

Preparation of Nitrogen-Doped Graphene Aerogel/Epoxy Nanocomposites and Experimental Study of Mechanical Properties

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Abstract: Nitrogen-Doped Graphene Aerogel (N-GA) nanomaterials can significantly improve the functional efficiency of polymer composites due to its three-dimensional structure and suitable physical properties. The preparation process affects the performance improvement. In this study, the effect of preparation method and the mechanisms affecting the strength behavior of Nitrogen-doped Graphene Aerogel/Epoxy (N-GA/E) nanocomposites was investigated. For this purpose, nanoparticles of Graphene Oxide (GO) were produced using Hummers' method; then, the N-GA was synthesized using the hydrothermal method and the freeze-drying process. The characterization experiments were used in order to confirm the structure and quality of the synthesized nanomaterials. Then, specimens of nanocomposite were prepared by adding weight percentages of 0.05, 0.1, 0.2, 0.5, 1, and 2 from the synthesized N-GA to the epoxy resin. In other preparation processes, N-GA/E nanocomposite specimens were produced using auxiliary solvents. After tensile tests, the best strength performance was observed in the specimens with the preparation process in which acetone solvent was used. The tensile strength and modulus of these nanocomposite specimens have increased by 23% and 20% compared to neat epoxy specimens, respectively. Also, the optimal weight percentage of N-GA nanomaterials for distribution in epoxy is 0.1 wt.%. Microscopic images of the fracture surfaces of the specimens used in the tensile test showed that the placement of N-GA porous plates in epoxy with the creation of the mechanism for micro crack formation led to more energy absorption during the stretching process of the N-GA/E nanocomposites.

Keywords: Nitrogen-Doped Graphene Aerogel, Nanocomposite, Morphology of Fracture Surfaces, Tensile Properties

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1 INTRODUCTION

Carbon atoms are involved in the structure of many important chemical compounds and, thus, the basis of various technologies. Graphene is the newest member of the family of carbon materials which includes fullerene as the next zero nanoparticle, carbon nanotubes as a one-dimensional nanowire, and graphite as a three-dimensional material. Graphene is a two-dimensional material in a honeycomb structure where carbon atoms are bonded together with sp^2 hybridization [1]. In graphene composites, the electrical conductivity is limited due to the lack of a bond between the graphene plates randomly distributed in the field. In addition, strong π - π reactions between graphene plates lead to severe cracking and a decrease in their specific surface area. Both of these deficiencies limit the performance of graphene.

However, the use of three-dimensional graphene structures can overcome these limitations [2]. Triple graphene is a spongy nanomaterial with a higher specific surface than carbon nanotubes and graphene nanosheets. Due to the combination of excellent graphene properties and a three-dimensional porous structure, this nanoscale material has unique properties such as high surface area, low density, suitable mechanical properties, and high electrical conductivity [3]. Doping graphene with other atoms is an effective way to modify the properties of three-dimensional structures. Nitrogen is one of the most important elements for dipping the graphene network. The peak effect of the use of a three-dimensional nitrogen-doped graphene grid can be observed in the electromagnetic field [4]. Nanocomposites fabricated using such a 3-D network produce far higher properties than conventional graphene nanocomposites.

The interest in graphene nanoparticles has led academia and industry to be ideal candidates for the design of new nanosized transistors, display screens, eco-friendly light emitting diodes, main chips next generation computers, color technology, adhesive and related derivatives, solar cells, and other inventions. The rapid progress of research on graphene leaves no doubt that it will revolutionize markets such as electronics, medicine, energy, and aerospace in the near future [5-10]. Triple graphene-based compounds such as foam, sponge, and graphene aerogel are a new generation of porous carbon materials.

Numerous studies have been performed on the properties and structure of this category of nanomaterials [11-13]. The loading of nanoparticles on the surface of irregular graphene prevents the accumulation and agglomeration of nanoparticles and increases stability, size control, and uniform distribution, all of which can affect ultimate morphology [14]. The results of research on the properties of nanocomposites containing graphene aerogel with

suitable thermal, electrical, magnetic, and mechanical properties confirm the structure of this compound [15-16].

