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Mechanical properties of epoxy composites reinforced with ammonia-treated graphene oxides

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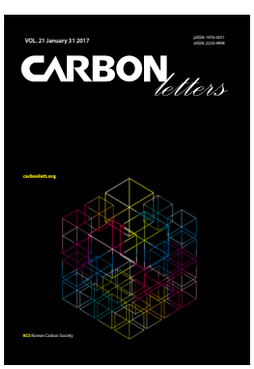

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Abstract

The effects of ammonia-treated graphene oxide (GO) on composites based on epoxy resin were investigated. Ammonia solutions of different concentrations (14–28%) were used to modify GO. Nitrogen functional groups were introduced on the GO surfaces without significant structural changes. The ammonia-treated GO-based epoxy composites exhibited interesting changes in their mechanical properties related to the presence of nitrogen functional groups, particularly amine ($C\text{-}NH_2$) groups on the GO surfaces. The highest tensile and impact strength values were 42.1 MPa and 12.3 J/m, respectively, which were observed in an epoxy composite prepared with GO treated with a 28% ammonia solution. This improved tensile strength was 2.2 and 1.3 times higher than those of the neat epoxy and the non-treated GO-based epoxy composite, respectively. The amine groups on the GO ensure its participation in the cross-linking reaction of the epoxy resin under amine curing agent condition and enhance its interfacial bonding with the epoxy resin.

Key words: graphene oxide, nitrogen, surface treatment, epoxy composites, mechanical properties

1. Introduction

The demand for advanced materials with improved properties to meet new requirements, or to replace existing materials, has been steadily increasing. Among advanced materials, polymer composites possess superior strength, stiffness, toughness, hardness, and heat distortion temperature compared with the material properties of metals [1,2]. Currently, polymer composites are being investigated for use in a wide range of applications, including products and components in the biotech, automotive, and aerospace industries [3]. Among the polymer resins being used in such composites, epoxy resin is an important polymer matrix with superior mechanical properties, thermal stability, adhesion properties, and chemical resistance. For these reasons, epoxy composites have been extensively applied in a variety of industrial applications, especially for automobile parts, aircraft components, and electronic components such as supercapacitors and transistors [4-7].

Although epoxy resin-based composites frequently have outstanding properties, they are also brittle and low in strength compared with composites formed with other resins. To resolve these problems, it has become a common practice to add fillers to enhance the properties of the epoxy composites. More specifically, both micro- and nano-scale fillers have been developed as additives to epoxy composites to achieve high performance. Various carbon materials, such as graphene, graphene oxide (GO), carbon nanotubes, chopped fibers, and long fibers, have been used as additives to compensate for the weak and brittle properties of epoxy composites [8-11]. These carbon materials enhance the properties of epoxy composites by providing support or forming a network structure.

Unfortunately, in terms of volume and weight ratios, these additives must be introduced

into the epoxy resin in rather high amounts. To address this problem, a surface treatment method has recently been studied with the goal of improving the interface between the epoxy resin and the additives, with the introduction of only a limited amount of material [12]. The resulting improvement in interface adhesion has led to a significant enhancement in the mechanical properties of the final composites.

GO materials, which consist of graphite sheets with an enlarged interplanar distance, have been used as fillers in polymer composites to improve their mechanical properties [3]. When GO is used as an additive, crack propagation is hindered by the GO network [3]. In addition, GO is amenable to the introduction of hetero-atoms such as nitrogen and fluorine and to surface treatment. In particular, the presence of nitrogen on GO can improve its interfacial adhesion in epoxy composites when amine curing agents are used.

In this study, samples of GO were treated with ammonia solutions and then used as additives in epoxy composites. The epoxy composites that were produced using the surface-treated GO were evaluated in terms of their mechanical and chemical properties.

