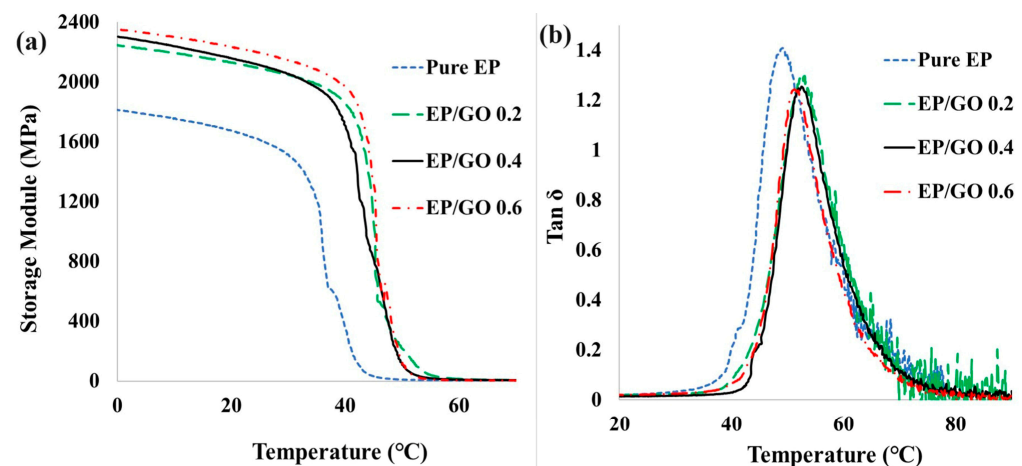
**Figure 6.** SEM images of fracture surfaces after tensile testing of (a,b) pure PE, (c,d) EP/GO 0.2, (e,f) EP/GO 0.4, and (g,h) EP/GO 0.6.

The highest weight percentage of GO content (0.6 wt%) shows a very rough fracture surface, dominated by many microcracks, crack pinning, and deflection (Figure 6g,h); they are responsible for high energy dissipation and nanocomposite toughness [37–39]. Figure 6g,h demonstrate many fracture ditches and obvious plastic deformations that led

to rougher fracture surfaces. At 0.6 wt% of GO incorporation, due to shorter inter-particle distances than both EP/GO 0.2 and EP/GO 0.4, the microcracks were pinned again before joining the primary crack.

### 3.5. Thermomechanical Properties

Dynamic mechanical analysis (DMA) was used to study the thermomechanical properties of the composites. Figure 7 and Table 3 provide the results. Table 3 also gives the T<sub>g</sub> values obtained with DSC analysis. The results indicate that the storage module of the pure epoxy in the glassy state at 0 °C was about 1800 MPa. This was greater for nanocomposite EP/GO 0.2, reaching 2230 MPa. By increasing the content of GO, the storage module of the nanocomposites gradually increased to 2245 and 2255 MPa for EP/GO 0.4 and EP/GO 0.6, respectively. In the glassy region, the storage module indicates an increase of about 25% for the EP/GO 0.6 nanocomposite. The considerable influence of GO on the storage module was probably due to the good dispersion of GO nanosheets and the strong epoxy–GO interface, which, to some extent, decreased the mobility of local polymer chains around the GO nanosheets. Some authors have shown that the incorporation of GO nanoparticles into the epoxy has a negligible effect on the storage module of the epoxy due to the agglomeration of nanoparticles in the epoxy resin [40].