Most research on graphene aerogel-reinforced composites has focused on the electrical and magnetic properties of these nanocomposites and only a limited number of researchers have studied their mechanical properties. In addition, no study has investigated the effect of the preparation process on the mechanical performance of N-GA/E nanocomposites. Therefore, the study of mechanical behavior and recognition of the mechanisms affecting it in graphene aerogel nanocomposites is considered as a valuable research field. Accordingly, the main purpose of this study is to evaluate the effect of preparation processes and mechanisms affecting the strength behavior of N-GA/E nanocomposites.

2 MATERIALS AND METHODS

2.1. Preparation of N-GA Nanomaterials

In this research, GO nanomaterials was made by the Hummer's manner [17]. For synthesis of N-GA nanomaterials, 0.2 g of GO nanomaterials was firstly added to 130 mL of water under ultrasonic vibration for 60 min. Then 1.4 mmol of dicyandiamide was dispersed in the solution and the blend was exposed to ultrasonication for 300 s. Next, the blend was placed in autoclave at 180 °C for 720 min. Finally, the prepared mixture was freeze-dried to form N-GA nanomaterials [18].

2.2. Preparation of Epoxy Resin Specimens

Epoxy resin (Bisphenol-A) was used with 15 wt.% hardener (Polyamine) to obtain the suitable physical properties for extensive use in automotive and aerospace industries to capture nanoparticles. The preparation of pure epoxy resins has been carried out according to literature.

Initial modeling and production of molds based on the dimensions mentioned in the ASTM D638 standard were performed for tensile tests of the samples. In this model, the width of the narrow section and the thickness of the sample were 13 and 3 mm, respectively. Then, the 15 wt.% hardening agent was mixed with epoxy resin using an agitator for 300 s at 100 rpm.

The resulting mixture was bubbled in a vacuum chamber for 300 s and then injected into metal molds. All specimens were cured at the ambient temperature for 2 days and post cured for 360 min at 80 °C.

2.3. Preparation of N-GA/E

After the synthesis of N-GA nanomaterials and the use of epoxy resin, the process for preparing nanocomposites of N-GA/E nanocomposites was carried

out as follows. In the beginning, pure epoxy was mixed with 0.1 wt.% N-GA nanomaterials powder using an agitator for 720 min at 1000 rpm. The blend was put in the bath-ultrasonic for 30 min and then again, using the mechanical agitator for 120 min, the process of coagulation continued. This step was repeated for 3 time. The blend was sonicated at power of 100 W using a probe-sonicator for 60 min and then stirred using a magnetic stirring. Then, the 15 wt.% hardening agent was mixed with the resulting blend using an agitator for 300 s at 100 rpm. The mixture was bubbled in a vacuum chamber for 300 s and then injected into metal molds. All specimens were cured at the ambient temperature for 2 days and post cured for 360 min at 80 °C. The N-GA/E nanocomposites preparation process for 0.05, 0.1, 0.2, 0.5, 1, and 2 wt.% of N-GA nanomaterials is similar to the above steps.

2.4. Preparation of N-GA/E by Co-Solvent

In this study, to investigate the dispersion of the N-GA nanomaterials in the epoxy resin and to achieve higher mechanical properties, the preparation of N-GA/E nanocomposite with 0.1% weight ratio was accomplished using two solvents including acetone and THF. Initially, N-GA nanomaterials were immersed in 100 mL acetone solvent and stirred at 2000 rpm for 2 h. The resulting mixture was placed in an ultrasound bath for 90 minutes. The mixture was added to the suitable amount of epoxy resin, and stirred by an agitator at 800 rpm for 90 min. The process of dispersing nanostructure was continued by controlling the temperature for 30 min in the ultrasonic bath. To ensure that whole of acetone solvent was removed from the resin, the solution was placed in a vacuum oven for 12 h to evaporate the remaining solvent. Subsequently, the mixture was subjected to ultrasound irradiation using an ultrasonic probe with a power output of 100 W for 30 min. Then, the mixture was slowly stirred for 10 min.

In another case, acetone solvent was replaced with THF, and the above steps were performed to obtain the samples.

2.4. Experimental Tests

In this study, a Transmission Electron Microscopy (TEM, Zeiss EM10C) was used to examine nanoparticle dispersion on polymer. Raman spectroscopy (Takram P50C0R10) was employed to confirm the nanostructures of N-GA. In order to determine the fractures mechanism, Field Emission Scanning Electron Microscopy (FESEM) analysis was done using a Tescan MIRA3 FESEM instrument ("Fig. 1a"). To do this without injuring the fracture area of specimens, a small fraction of the fracture area was cut. The fracture surfaces were made by creating a thin layer of gold using the sputtering method ("Fig. 1b").