2. Experimental

2.1. Preparation of GO

The GO used in this study was synthesized via the oxidation of graphite powder using the modified Hummers' method [13]. Graphite powder of 99.99% purity, (L_a = 150 μm; Aldrich, USA) was used as the starting material. The graphite powder (3 g) was first stirred into sulfuric acid (360 mL, 95.0%) while being cooled in an ice bath. Then, potassium permanganate (4.5 g, 99.0%) was slowly added to the mixture. The temperature of the suspension was increased to 70°C, and the suspension was then stirred for 12 h. After the addition of distilled water (400 mL), the suspension was stirred for an additional 12 h. Hydrogen peroxide (8 mL, 34.5%) was then slowly added, and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was then filtered and washed with HCl (35%) and distilled water until the pH of the filtrate was neutral. All the chemical reagents were purchased from Samchun Chemical, Korea. After being washed, the GO was freeze-dried under vacuum [14].

2.2. Ammonia treatment of GO

The prepared GO was treated with ammonia solutions of different concentrations (14, 21, and 28%) at room temperature. A 100 mL volume of ammonia solution was mixed with 1 g of GO and the mixture was stirred for 48 h. After stirring, aminated GO was obtained in powder form following vacuum filtration and washing with distilled water. The non-treated and aminated GO samples were labeled GO, A14-GO, A21-GO, and A28-GO, respectively, depending on the concentration of the ammonia solution used. This series of GO materials was then used as additives to improve the mechanical properties of epoxy composites.

2.3. Preparation of epoxy composites

An epoxy resin with diglycidyl ether of bisphenol A (DGEBA) (YD128, viscosity, 11,500–13,500 cps; Kukdo Chemical Co. Ltd., Korea) as the epoxy monomer was used as the polymer matrix and was cured with an amine curing agent (G-640, viscosity, 11,500–13,500 cps; Kukdo Chemical Co. Ltd.). The prepared GO was blended into the epoxy resin under powerful sonication for 3 h to achieve a uniform dispersion. The GO/epoxy resin blend (weight ratio, 0.5:100; 0.5 phr) was mixed with an appropriate amount of the hardener using a high-speed mechanical stirrer for 10 min. To remove the air bubbles that formed during the mixing process, which would have had detrimental effects on the final product, a deformation procedure was performed at room temperature for a duration of 40 min using a vacuum rotary pump. Once the bubbles had been completely removed, the GO/epoxy mixtures were transferred into metal molds to obtain analytical specimens. The mold assembly was placed in an oven to cure at 100ºC for 1 h.

2.4. Characterization

X-ray photoelectron spectroscopy (XPS) (MultiLab 2000 spectrometer, Thermo Electron Corporation, England) was conducted to investigate the elemental compositions of the aminated GO surfaces. Al Ka (1485.6 eV) was used as the X-ray source, with an anode voltage of 14.9 keV, a filament current of 4.6 A, and an emission current of 20 mA. Fourier-transform infrared (FT-IR) spectroscopy (FTS-175C; Bio-Rad Laboratories, Inc., USA) was performed to confirm the functional groups on the GO. The infrared spectra were recorded over a wavenumber range from 500 to 4000 cm^{-1}. The structural changes that occurred after the amination of the GO were investigated using X-ray diffraction (XRD) spectroscopy, (D8 Discover; Bruker AXS, Germany) and Raman spectroscopy (LabRAM HR; Horiba Jobin-Yvon, France). The XRD and Raman analyses were conducted using CuKα radiation and an Ar-ion laser with a wavelength of 514.532 nm, respectively.

Tensile strength tests were performed on an Instron model 8500 servohydraulic mechanical tester in accordance with the American Society for Testing and Materials (ASTM) D638 standard. The tests were conducted at a crosshead speed of 5 mm/min. The strains were recorded using strain gages. Impact strength tests were performed in accordance with the ASTM D256 standard using a testing machine at an impact speed and impact hammer energy of 3.5 m/s and 6.8 J, respectively. The dimensions of the typical molded notched Izod impact test specimens were 63 mm × 12.7 mm × 3 mm. To ensure meaningful results, at least five specimens were tested for each set of conditions and the averages were computed.