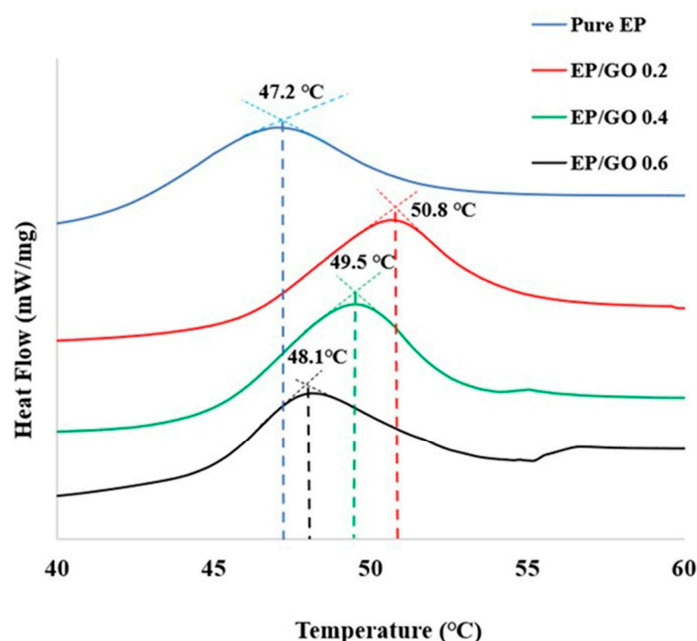
**Figure 7.** Dynamic mechanical properties of neat PE and nanocomposites: (a) storage module and (b) the loss factor of samples.

**Table 3.** Storage modulus and glass transition temperature (T<sub>g</sub>) values of pure EP and nanocomposites.

| Sample                        | Pure EP | EP/GO 0.2 | EP/GO 0.4 | EP/GO 0.6 |
|-------------------------------|---------|-----------|-----------|-----------|
| Storage module at 25 °C (MPa) | 1810    | 2230      | 2295      | 2350      |
| T <sub>g</sub> (°C) (DMA)     | 49.3    | 53.1      | 52.7      | 51.5      |
| T <sub>g</sub> (°C) DSC       | 47.2    | 50.8      | 49.5      | 48.1      |

The alterations of glass transition temperature in a polymer matrix have special significance, not only because they provide real insights into the fundamental changes in polymer chain dynamics but also due to the changes in thermal stability, playing crucial roles in several applications [41]. Table 3 gives the T<sub>g</sub> values of various samples determined from the maximum of tan δ versus temperature plots (Figure 7b). The T<sub>g</sub> of the prepared GO/epoxy nanocomposite was influenced by three competing factors: (1) massive surface area and wrinkled/folded configuration of GO nanosheets, as observed in SEM pictures of as-prepared GO nanosheets (Figure 3); (2) the dispersion of GO nanoparticles in the epoxy matrix; and (3) chemical interaction/bonding between the GO nanoparticles and epoxy resin. The wrinkled construction of the GO nanosheets probably improves mechanical interlocking among the GO sheets and resin, noticeably hindering the mobility of the epoxy chains. Nevertheless, restricting the mobility of the polymer chains was effectively reduced

because of the poor exfoliation/distribution of nanoparticles. The covalent bonding between the GO nanoparticles and epoxy resin can create an ideal GO sheet/resin interfacial zone, leading to improved thermal stability [41]. Adding 0.2 wt% of GO to pure resin increased its  $T_g$  from 49.3 °C to 53.1 °C, revealing the probable synergistic effect of the aforementioned factors. This can be attributed to the good exfoliation and dispersion of sheets, mechanical interlocking between the GO sheets and epoxy, and the possible covalent bonding between the epoxy matrix and graphene oxide sheets. This significantly restricted the mobility of the surrounding polymer chains, causing the improved thermal resistance of the nanocomposite. In contrast, by increasing the loading of GO sheets to 0.4 wt% and 0.6 wt%, the  $T_g$  of the nanocomposites decreased slightly to 52.7 °C and 51.5 °C, respectively. The  $T_g$  values obtained from DSC measurements revealed a similar trend to those from DMA. Figure 8 shows the nanocomposite with 0.2 wt% GO loading having the highest  $T_g$  (50.8 °C), which, by exceeding this amount, gradually reduced the  $T_g$  of the nanocomposites.