Fig. 1 (a): FESEM device, and (b): samples prepared for testing.

Tensile test was performed using ASTM D638 standard instructions on neat epoxy specimens and N-GA/E nanocomposites ("Figs. 2a and b") by the STM-150 device. The tensile modulus of the samples was obtained using an extensometer during the tests. The loading speed of the parts in the tensile tests were adjusted at 5 mm/min.

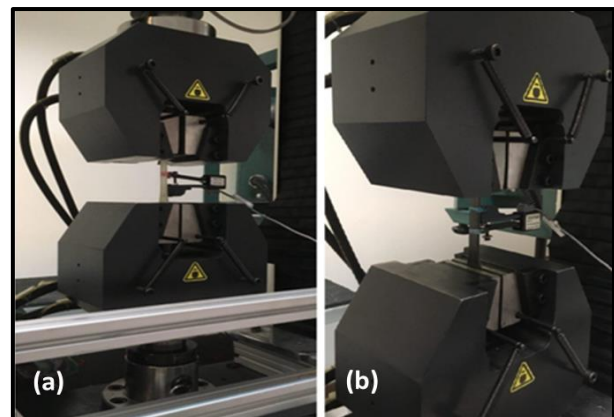


Fig. 2 Images of the device used in the tensile test: (a): tensile test of pure epoxy specimen, and (b): tensile test of N-GA/E specimen.

3 RESULTS AND DISCUSSION

3.1. FESEM Analysis

Figures 3a and b show the FESEM images of GO and N-GA nanomaterials, respectively. To verify the quality of the synthesized GO nanosheets, FESEM analysis was employed which clearly depicted the exfoliated GO nanosheets with the size in the range of several micrometers ("Fig. 3a"). In "Fig. 3b", the FESEM image of N-GA nanomaterials confirms the porosity and the approximate size of the pores of the 3D graphene [19].

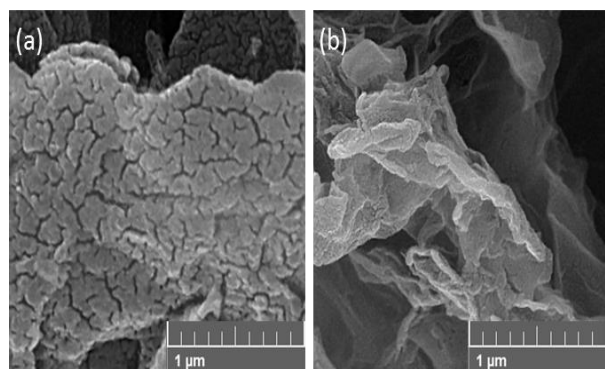


Fig. 3 FESEM images of: (a): GO nanomaterials, and (b): N-GA nanomaterials.

3.2. Raman Spectroscopy Analysis

Raman spectroscopy is one of the most powerful non-destructive detection methods used to identify the structures of carbon materials, especially the detection and identification of regular and irregular crystalline structures [20]. The Raman spectra of GO and N-GA nanomaterials are presented in “Fig. 4a and b”, respectively. The Raman spectrum shows two bands at 1601 and 1362 cm^{-1} according to the G-band and D-band of GO nanomaterials, respectively. In the case of N-GA nanomaterials, the G-band and D-band are located at 1586 and 1353 cm^{-1} respectively [21]. The ratio (I_D/I_G) in the spectrum of GO nanomaterials (“Fig. 4a”) is about 0.9 and that of N-GA nanomaterials (“Fig. 4b”) is about 1.02. The amount of ratio (I_D/I_G) increases with a reduction of GO [22]. Therefore, the G-band in GO is about 1601 cm^{-1} , while in N-GA, G-band moves toward lower bands (1586 cm^{-1}) [23].