3. Results and Discussion

3.1. Surface chemical compositions of the aminated GO samples

The GO was aminated using ammonia solutions of different concentrations to introduce nitrogen functional groups. It was

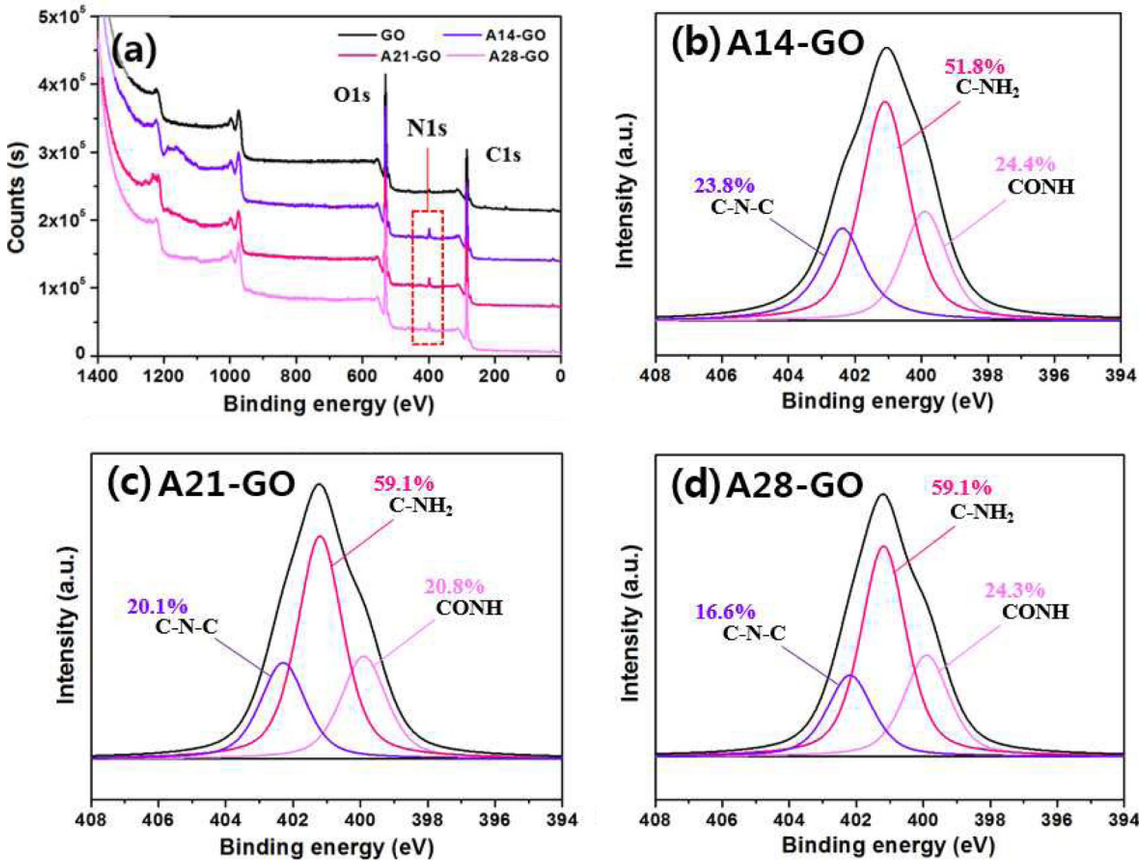

Fig. 1. (a) Wide X-ray photoelectron spectroscopy spectra and (b-d) curve fitting of the N1s spectra of aminated graphene oxide (GO).

necessary to confirm that the amine groups were covalently attached to the GO surfaces, not simply adsorbed onto them. The elements present on the GO surfaces were identified via XPS [15]. Fig. 1a shows the XPS spectra related to C1s, N1s, and O1s on the aminated GO surfaces. The aminated GO exhibited an N1s peak at 400 eV after ammonia treatment, which confirmed the successful amino-group functionalization of the GO surfaces.