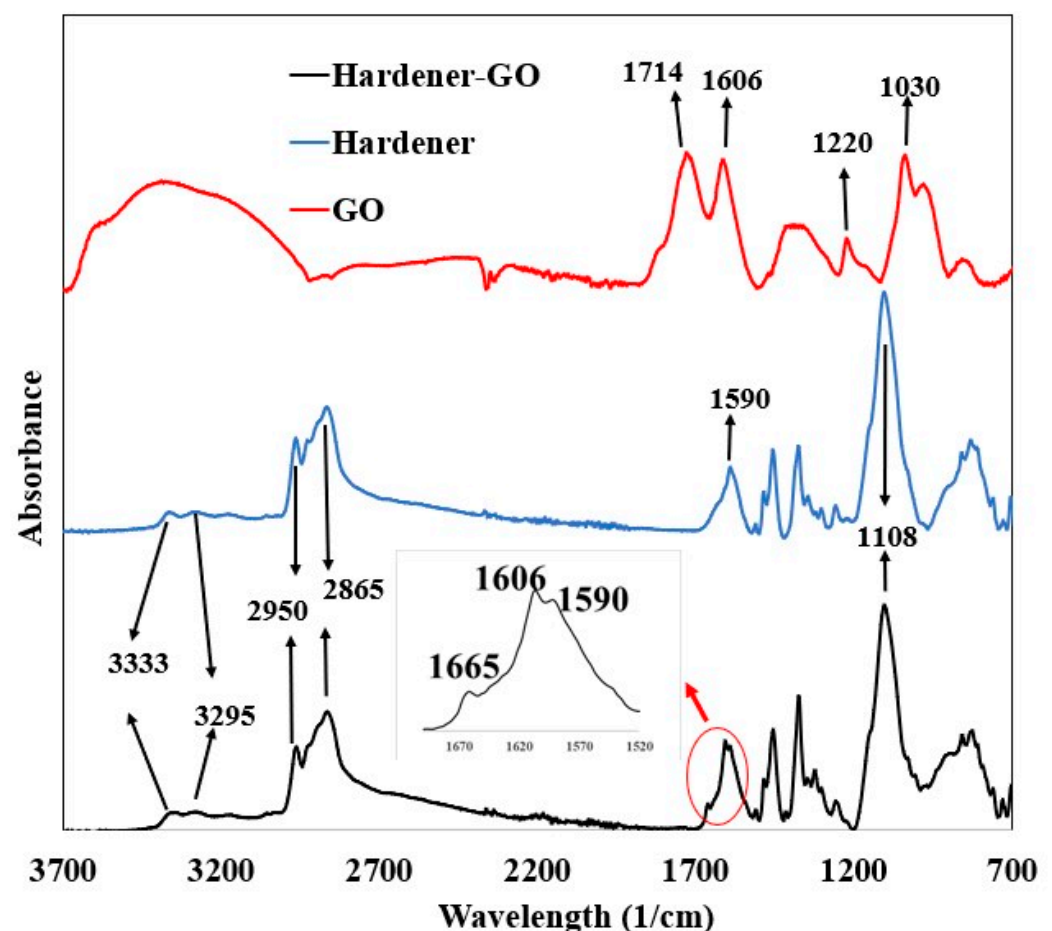


**Figure 8.** DSC cures for pure EP and nanocomposites.

The thorough investigation of the microstructure of samples under TEM (Figure 4) and SEM (Figure 6) indicates that not only did any agglomerations of GO nanosheets appear when the GO content was increased to 0.4 wt% and 0.6 wt% but the roughness of the fracture surface of the nanocomposites increased remarkably. This reveals the high quality of the GO sheet/epoxy interface as well as the exfoliation and dispersion of nanoparticles in the matrix. Therefore, the covalent bonding probably played an effective role in a small reduction in the  $T_g$  in EP/GO 0.4 and EP/GO 0.6. This indicates that GO sheets probably bonded chemically with the amine group of the curing agent during the mixing and sonication processes, which tended to increase the  $T_g$  of the epoxy resin. On the other hand, increasing the content of GO nanosheets resulted in an increasing number of curing agent molecules reacting with GO sheets. This led to an alteration in the curing stoichiometric ratio, decreasing the cross-linking density of the cured nanocomposite to some extent, which slightly reduced the  $T_g$  of the nanocomposites. To evaluate the probability of this phenomenon, the FTIR of the GO, curing agent, and the mixture of the GO/curing agent after mixing and sonication was obtained and is discussed in the next section.