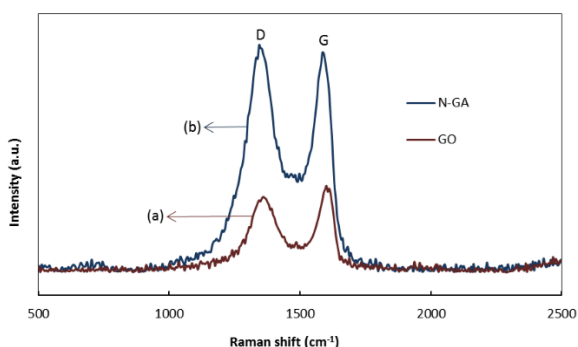


Fig. 4 Raman spectra of: (a): GO nanomaterials, and (b): N-GA nanomaterials.

3.3. TEM Analysis

Figure 5 shows the TEM image of N-GA/E nanocomposite. The binding of 3D structure graphene with epoxy resin causes the dispersion and uniform distribution of nanoparticles and increases their activity [24]. The distribution of porous structure of N-GA nanomaterials in epoxy resin can be observed in the TEM image.

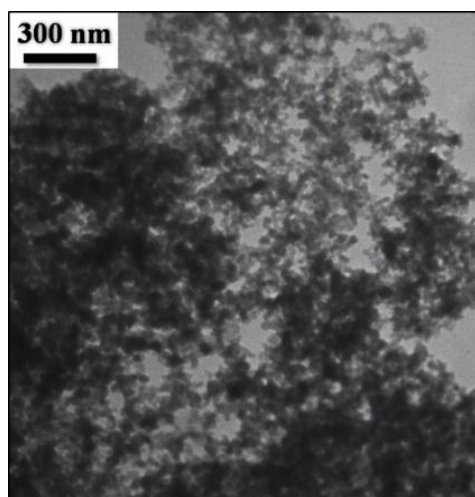


Fig. 5 TEM image of dispersed N-GA in epoxy resin.

3.4. Tensile Experiment Results

The tensile test results regarding the pure epoxy and N-GA/E nanocomposites with different weight percentages of the N-GA nanomaterials are depicted in “Fig. 6”. According to the calculations, the average tensile strength of the pure epoxy specimens was 57.98 MPa, and the calculated tensile modulus was equal to 2.62 GPa. The average tensile strength and modulus for 0.1 wt.% N-GA/E nanocomposites were 68.96 MPa and 2.91 GPa, respectively.

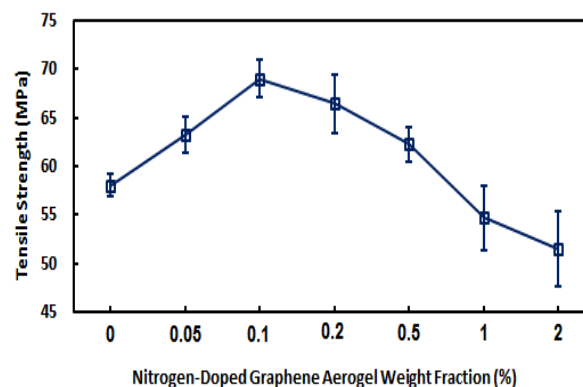


Fig. 6 Tensile strength of N-GA/E with different weight percentages of N-GA.

The good effect of N-GA nanomaterials can be explained by the use of the proper properties of the nanoparticle and polymer joint. Moreover, the presence of porous N-GA plates in epoxy and the formation of relatively strong bonds caused a transfer of stress from the resin to the nanoparticles in the applied phase, which increased the tensile strength of the specimen [25]. According to calculations, the average tensile strengths for N-GA/E nanocomposites with the different weights of 0.05, 0.2, 0.5, 1, and 2 wt.% N-GA nanomaterials were 63.22 MPa, 66.42 MPa, 62.22 MPa, 54.65 MPa, and 51.46 MPa, respectively.

Comparison of specimen tensile strength (“Fig. 6”) showed that the highest tensile strength was recorded in the specimen with 0.1 wt.% N-GA nanomaterials. With the addition of N-GA nanomaterials to epoxy resin, the properties of the resin varied in the vicinity of the nanoparticle phase (middle phase). In fact, the mid-phase was formed around the interconnected phase, between the phase and the amplifier, and increased the strength of this joint area to transfer the control force and the tensile strength of the nanocomposite specimen. By increasing the percentage of the N-GA due to the increased probability of poor distribution of nanoparticles and the formation of clumping conditions, the strength of the specimens decreased sharply; when more than 1 wt.% of the N-GA nanomaterials was added to the epoxy resin, the tensile strength of the nanocomposite specimen was less than even pure epoxy [26].

