International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075 (Online), Volume-8 Issue-4, February 2019

Microstructure and Elemental Investigation of Graphene/ CNT Epoxy Composite

Manoj Kumar Shukla, Kamal Sharma

***Abstract:** Epoxy based graphene/ CNT reinforced hybrid composite was prepared using sonication method with equal ratio of nano-fillers at weight percent of 0 and 0.25 wt. % are fabricated. In the present work, the influence of graphene/ CNT substitution on the microstructure and element distribution on hybrid epoxy composite is reported. The composite was characterized for their morphological properties by Scanning Electron Microscopy (SEM). The distribution of elements and elemental composition was also evaluated using Energy Dispersive X-Ray Spectroscopy (EDX). The reaction progress and compositions of elements were analyzed as a function of microstructure. The presence of functionalized filler and formation of copolymerization of polymer was confirming with the help of the EDX spectra of the hybrid composite. Hybrid composite confirmed the presence of Carbon, Chlorine, Silicon and other elements. Variation in the ratio of elements present in pristine and hybrid epoxy composite confirms the occurrence of chemical reaction during processing of composite sample. SEM-EDX analysis show better adhesion in hybrid composite as compared to pristine composite. The detailed results will be presented and discussed.*

***Keywords:** Graphene, CNT, epoxy, hybrid composite, EDX, SEM.*

I. INTRODUCTION

Epoxy resin is widely used for structural application dues to its favorable structural properties [1]. Epoxy is a member of epoxide group known as polyepoxide which forms polymer chain by polymerization. Epoxy is produced by reacting epichlorohydrin and bisphenol A to obtain bisphenol A diglycidyl ethers, a building block for formation of epoxy resin. Various forms of epoxy are shown in Figure1 [2].

Epoxy resin are normally reinforced with graphene and CNT (Carbon nano tube) for improving its strength to weight ratio for structural properties thus forming epoxy based composite material [3][4]. Implication of both graphene and CNT simultaneously forms 3-D which further improves microstructure of hybrid composite [5]. Interaction of elements whose combination produces effect that is improved in comparison to the effect of individual elements is referred to synergy. The synergy of the reinforcing materials is characterized, indicating a positive synergistic effect [6].

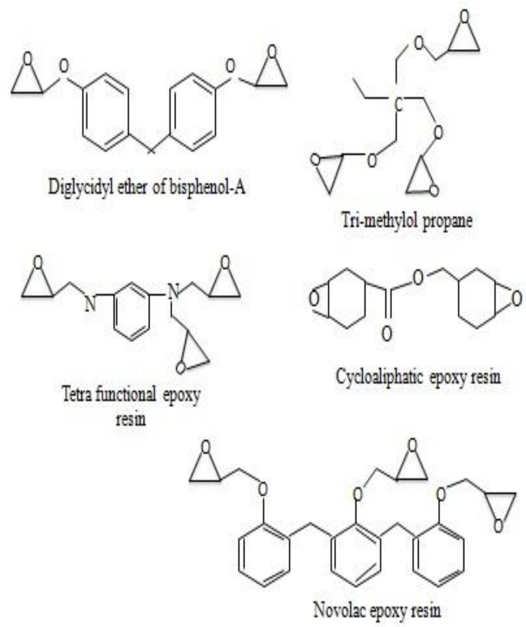


Figure 1: Different types of epoxy resin [2]

Dispersion is of prime importance for improving microstructure of composite which can be obtained by functionalization of graphene and CNT [7][8]. Various aspects of composite such as morphological [9] and chemical [10] can be analyzed through advanced testing methods such as SEM and EDS respectively. Variation in microstructure and dispersion is due to various elements which can be analyzed by chemical composition analysis [10][11]. Chemical analysis of epoxy composite is still not explored as per literature survey. Therefore the combined effect of graphene and CNT on microstrucure and elemental composition of aforementioned hybrid composites has been investigated.

II. EXPERIMENTAL

A. Materials and Sample preparation

Graphene and CNT particles were used as filler material. Both the fillers were amine functionalized. Diglycidyl ether bisphenol A (DGEBA) form of epoxy resin was used as matrix. Filler particles with equal ratio are reinforced in epoxy resin to fabricate hybrid composite. The amount of filler reinforced in epoxy resin is 0 and 0.25 weight %. Elemental constituents of both the fillers are given in Table 1.