### 3.6. FTIR Spectroscopy

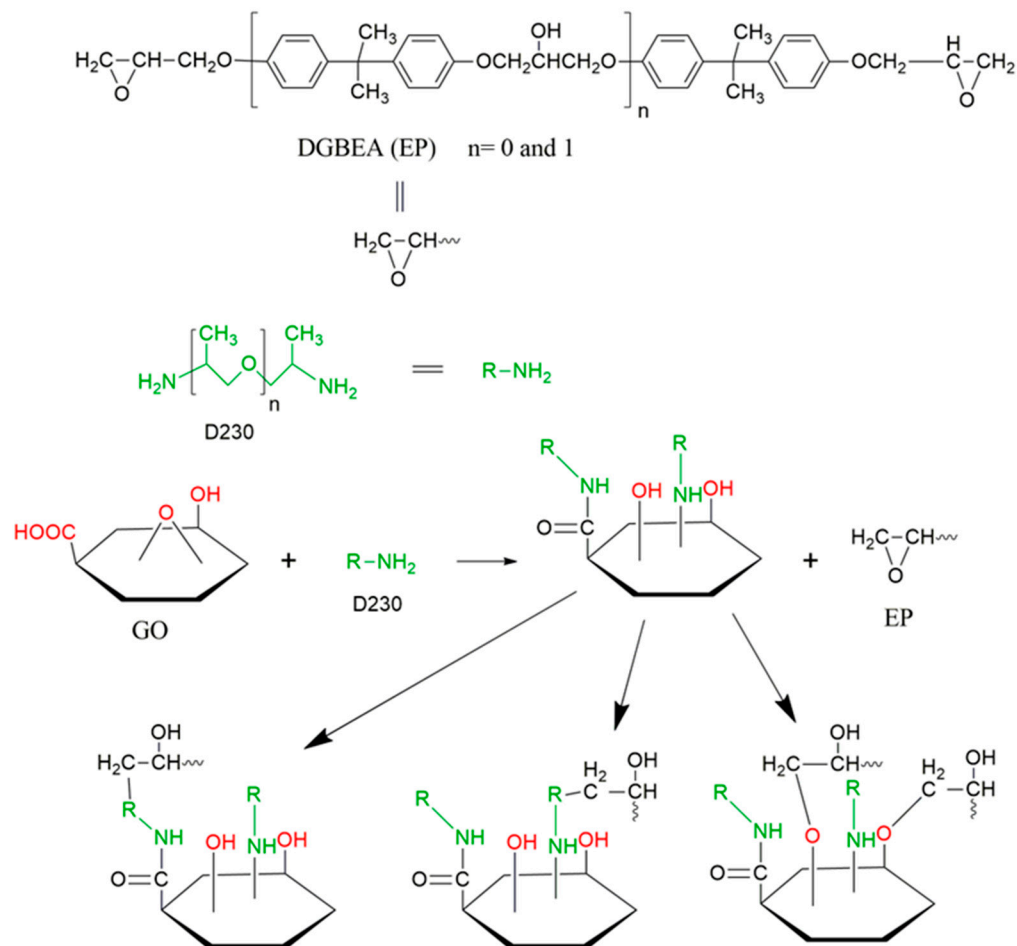
FTIR spectroscopy was used to verify the covalent functionalization of GO sheets by hardener molecules. Figure 9 shows the FTIR spectra of the as-prepared graphene oxide, hardener, and GO/hardener. Obviously, FTIR spectroscopy of the GO confirmed the presence of oxygen-containing functional groups by indicating the absorption bonds corresponding to C–O–C stretching from epoxy groups at  $1220\text{ cm}^{-1}$ , unoxidized  $\text{sp}^2$  C=C at almost  $1606\text{ cm}^{-1}$ , and C=O stretching vibrations from carboxylic and carbonyl around  $1714\text{ cm}^{-1}$  [42,43]. In addition, the peak at around  $1030\text{ cm}^{-1}$  is related to alkoxy (C–O) stretching [42]. The spectrum of the hardener shows a strong characteristic peak at  $1108\text{ cm}^{-1}$  attributed to the aliphatic ether of polyetheramine [44], a peak at  $1582\text{ cm}^{-1}$  was related to bending  $\text{-NH}_2$ , and there were typical  $\text{-NH}_2$  stretching vibrations at  $3295$  and  $3333\text{ cm}^{-1}$  [45,46]. Furthermore, the peaks at around  $2865$  and  $2950\text{ cm}^{-1}$  are related to the asymmetric and symmetric stretching vibrations of methylene groups in hardener molecules [47].