Figure 7 depicts the comparison diagram of the tensile modulus of N-GA/E nanocomposites with various percentages of N-GA nanomaterials. The mean tensile modulus for 0.05, 0.2, 0.5, 1, and 2 wt.% N-GA nanomaterials were found to be 2.71 GPa, 2.97 GPa, 3.01 GPa, 2.93 GPa, and 2.83 GPa, respectively.

An increase in the tensile modulus of a material means increasing the rigidity of the material and, consequently, the toughness of that material. By comparing the tensile modulus values of the nanocomposite specimens, it was observed that adding N-GA nanomaterials to resin increased the tensile modulus. This result was observed with increases up to 0.5 wt.% nanomaterials to resin, and then it slightly decreased.

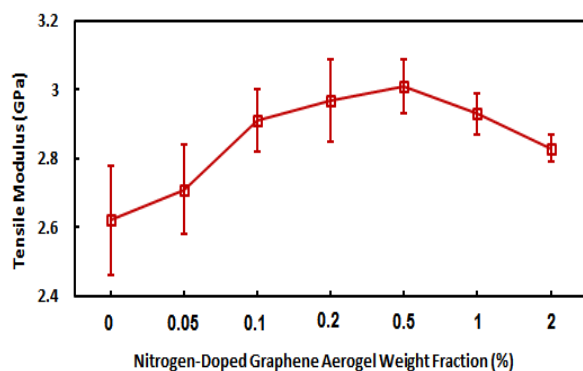


Fig. 7 Tensile modulus of N-GA/E with different weight percentages of N-GA.

In another assessment of the results of the tensile test, the effects of the use of an auxiliary solvent could be seen (“Fig. 8”). According to the results, when acetone solvent was used to distribute 0.1 wt.% N-GA nanomaterials in epoxy resin, the tensile strength and modulus were 71.38 MPa and 3.15 GPa, respectively. For the samples used from the THF auxiliary solvent, these values were 64.26 MPa and 2.93 GPa, respectively.

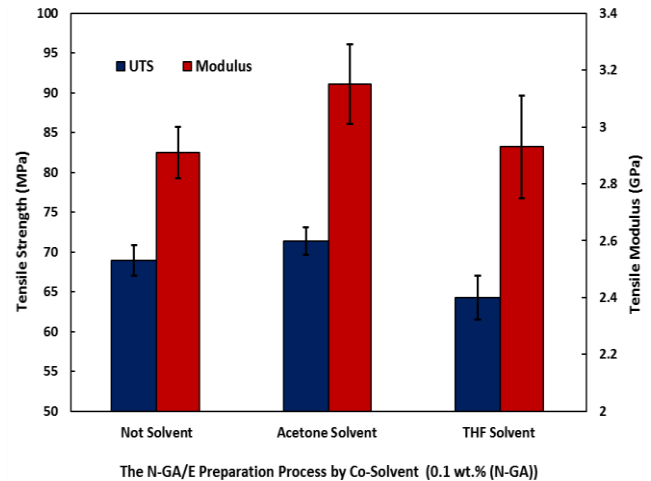


Fig. 8 Tensile strength and modulus of N-GA/E (0.1 wt.% (N-GA)) by using solvent in preparation process.

The results showed that for the selected materials in this study, the use of acetone solvent had a more positive effect on the more uniform distribution of the N-GA nanomaterials within the resin, and the nanocomposite with higher tensile properties resulted from this process. The destructive effects of THF solvent, due to its imperfect evaporation, reduced the tensile strength of the nanocomposite.

In epoxy resin, a covalent bond is seen between the particles of each layer, and the bond between the layers is of the van der Waals type. Given that the van der Waals bond is much weaker than the covalent bond, when the resin is loaded first, the van der Waals bonds break down, causing the layers to slip on each other. With precision in the form indicating the fracture area of the pure epoxy sample, the slip of the layers on each other is clearly visible. Adding N-GA nanoparticles to the epoxy resin enhanced the bond between the resin layers, which prevented the layers from slipping slip easily onto each other. When the layers cannot easily slip over each other, each layer suffers more power, and this causes microcracks to occur in the layers. Microcracks reduce the growth rate of the major cracks that result in a specimen being defeated; in other words, these cracks increase the energy needed to break the specimen [27].