Manuscript published on 28 February 2019.
***Correspondence Author(s)**
Manoj Kumar Shukla, Department of Mechanical Engineering, Institute of Engineering & Technology, GLA University, Mathur, India,
KNPC (Rajiv Gandhi Technical University), Jabalpur- 482001, India.
Kamal Sharma, KNPC (Rajiv Gandhi Technical University), Jabalpur- 482001, India

Table 1: Chemical composition of Graphene and CNT (Ref: United nanotech Innovations, Bangalore, India)

Element / Filler	Carbon	Chlorine	Oxygen	Hydrogen	Nitrogen	Trace metals	Ash
Graphene	≥ 72 %	≤ 0.8 %	≥ 0.2 %	18 %	9 %	≤ 0.5 %	≤ 0.1 %
CNT	≥ 72 %	≤ 1 %	≥ 0.2 %	16 %	8 %	≤ 1.5 %	≤ 0.1 %

Configurations of constituents of mixture are given in Table 2. For preparation of matrix composite first epoxy resin and ethanol is mixed. The mixture is stirred for 10 min and after this as per Table 2, pre weighted quantity of filler is added with the mixture. Degassing for 30 minutes is performed for removing accumulated bubbles in the mixture. The mixture is then poured in aluminum moulds and cured at room temperature for 24 hours to finally obtain composite sample.

Table 2: Sample code corresponding to composition composites

Sample code	Epoxy resin (wt. %)	Filler (wt. %)	Carbon nano-filler composition	
			Graphene	CNT
A	100	0	0	0
B	99.75	0.25	0.125	0.125

B. Characterization

Microstructure of fractured surface of sample is analyzed through SEM (scanning electron microscopy) images. Energy dispersive X-ray spectroscopy (EDX) is performed for elemental analysis or chemical characterization of sample. An energy dispersive spectrum is obtained comprising x-ray beam energy (0 to 10 keV) in x-axis and number of counts per second (cps) in y-axis. Usually spectrum is set at a point in SEM image, at this particular point chemical composition is being analytically obtained. The incident beam excites an electron in an inner shell, ejecting it from the shell while creating an electron-hole which is filled by an electron from an outer (higher energy) shell and the difference in energy between the higher and the lower energy shell can be released in the form of an X-ray. The energy of the X-rays is characteristic of the difference in energy between the two shells.

III. RESULTS AND DISCUSSION

A. Microstructure analysis

This segment is dedicated to analyzing the influence of graphene/ CNT fillers at epoxy matrix regime. The SEM micrograph taken up on microstructure of composite is analyzed for presence of elements at that regime. Influence of chemical reaction between filler, epoxy resin and hardener occurred during fabrication process on the difference in microstructure of pristine and hybrid composite is revealed by this investigation. For this the SEM micrograph of both pristine and hybrid composite is compared, showing changes in the microstructure.

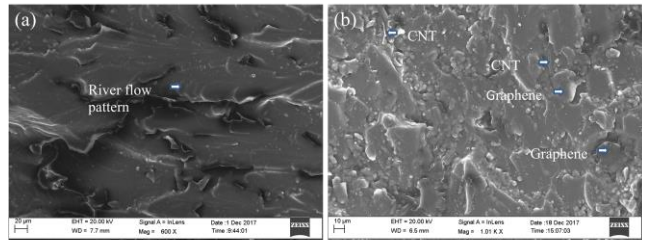


Figure 2: SEM Images of (a) pristine and (b) hybrid epoxy composite.

The analysis of microstructure of pristine and hybrid epoxy composite was conducted to compare the change before and after chemical reaction as a result of reinforcement of fillers in epoxy resin. SEM micrographs of pristine and hybrid epoxy composite are shown in Figure 2. Microstructure of pristine epoxy composite sample shown in Figure 2 (a) reveals river flow pattern with no evidence of resistance to fracture. In contrast the microstructure of hybrid composite sample shown in Figure 2 (b) indicates evidence of disruption of structure with distribution of graphene/ CNT filler particles at the grain boundaries which resists the fracture process. This may be attributed to the dispersion of fillers in the vicinity of epoxy matrix. SEM images are further analyzed to investigate the elements present in the fabricated samples. This is validated by EDX analysis of both the images due to incorporation of new elements.