**Figure 9.** FTIR spectra of as-prepared GO, hardener, and GO/hardener.

With the functionalization of GO sheets by the hardener, the peaks at  $1220$  and  $1030\text{ cm}^{-1}$  disappeared, illustrating the removal of the O–H and epoxied groups attached to the surface of graphene oxide sheets. Ferreira et al. grafted hexamethylenediamine onto GO and reported a similar result [47]. Moreover, the peak of C=O at  $1714\text{ cm}^{-1}$  on the GO disappeared; a new peak appeared at around  $1665\text{ cm}^{-1}$ , which is the characteristic feature of amide groups (N–C=O) [19]. This finding reveals that some of the amine groups (N–H) in the curing agent reacted with carboxylic groups in the GO, and amide groups were created. These results suggest that the harder molecules were successfully grafted onto the surface of the graphene oxide.

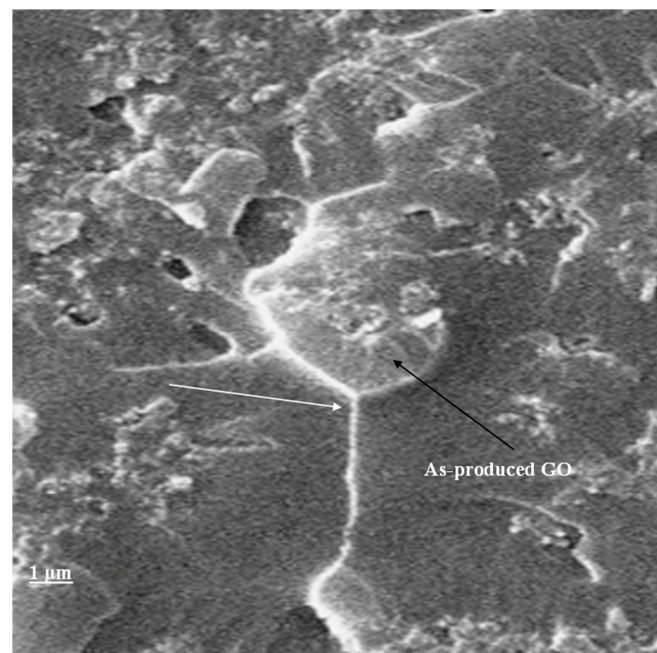
In this study, curing agent (D230)-based polyetheramine was used as the curing agent. The possible reactions of the functional groups on the surface of GO and some amine groups of polyetheramine are proposed in Figure 10. This figure also predicts the probable cure reactions in the GO/epoxy/hardener system.