3.5. Microscopic Analysis of Fracture

By observing FESEM images, the fracture surface of the neat epoxy resin sample and the N-GA/E nanocomposites are indicated, in the pure epoxy specimen, the plate deflection is smooth and even (“Figs. 9a and b”). While in the N-GA/E nanocomposites, the fracture surface looks like a cloud and rugged (“Figs. 9c and d”). The random dispersion of the crack plates in this state indicates higher energy absorption to the final failure of the test specimen [28].

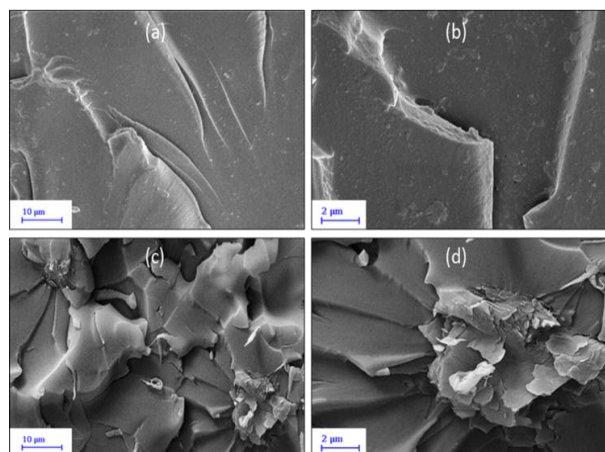


Fig. 9 FESEM images of: (a) and (b): fracture surfaces of neat epoxy, (c) and (d): fracture surfaces of N-GA/E nanocomposites.

4 CONCLUSION

In epoxy resin, the bond between the layers is weak. The addition of porous N-GA nanomaterials to epoxy resin enhances the bond between the resin layers, making it impossible for the layers under load to slip easily over each other. Due to the high specific surface area of N-GA nanomaterials, a good bond between the resin and the nanomaterials is formed, and the possibility of using the properties of the joint chains increases.

At first, the GO nanomaterials were produced by the Hummers method, and then using the hydrothermal method and the freeze drying process, the N-GA nanomaterials synthesis. Dicyandiamide was used to convert GO into N-GA nanomaterials. Due to high nitrogen density, dicyandiamide can interact with the oxygen groups of GO nanosheets and allow an idealized N-GA nanomaterial to be produced. The formation of GO and N-GA nanomaterials was investigated and verified by FESEM and Raman spectroscopy.

Tensile test was performed on neat epoxy, and the average values of 2.62 GPa and 57.98 MPa were obtained for tensile modulus and tensile strength, respectively. Tensile tests were also carried out on N-GA/E nanocomposites with weight percentages of 0.05, 0.1, 0.2, 0.5, 1, and 2 nanomaterials in resin. According to the calculations, the highest tensile strength (68.96 MPa) was obtained in samples with 0.1 wt.% N-GA nanomaterials, indicating a 19% growth compared to the epoxy specimen. The highest tensile modulus was recorded for the specimen with 0.5 wt.% nanomaterials and was reported as 3.01 GPa, which represents a 15% increase. It was also observed that the use of acetone solvent in the preparation process improves the strength performance of the N-GA/E nanocomposite by 23%. The application of acetone solvent in the preparation process causes a more uniform distribution of

nanomaterials within the epoxy resin and, the transfer of stress from the resin to the nanomaterials is done more widely. Therefore, the tensile strength of N-GA/E nanocomposites increases.

By observing the FESEM images, the fracture surfaces can be seen. In the pure epoxy specimen, the fracture surface is smooth and uniform, while in the N-GA/E nanocomposites specimen, the fracture surface looks rugged and like a cloud. The random dispersion of the crack plates in this state indicates higher energy absorption to the final failure of the test specimen.