In the non-treated GO, the atomic concentrations of carbon and oxygen were 60.65 and 39.35 at%, respectively, as shown in Table 1. The elemental oxygen contents of the aminated GO samples decreased as the ammonia concentration increased, down to 31.67 at%, whereas, the nitrogen contents increased to 3.78, 4.35, and 4.73 at% for A14-GO, A21-GO, and A28-GO, respectively. Moreover, it is found from Fig. 1b-d that the N1s peaks of the aminated GO samples could be fitted to three component peaks at 399.9 eV (C-N-C), 401.0 eV (C-NH_2), and 402.3 eV (CO-NH) [16]. These peaks were differently formed depending on the concentration of the ammonia solution. Only the C-NH_2 peak exhibited a meaningful change; the others were randomly formed regardless of the concentration.

The quantity of amine increased as the concentration of ammonia solution increased. Of the N atoms on the GO, a N content of 1.95 at% (51.8% of the total 3.78 at% N content) was present in the form of C-NH_2 when the GO was treated with the 14% ammonia solution. When treated with the ammonia solutions of 21 and 28%, the GO had N contents of 2.57 and 2.79 at%, respectively, in the form of C-NH_2. The presence of these amine groups was expected to improve the mechanical properties of the GO-based epoxy composites.

Table 1. Surface element analysis results of X-ray photoelectron spectroscopy for aminated graphene oxide

Sample	Elemental contents (at%)		
	C1s	O1s	N1s
GO	60.65	39.35	-
A14-GO	64.35	31.87	3.78
A21-GO	63.98	31.67	4.35
A28-GO	63.01	32.26	4.73

GO, graphene oxide.

FT-IR analysis was performed to characterize the functional groups of the GO samples, as shown in Fig. 2. A distinctive peak at 1630 cm^{-1}, which was observed for the aminated GO samples but mostly absent in the case of GO, corresponded to N-H bending vibrations. There were also hints of the am-

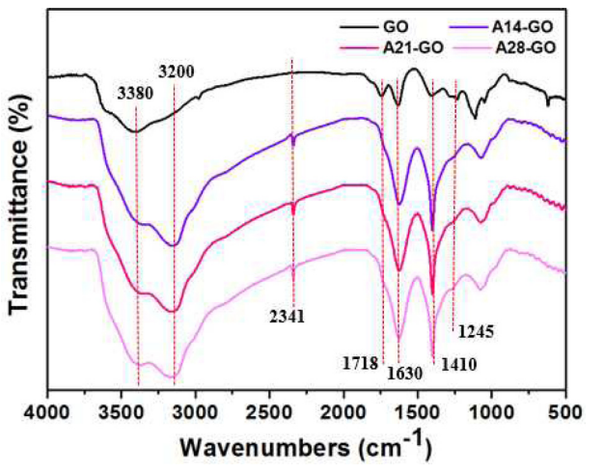

Fig. 2. Fourier-transform infrared spectra of the aminated graphene oxide (GO).

ide III band at 1245 cm^{-1} in the spectra of the aminated GO samples. All samples had common bands at 3380 and 3200 cm^{-1}, which were assigned to the stretching vibrations of O-H bonds in the GO, or of N-H bonds in the aminated GO samples [17,18]. Other bands at 1718 and 1410 cm^{-1} were attributed to the C=O stretching vibrations of carboxylic groups and O-H bending vibrations, respectively, suggesting the presence of non-amine groups in the aminated GO after ammonia treatment.

The band observed at 2341 cm^{-1} is characteristic of GO with hetero-atoms such as fluorine and nitrogen [14]. These results further confirmed that nitrogen functional groups had been introduced onto the surfaces of the GO samples, supporting the results obtained in the XPS analysis.