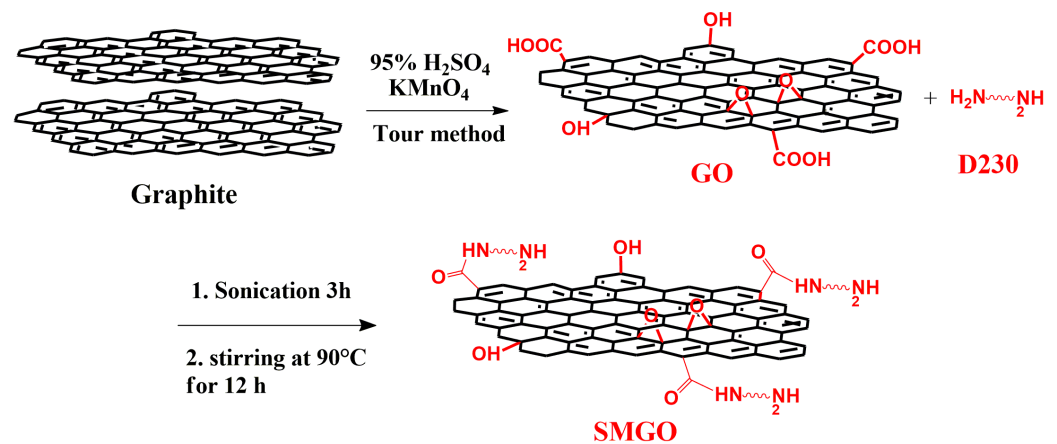
**Figure 10.** Proposed reaction mechanism of GO/TETA/EP.

As suggested, amide bonding can be created by the carboxylic acid groups of GO reacting with some amine groups in the curing agent, leading to the surface modification of graphene. Surface modification is one of the most effective methods used for reducing the tendency of graphene nanoparticles to agglomerate [47]. Careful observations of the highly magnified SEM images of the fracture surface (Figure 11: the black arrow points to GO sheet, and the white arrow indicates the crack pinning when a crack encounters GO sheets) reveal that functionalization increases compatibility and the interfacial interaction between the graphene oxide nanosheets with the epoxy matrix, improving the reinforcing effect [19].

This image clearly shows the improved quality of the interface between the epoxy matrix and GO sheets. The sheet surface is covered with the matrix, leaving no obvious gaps between the sheets and the epoxy matrix. In contrast, other authors have reported obvious agglomeration in GO/epoxy nanocomposites that are prepared by dispersing GO in solvents. The presence of GO agglomerations indicates the clean surface of GO nanosheets with some gaps between the sheets and matrix, revealing poor interfacial interaction between the epoxy and GO [48]. Figure 12 shows a schematic preparation of the graphene oxide and its surface modification (SMGO) in this study.



**Figure 11.** Highly magnified SEM images of the fracture surface of sample EP/GO 0.4.



**Figure 12.** Schematic of the preparation of graphene oxide by the Tour method (GO) and surface modification using polyetheramine (SMGO).

#### 4. Conclusions

This research introduced a new class of high-performance epoxy nanocomposites from dispersing as-prepared GO into a hardener. The covalent bonding between a GO and hardener molecules creates a strong interface and plays a vital role in the performance of composites. The TEM images of the EP/GO nanocomposites show a relatively homogeneous distribution of GO nanosheets without clear agglomerates of nanoparticles. The Young's modulus, strength, and toughness of the neat epoxy were 2.1 GPa, 37 MPa, and  $0.66 \text{ MJ m}^{-3}$ , respectively. Loading just 0.6 wt% of GO into resin increased these values to 2.9 GPa, 54 MPa, and  $1.62 \text{ MJ m}^{-3}$ , respectively. The SEM images of the fracture surfaces of samples show that crack deflection, crack branching, and crack bowing mechanisms were responsible for the higher fracture toughness of the nanocomposites. Studying the glass transition temperature ( $T_g$ ) of samples with both DMA and DSC clarified that the  $T_g$  of the nanocomposites with a loading of 0.2 wt% of GO increased, while the  $T_g$  gradually reduced when this amount of nanofiller was exceeded. The FTIR findings reveal that some of the hardener amine groups reacted with GO carboxylic groups. Amide groups were created, revealing that the molecules of the hardener were successfully grafted onto the surface of

the graphene oxide. This innovative approach to synthesizing GO/epoxy nanocomposites is appropriate for upscaling for use in structural FRP composites in civil engineering applications (bridges and buildings), aerospace, marine, and automotive industries.

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