REFERENCES

- [1] Geim, A. K., Novoselov, K. S., *The Rise of Graphene*, Nanoscience and Technology, 2009, pp. 11-19, 10.1142/9789814287005_0002.
- [2] Chen, P., Yang, J., Li, S., Wang, Z., Xiao, T., Qian, Y., and Yu, S., Hydrothermal Synthesis of Macroscopic Nitrogen-Doped Graphene Hydrogels for Ultrafast Supercapacitor, *Nano Energy*, Vol. 2, No. 11, 2013, pp. 249-256, 10.1016/j.nanoen.2012.09.003.
- [3] Gorgolis, G., Galiotis, C., *Graphene Aerogels: A Review*, 2D Materials, Vol. 4, 2017, 032001, 10.1088/2053-1583/aa7883.
- [4] Wang, H., Maiyalagan, T., and Wang, X., Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and its Potential Applications, *Acs Catalysis*, Vol. 2, No. 5, 2012, pp. 781-794, 10.1021/cs200652y.
- [5] Rowley Nealea, S. J., Randviir, E. P., Abo Dena, A. S., and Banksa, C. E., An Overview of Recent Applications of Reduced Graphene Oxide as a Basis of Electroanalytical Sensing Platforms, *Applied Materials Today*, Vol. 10, March 2018, pp. 218-226, 10.1016/j.apmt.2017.11.010.
- [6] Kumar, A., Sharma, K., and Dixit, A. R., A Review of the Mechanical and Thermal Properties of Graphene and Its Hybrid Polymer Nanocomposites for Structural Applications, *Journal of materials science*, Vol. 54, 2019, pp. 5992-6026, 10.1007/s10853-018-03244-3.
- [7] Bafana, A. P., Yan, X., Wei, X., Patel, M., Guo, Z., Wei, S., and et al., Polypropylene Nanocomposites Reinforced with Low Weight Percent Graphene Nanoplatelets, *Compos Part B- Engineering*, Vol. 109, 15 January 2017, pp. 101-107, 10.1016/j.compositesb.2016.10.048.
- [8] Cong, L., Li, X., Ma, L., Peng, Z., Yang, C., Han, P., Wang, G., Li, H., Song, W., and Song, G., High-Performance Graphene Oxide/Carbon Nanotubes Aerogel-Polystyrene Composites: Preparation and Mechanical Properties, *Materials Letters*, Vol. 214, 1 March 2018, pp. 190-193, 10.1016/j.matlet.2017.12.015.
- [9] Phetarporn, V., Loykulnant, S., Kongkaew, C., Seubsai, A., and Prapainainar, P., Composite Properties of Graphene-Based Materials/Natural Rubber Vulcanized