3.2. Structural properties of the aminated GO samples

XRD analysis was performed to investigate the structural changes that occurred in the GO as a result of the ammonia treatment. After treatment, the structural orientations of the aminated GO samples showed no significant changes regardless of the treatment concentration, as shown in Fig. 3a. The (001) and (101) peaks were still present at θ = 10.4° and 42°, respectively. The (001) peaks of the aminated GO samples were slightly shifted to the right, indicating that the gap between the crystal planes had decreased after treatment. This gap decreased from 0.8529 nm for GO to 0.7695 nm for A28-GO, as listed in Table 2. The *d*-spacings were calculated using the following equation:

$$d_{002} = \lambda/(2\sin\theta) \quad (1)$$

, where λ is the wavelength of the X-rays used and θ is the corresponding scattering angle [19,20]. This decrease in *d*-spacing was interpreted to be a result of the ammonia treatment decreasing the number of oxygen functional groups on the GO surfaces, thereby also decreasing the repulsion between the (001) crystal planes.

Raman analysis, which provides information about atomic

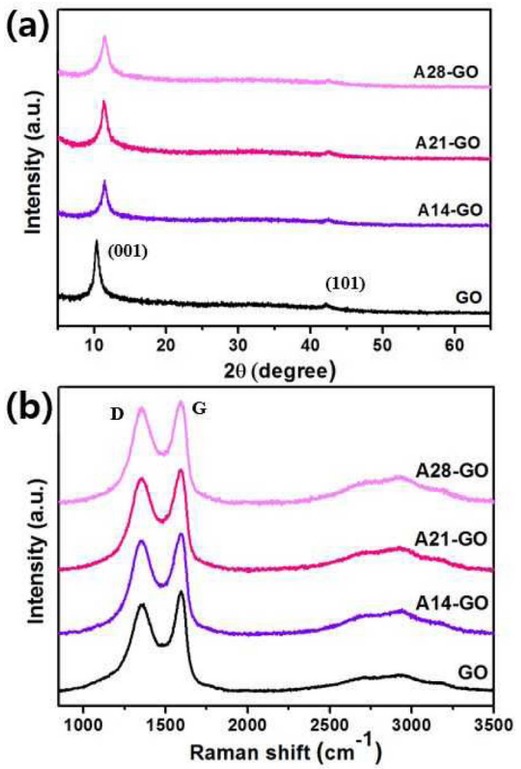

Fig. 3. (a) X-ray diffraction pattern and (b) Raman spectra of aminated graphene oxide (GO).

Table 2. X-ray diffraction and Raman analysis results of aminated graphene oxide

Sample	GO	A14-GO	A21-GO	A28-GO
2θ (°)	10.36	11.43	11.31	11.49
d_{001} (nm)	0.8529	0.7734	0.7813	0.7695
I_D/I_G	0.86	0.93	0.92	0.94

GO, graphene oxide; I_D/I_G, ratio of the integrated areas of the D and G bands.

structure, is particularly useful for characterizing graphene-related materials. To examine the structural changes of the aminated GO samples in detail, Raman analysis was conducted, and the results are shown in Fig. 3b. We confirmed the D and G bands in the GO samples, corresponding to a weak band at ~1340 cm^{-1} (D band) and a strong band at ~1581 cm^{-1} (G band). The D band in the Raman spectra is attributed to disordered structures resulting from atomic-scale defects on the graphitic plane, and the G band is well known to represent the E_{2g} vibrational mode of sp^2-bonded graphitic carbon.

Additionally, the distortion of aromatic clusters, aromatic rings, and crystallites can be confirmed based on the position of the D band and the I_D/I_G ratio [21]. Generally, the reduction of GO and the introduction of hetero-atoms into GO can cause structural defects [22]. The I_D/I_G value for the aminated GO sam-

ples following ammonia treatment was 0.93, which was larger than that for the non-treated GO. This result revealed that the nitrogen functional groups were well introduced into the GO.

It is possible to confirm layers of graphene based on high and symmetrical 2D bands [23], but in this study, the aminated GO contained several layers of graphene. Therefore, the ammonia treatment can introduce amine groups onto the GO without major structural changes.