B. Elemental analysis

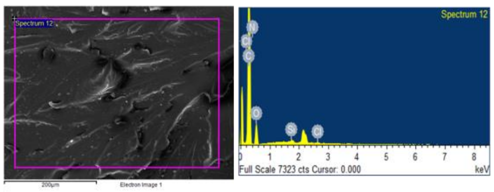
The atomic elements present in pristine and hybrid epoxy composite has been characterized by Energy dispersive analysis of X-rays (EDX). EDX spectrum of pristine and hybrid epoxy composite is shown in the Figure 3 and 4 respectively. Examination of peaks in the spectra of EDX elemental X-ray mapping shows segregation of various chemical elements along the boundaries of epoxy matrix. The distribution of various elements in the aforementioned composite in the SEM image is shown in the Table 4. Figure 4 shows the EDX spectra of hybrid composite which confirms the presence of carbon and oxygen observed at 0.15 eV (Kα) and 0.45 eV (Kα). The peak of oxygen with increased intensity confirms the presence of oxide group in the composite sample. The weight percentage of the oxygen in hybrid composite is 23.46 % whereas in pristine epoxy composite it is 20.97 % which is 12 % due to the strong oxidation of the graphene structure by the oxidizing agents. The reason may be due to thermal exfoliation of fillers which can be verified by morphology and composition of composite sample.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

Similarly hybrid composite confirm the presence of oxygen, carbon and catalyst particles.

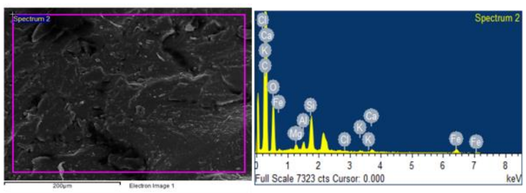
Chemical composition as investigated from EDX spectra can be correlated with SEM images. The dark areas in SEM micrographs of Figure 2 are due to presence of carbon whereas white areas indicate presence of oxygen element. The diffused grey regions constitutes remaining element.

EDX analysis of pure epoxy composite as shown in Figure 3 shows presence of carbon and oxygen as main elements as expected as given in Table 4, carbon and oxygen constitute 97.16 % of elemental composition. However other elements such as silicon and chlorine are also present. Similarly EDX analysis of hybrid composite shown in Figure 4, shows presence of carbon and oxygen as main elements as expected which constitute 99.65 % of total elemental composition as seen from Table 4. Elements present in the substrate, due to chemical reaction and impurities constitutes for remaining 0.35% weight percentage, accumulating other elements such as magnesium, aluminum, silicon, chlorine, potassium, calcium and iron.



Element	Weight %	Atomic %
CK	76.19	80.88
NK	2.49	2.27
OK	20.97	16.71
SiK	0.17	0.08
ClK	0.18	0.07
Totals	100.00	

Figure 3: Combined SEM micrograph & EDX spectra of pristine epoxy composite.



Element	Weight %	Atomic %
CK	72.85	79.34
OK	23.46	19.18
MgK	0.29	0.16
AlK	0.37	0.18
SiK	1.66	0.77
ClK	0.09	0.03
KK	0.09	0.03
CaK	0.23	0.08
FeK	0.96	0.22
Totals	100.00	

Figure 4: Combined SEM micrograph & EDX spectra of hybrid epoxy composite.

Table 4: EDX analysis of pristine and hybrid epoxy composite

	Weight percentage									
Elements	C	O	N	Si	Cl	Mg	Al	K	Ca	Fe
Pristine epoxy composite	76.19	20.97	2.49	0.17	0.18	---	---	---	---	---
Hybrid epoxy composite	72.85	23.46	---	0.18	0.09	0.29	0.37	0.09	0.23	0.96

Table 3: EDX spectrum element ratio for pristine and hybrid epoxy composite

Element ratio	Pristine epoxy composite element atomic %	Hybrid epoxy composite element atomic %
C/ O	3.63	3.10
C/ Cl	423.27	849.56
C/ Si	448.17	45.89

Ratio of elements present in pristine and hybrid epoxy composite is obtained by EDX analysis, shown in Table 3. There is a decrease in C/ O and C/ Si ratio, however an increase in ratio of C/Cl is observed. This indicates the occurrence of chemical reactions in pristine and hybrid epoxy composite. There is slight variation in C/ O ratio indicating identical variation due to oxygen element in both the composite. C/ Cl ratio is higher for hybrid epoxy composite may be due to constituent elements of higher chemical compositions of the same. A drastic decrease in the ratio C/ Si is observed for hybrid epoxy composite.