- Using Electron Beam Irradiation, *Materials Today Communications*, Vol. 19, June 2019, pp. 413-424, 10.1016/j.mtcomm.2019.03.007.
- [10] Bhasin, M., Wu, S., Ladani, R. B., Kinloch, A. J., Wang, C. H., and Mouritz, A. P., Increasing the Fatigue Resistance of Epoxy Nanocomposites by Aligning Graphene Nanoplatelets, *International Journal of Fatigue*, Vol. 113, August 2018, pp. 88-97, 10.1016/j.ijfatigue.2018.04.001.
- [11] Yang, M., Zhao, N., Cui, Y., Gao, W., Zhao, Q., Gao, C., Bai, H., and Xie, T., Biomimetic Architected Graphene Aerogel with Exceptional Strength and Resilience, *ACS Nano*, Vol. 11, No. 7, 2017, pp. 6817-6824, 10.1021/acsnano.7b01815.
- [12] Huang, Z. M., Liu, X. Y., Wu, W. G., Li, Y. Q., and Wang, H., Highly Elastic and Conductive Graphene/Carboxymethylcellulose Aerogels for Flexible Strain-Sensing Materials, *Journal of Materials Science*, Vol. 52, 2017, pp. 12540-12552, 10.1007/s10853-017-1374-1.
- [13] Wang, M., Shao, C., Zhou, S., Yang, J., and Xu, F., Super-Compressible, Fatigue Resistant and Anisotropic Carbon Aerogels for Piezoresistive Sensors, *Cellulose*, Vol. 25, 2018, pp. 7329-7340. 10.1007/s10570-018-2080-0.
- [14] Ma, Y., Chen, Y., Three-Dimensional Graphene Networks: Synthesis, Properties and Applications, *National Science Review*, Vol. 2, 2015, pp. 40-53, 10.1093/nsr/nwu072.
- [15] Kim, J., Han, N. M., Kim, J., Lee, J., Kim, J. K., and Jeon, S., Highly Conductive and Fracture-Resistant Epoxy Composite Based On Non-Oxidized Graphene Flake Aerogel, *ACS Applied Materials & Interfaces*, Vol. 10, No. 43, 2018, pp. 37507-37516. 10.1021/acсами.8b13415.
- [16] Chiou, Y. C., Chou, H. Y., and Shen, M. Y., Effects of Adding Graphene Nanoplatelets and Nanocarbon Aerogels to Epoxy Resins and Their Carbon Fiber Composites, *Materials & Design*, Vol. 178, 15 September 2019, pp. 107869, 10.1016/j.matdes.2019.107869.
- [17] Hummers Jr, W. S., Offeman, R. E., Preparation of Graphitic Oxide, *Journal of the American Chemical Society*, 1958, pp. 1339-1339, 10.1021/ja01539a017.
- [18] Panchakarla, L., Subrahmanyam, K., Saha, S., Govindaraj, A., Krishnamurthy, H., Waghmare, U., and Rao, C., Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene, *Advanced Materials*, Vol. 21, No. 46, 2009, pp. 4726-4730, 10.1002/adma.200901285.
- [19] Hosseini, S. G., Gholami, S., and Mahyari, M., Highly Dispersed Ni-Mn Bimetallic Nanoparticles Embedded in 3D Nitrogen-Doped Graphene as an Efficient Catalyst for the Thermal Decomposition of Ammonium Perchlorate, *New Journal of Chemistry*, No. 8, 2018, pp. 5889-5899, 10.1039/C8NJ00613J.
- [20] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., and Ruoff, R. S., Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide, *Carbon*, Vol. 45, No. 7, 2007, pp. 1558-1565, 10.1016/j.carbon.2007.02.034.
- [21] Tuinstra, F., Koenig, J. L., Raman Spectrum of Graphite, *The Journal of Chemical Physics*, Vol. 53, No. 3, 1970, pp.1126-1130, 10.1063/1.1674108.
- [22] Qiu, B., Xing, M., and Zhang, J., Mesoporous TiO₂ Nanocrystals Grown in Situ On Graphene Aerogels for High Photocatalysis and Lithium-Ion Batteries, *Journal of the American Chemical Society*, 2014, pp 5852-5855, 10.1021/ja500873u.
- [23] Pimenta, M., Dresselhaus, G., Dresselhaus, M. S., Cancado, L., Jorio, A., and Saito, R., Studying Disorder in Graphite-Based Systems by Raman Spectroscopy, *Physical Chemistry Chemical Physics*, No. 11, 2007, pp. 1276-1290, 10.1039/B613962K.
- [24] Chandrasekaran, S., Seidel, C., and Schulte, K., Preparation and Characterization of Graphite Nano-Platelet (GNP)/Epoxy Nano-Composite: Mechanical, Electrical and Thermal Properties, *European Polymer Journal*, Vol. 49, No. 12, 2013, pp. 3878-3888, 10.1016/j.eurpolymj.2013.10.008.
- [25] Abdullah, S. I., Ansari, M. N. M., Mechanical Properties of Graphene Oxide (GO)/Epoxy Composites, *HBRC Journal*, Vol. 11, No. 2, 2015, pp. 151-156, 10.1016/j.hbrcj.2014.06.001.
- [26] Ni, Y., Chen, L., Teng, K., Shi, J., Qian, X., and Xu, Z., Superior Mechanical Properties of Epoxy Composites Reinforced by 3D Interconnected Graphene Skeleton, *ACS Applied Materials & Interfaces*, Vol. 7, No. 21, 2015, pp. 11583-11591, 10.1021/acсами.5b02552.
- [27] Bortz, D. R., Heras, E. G., and Martin-Gullon, I., Impressive Fatigue Life and Fracture Toughness Improvements in Graphene Oxide/Epoxy Composites, *Macromolecules*, Vol. 45, No. 1, 2012, pp. 238-245, 10.1021/ma201563k.
- [28] Loos, M. R., Yang, J., Feke, D. L., Manas, I., Unal, S., and Younes, U., Enhancement of Fatigue Life of Polyurethane Composites Containing Carbon Nanotubes, *Elsevier*, Vol. 44, 2013, pp. 740-744, 10.1016/j.compositesb.2012.01.038.

CONFLICTS OF INTEREST

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