3.3. Mechanical properties of the aminated GO/epoxy composites

Tensile tests of the GO- and aminated GO-based epoxy composites were performed at ambient temperature to investigate their tensile strengths and moduli. The test results revealed that the addition of GO and aminated GO resulted in somewhat different stress-strain curves, as shown in Fig. 4a. All specimens broke immediately after the stress reached the maximum point. In addition, no yield points were observed for any of the specimens. This result can be attributed to the brittleness of epoxy resin. The mechanical properties of such composites can be improved by adding fillers, which interact differently with the polymer resin depending on their interfacial bonding properties. Therefore, the addition of GO could enhance the mechanical properties of the resulting epoxy composites. However, the use of aminated GO resulted in an increase in the maximum load.

For a detailed investigation of the tensile properties in relation to the presence of amine groups on the GO, the tensile modulus (E) values of the composites were calculated using the following equation:

$$E = \frac{\sigma}{\varepsilon} \quad (2)$$

, where σ is the stress and ε is the strain. The tensile strengths, strains, and moduli of the neat epoxy and the epoxy composites are shown in Table 3. When GO was added, the resulting epoxy composite exhibited a remarkable improvement in tensile strength compared with the neat epoxy, from 19.1 to 30.5 MPa. With further ammonia solution treatment of the GO, the tensile strength increased to 35.3, 41.9, and 42.1 MPa for the A14-GO, A21-GO, and A28-GO-based epoxy composites, respectively.

GO itself possesses various oxygen functional groups. Among them, carboxylic groups (-COOH) are favorable for improving its dispersion in and interfacial adhesion with an epoxy matrix [24]. In addition, the platelet shape of GO reinforces the adhesion in the matrix, increasing its roughness and surface area [25]. As a result, the tensile modulus of the epoxy composite prepared with GO increased from 1.0 to 1.7 GPa.

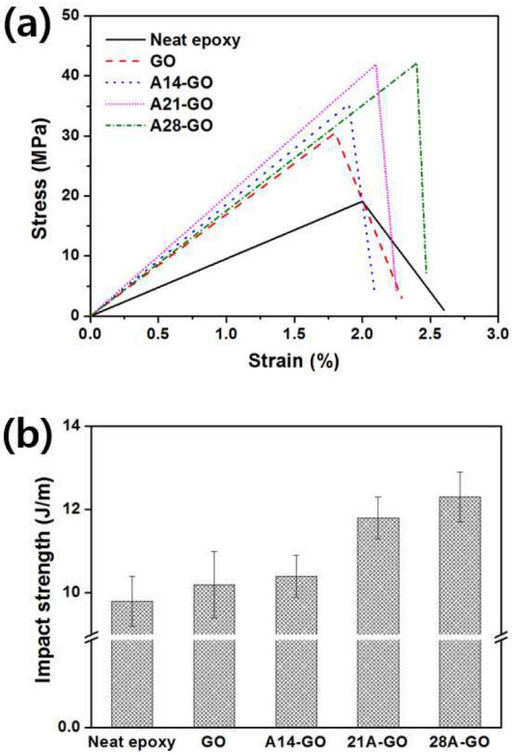

Fig. 4. (a) Tensile and (b) impact test results of aminated graphene oxide (GO) based epoxy composites.

At the same time, the epoxy composites prepared with aminated GO exhibited even better tensile properties, although their oxygen contents were lower. This fact can be attributed to the newly formed nitrogen functional groups on the GO surfaces. The tensile strengths of the aminated GO-based epoxy composites were concluded to have improved as a result of their increased amine ($C\text{-}NH_2$) contents, considering that the variations in the other nitrogen functional groups, such as C-N-C and CONH, were random. Amine groups are sufficiently strongly nucleophilic to cause epoxide groups to open in the presence of an amine curing agent, unlike other oxygen and nitrogen functional groups. The mechanism is illustrated in Fig. 5. Amine groups can undergo cross-linking reactions in an epoxy resin system [26,27]. This reaction is considered to prevent GO agglomeration in an epoxy composite, by acting as a protective layer. With the increase in interfacial bonding between the ami-

Table 3. Tensile test results for the aminated graphene oxide based epoxy composites

Sample	Neat epoxy	GO	A14-GO	A21-GO	A28-GO
Tensile strength (MPa)	19.1 (±1.35)	30.5 (±0.95)	35.3 (±2.10)	41.9 (±1.81)	42.1 (±1.90)
Tensile strain (%)	2.0 (±0.20)	1.8 (±0.10)	1.9 (±0.02)	2.1 (±0.04)	2.3 (±0.05)
Tensile modulus (GPa)	1.0 (±0.40)	1.7 (±0.05)	1.9 (±0.11)	2.0 (±0.05)	1.8 (±0.04)

Value are presented as mean (±standard deviation).
GO, graphene oxide.