IV. CONCLUSION

From current investigation it can be concluded by SEM and EDX analysis that chemical reactions takes place during composite processing with presence of different elements in the composite sample. Chemical characterization using EDX analysis reveals the increase in composition of oxygen and other heavy metals in hybrid composite as compared to pure epoxy composite. SEM micrograph indicates traces of filler materials in hybrid composite showing resistance to fracture due to improved dispersion of constituent materials as compared to pristine epoxy composite. Combined SEM-EDX analysis helps in understanding the impact of chemical reaction on the microstructure of polymer composite. Increase in oxidation in hybrid composite is revealed by higher content of oxygen. Similarly traces of other elements such as magnesium, aluminum, silicon, chlorine, potassium, calcium and iron are seen due to presence of substrate and impurities. Ratio of elements present in pristine and hybrid epoxy composite is also analyzed indicating decrease in C/ O and C/ Si ratio, however an increase in ratio of C/Cl is observed.

Acknowledgments

I would thank Indian Institute of Science and Research, Bhopal for conducting advance tests of SEM and EDX.

REFERENCES:

1. R. Atif and F. Inam, “Influence of Macro-Topography on Damage Tolerance and Fracture Toughness of Monolithic Epoxy for Tribological Applications,” *World J. Eng. Technol.*, no. May, pp. 335–360, 2016.
2. Z. Anwar, A. Kausar, I. Rafique, and B. Muhammad, “Advances in Epoxy/Graphene Nanoplatelet Composite with Enhanced Physical Properties: A Review,” *Polym. Plast. Technol. Eng.*, vol. 2559, no. January, p. 03602559.2015.1098695, 2015.

3. A. K. Geim and K. S. Novoselov, "The rise of graphene.," *Nat. Mater.*, vol. 6, no. 3, pp. 183–91, 2007.
4. H. Nolte, C. Schilde, and A. Kwade, "Determination of particle size distributions and the degree of dispersion in nanocomposites," *Compos. Sci. Technol.*, vol. 72, no. 9, pp. 948–958, 2012.
5. S. Chatterjee, F. Nafezarefi, N. H. Tai, L. Schlagenhauf, F. A. Nüesch, and B. T. T. Chu, "Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites," *Carbon N. Y.*, vol. 50, no. 15, pp. 5380–5386, 2012.
6. U. Szeluga, B. Kumanek, and B. Trzebicka, "Synergy in hybrid polymer/nanocarbon composites. A review," *Compos. Part A Appl. Sci. Manuf.*, vol. 73, pp. 204–231, 2015.
7. J. Wang *et al.*, "Graphene and Carbon Nanotube Polymer Composites for Laser Protection," *J. Inorg. Organomet. Polym. Mater.*, vol. 21, no. 4, pp. 736–746, 2011.
8. Z. A. Ghaleb, M. Mariatti, and Z. M. Ariff, "Synergy effects of graphene and multiwalled carbon nanotubes hybrid system on properties of epoxy nanocomposites," *J. Reinf. Plast. Compos.*, vol. 0(0) 1–11, 2017.
9. P. J. Lu *et al.*, "Methodology for sample preparation and size measurement of commercial ZnO nanoparticles," *J. Food Drug Anal.*, vol. 26, no. 2, pp. 628–636, 2018.
10. C. Zhao, "Enhanced strength in reduced graphene oxide/nickel composites prepared by molecular-level mixing for structural applications," *Appl. Phys. A Mater. Sci. Process.*, vol. 118, no. 2, pp. 409–416, 2014.
11. C. C. C.S. Sipaut, N. Ahmed, R.Adnan, I. Rahman, MA Bakar, J Ismail, "2007 Properties and Morphology of Bulk Epoxy Composite filled with modified fumed silica-epoxy nanocomposite," *J. Appl. Sci.*, vol. 7, no. (1), pp. 27–34, 2007.