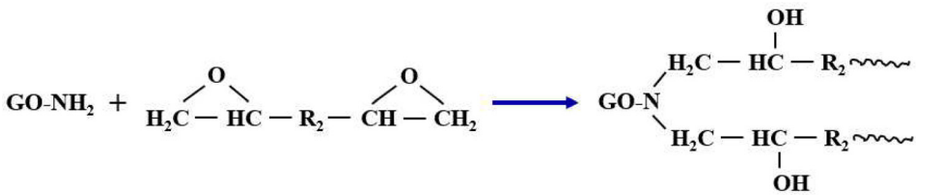

Fig. 5. Schematic of chemical reaction between GO-NH_2 and epoxy molecules. GO, graphene oxide.

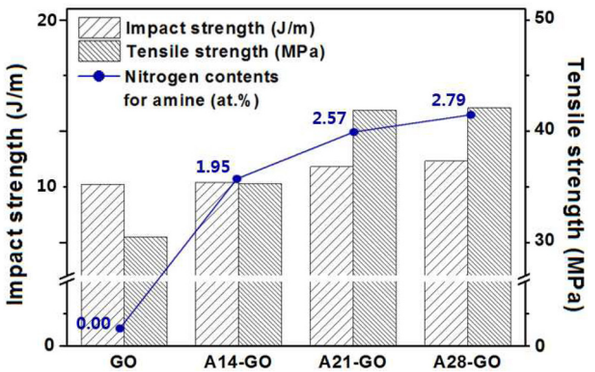

Fig. 6. Relationship diagram between amine groups on graphene oxide (GO) and mechanical properties of aminated GO based epoxy composites.

nated GO and the epoxy matrix, the tensile moduli accordingly increased to 1.8–2.0 GPa.

To explore the reinforcing effects of GO on the epoxy matrix as a function of amination, Izod impact tests were performed on the neat epoxy and the GO/epoxy composites, and the results are shown in Fig. 4b. The impact strength values of the epoxy composites increased with the addition of GO and aminated GO. The highest observed impact strength was 12.3 J/m for the A28-GO-based epoxy composite, and this value was enhanced by 25 and 20% compared with those for the neat epoxy and the GO-based epoxy composite, respectively. This result is attributed the addition and stable dispersion of the aminated GO platelets. These findings are similar to the tensile strength results presented above. Considering the relatively small observed differences in impact strength, however, the amine groups in the aminated GO exerted a stronger influence on the tensile properties of the epoxy composites, as shown in Fig. 6.

4. Conclusions

GO was aminated using ammonia solutions of different concentrations (14, 21, and 28%). Of the nitrogen atoms introduced onto the GO surfaces, only the N that was present in the form of amine (C-NH_2) groups exhibited significant changes. The number of amine groups present consistently increased as the concentration of the ammonia solution increased, resulting in N contents of 1.95, 2.57, and 2.79 at% in the form of C-NH_2 for the GO samples treated with ammonia solutions of 14, 21, and 28%, respectively. Despite the introduction of nitrogen functional groups, no significant structural changes occurred in the aminated GO. The GO- and aminated GO-based epoxy composites exhibited excellent mechanical properties related to the presence of amine groups. The tensile and impact strength values were the highest (42.1 MPa and 12.3 J/m, respectively) in the epoxy composite prepared with GO treated with a 28% ammonia solution. These findings are attributed to the effective interaction of the aminated GO with the epoxy matrix through the rigid interfacial bonding formed in the presence of an amine curing agent.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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