70(8A): 1-479; 2022. DOI: 10.18311/jmmf/2022/32011

Print ISSN : 0022-2755
Journal of Mines, Metals and Fuels
Contents available at: www.informaticsjournals.com/index.php/jmmf

Comparative Study on the Effect of Aluminium Trihydrate and Carbon Nanofillers on Thermal Properties of Glass Fiber Reinforced Epoxy Composites

Madhu B.M.*[1], Rashmi[1], Sailaja R R N[2], Sundara Rajan J[1]

[1]Department of Electrical and Electronics Engineering, Siddaganga Institute of Technology, BH. Road, Tumakuru, Karnataka-572 103, India.
[2]The Energy and Resources Institute, Southern Regional Centre, 4th Main, 2nd Cross, Bangalore, Karnataka, India.
**E-mail: madhubm@sit.ac.in*

Abstract

High performance glass fiber reinforced epoxy composites are in greater demand in several industrial applications, from civil structures to aviation industry. The epoxy has highly cross-linked structure and is found to be high performance polymer. Further, carbon nanofillers such as multi-walled carbon nanotubes (MWCNT), graphene nanoplatelets (GNP) and thermally stable microfiller aluminium trihydrate (ATH) are being used to improve the thermal properties. GNP and MWCNT posses high aspect ratio and specific surface area contributing to improvement in thermal properties of composites. In spite of this, there are difficulties connected with nanofiller addition, such as dispersion and interaction. The fabricated nanocomposites are based on ECR glass fiber and epoxy resin by adding GNP, MWCNT and ATH fillers using pultrusion process assisted by ultrasonication. For the purpose of comparison, composites containing only MWCNT, GNP and ATH were also tested. The XRD and SEM were used to study the fillers dispersion and interaction. The thermogravemetric analysis(TGA) was carried out to determine the thermal stability of composites. From the thermal analysis result, it is found that the epoxy-MWCNT-GNP-ATH composite has enhanced thermal stability due to the addition of ATH micro filler.

Keywords: *Differential Scanning Calorimetry, Thermal kinetics, GFRP composites*

1.0 Introduction

Glass fibre reinforced polymer (GFRP) composites are employed in a wide range of engineering applications, particularly in power transmission and distribution, aviation, infrastructures, and electronics [1]–[4]. Due to functional features specific to applications that require high strength, modulus, and resistance to high temperatures and corrosion, GFRP composites have become a popular choice [5]–[9]. Carbon nanofillers with excellent electrical and thermal conductivity have recently been flaunted as promising filler for improving thermal characteristics. Composite properties are influenced by fillers and fabrication methods [10]–[12]. Fillers with better mechanical and thermal properties are required to improve thermal characteristics and to overcome the limitations of GFRP composites. The conventional fire-retardant micro filler used in GFRP to enhance thermal and flame characteristics is aluminium trihydride. Physiochemical properties of nanofillers and their hybrids have drawn considerable attention. In

---

*Corresponding Author

combination with ATH microfiller, MWCNT and GNP carbon nanofillers exhibit excellent thermal and electrical properties. Though their basic structures differ, these two nanofillers have remarkable intrinsic qualities, and the primary goal of mixing them was to generate synergistic effects with the two fillers[13]–[15]. Several researchers in recent investigations also reported an improvement of thermal properties in their observations [16]–[19]. The strong covalent connections formed between the nanofillers and polymer chains in nanocomposites give them outstanding thermal characteristics. MWCNT posses electrical conductivity of 0.5S/m, tensile strength of 63GPa, and youngs modulus of 950GPa [19]–[22], whereas, GNP has 6×10^5 S/m, 130GPa and 1TPa respectively. The thermal conductivity of GNP is 290-380 $Wm^{-1}K^{-1}$ [29], [30]. Many authors investigated the thermal properties of epoxy added with GNP, MWCNT and ATH aiming at elevating thermal stability. TheTGA and DSC are commonly employed to investigate the thermal properties of composites by acquiescing them to increased thermal loads. Several researchers used DSC and TGA to examine the thermal stability of GFRP composites [25]–[29]. The DSC results of epoxy composites modified with GNP [29], [30], MWCNT [19]–[22] and ATH [30]–[33] were reported in the literature. In this research paper, a comparative study on the experimental results of composites containing ATH, MWCNT and GNP is carried with the values reported in literature. The most challenging aspect of integrating different carbon fillers is the tendency for these nanofillers to agglomerate together, increasing the viscosity of the epoxy matrix. Using an ultrasonication-followesd by pultrusion method, the aglomeration might be considerably decreased. The synergistic effect of carbon nanofillers improved the glass transisition temperature and thermal stability of GFRP composites.

2.0 Materials and methods

The GFRP composites were fabricated by mixing Lapox-12 epoxy (L-12) resin and K918 hardener. Continuous ECR glass fiber was used in the study and the average glass fiber diameter was 15/μm. These laboratory-grade components were supplied by Atul industries. Table 1 lists the various composites that have been fabricated and their constituents.

2.1 Materials

Graphene nanoplatelets with an approximate bulk density of 0.03-0.01 g/cm^3 was received in powder form from Sigma Aldrich. The GNPs have average diameter of 15μm and thickness of 2nm. Multi-walled carbon nanotubes produced by chemical vapour deposition was obtained from IENT, India. The MWCNT had a carbon content of about 98% atomic, and having an bulk density of 0.1-0.6 g/cm^3 approximately. They featured an average diameter of 10nm and length of 6 to 9μm, respectively. Continuous unidirectional ECR-glass fiber creels with an average fiber diameter of 20/ μm were supplied by Owens-Cornings, India having a surface density of $0.78/kg/m^2$. Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin Lapox-12 and the curing agent K918 were supplied by Huntsmen India.

2.2 Fabrication of composites

The process of fillers inclusion into epoxy resin and fabrication of composites using pultrusion is illustrated in Figure 1. Initially, the required amount of ATH was predispersed in epoxy resin using a mechanical agitator. The addition of nanofillers follows it, and then the MWCNT/GNP/ATH/epoxy mixture is ultrasonicated for 30 minutes at 20kHz (for each filler addition) to achieve homogeneous filler dispersion. Finally, the hardener is added to the modified epoxy matrix and transferred to the pultrusion resin bath, and composites of predetermined size and dimensions are pulled through a temperature-controlled die and cut into desired lengths.

2.3 Thermogravimetric analysis

A thermogravimetric analyzer (TGA/DTGA Q-50, TA Instruments, USA) was used to investigate the influence of fillers inclusion on the thermal performance of flax/epoxy composites. An alumina crucible was used to hold the composite sample, which weighed around 10mg. This was heated upto 850°C at a rate of 10°C min^{-1}, the weight loss of the composites was measured with respect to temperature. Experiments were conducted for each type of composite, and the values are provided.

3.0 Results

3.1 Scanning electron microscopy

The distribution of MWCNT, GNP and ATH fillers in the epoxy was investigated using SEM on the surfaces of pure and other composites, as shown in Figure 1(a-d). Figure 1(a) shows a transverse section of a glass fibre wrapped in polymer, demonstrating strong adhesion between the polymer and the glass fibres. The

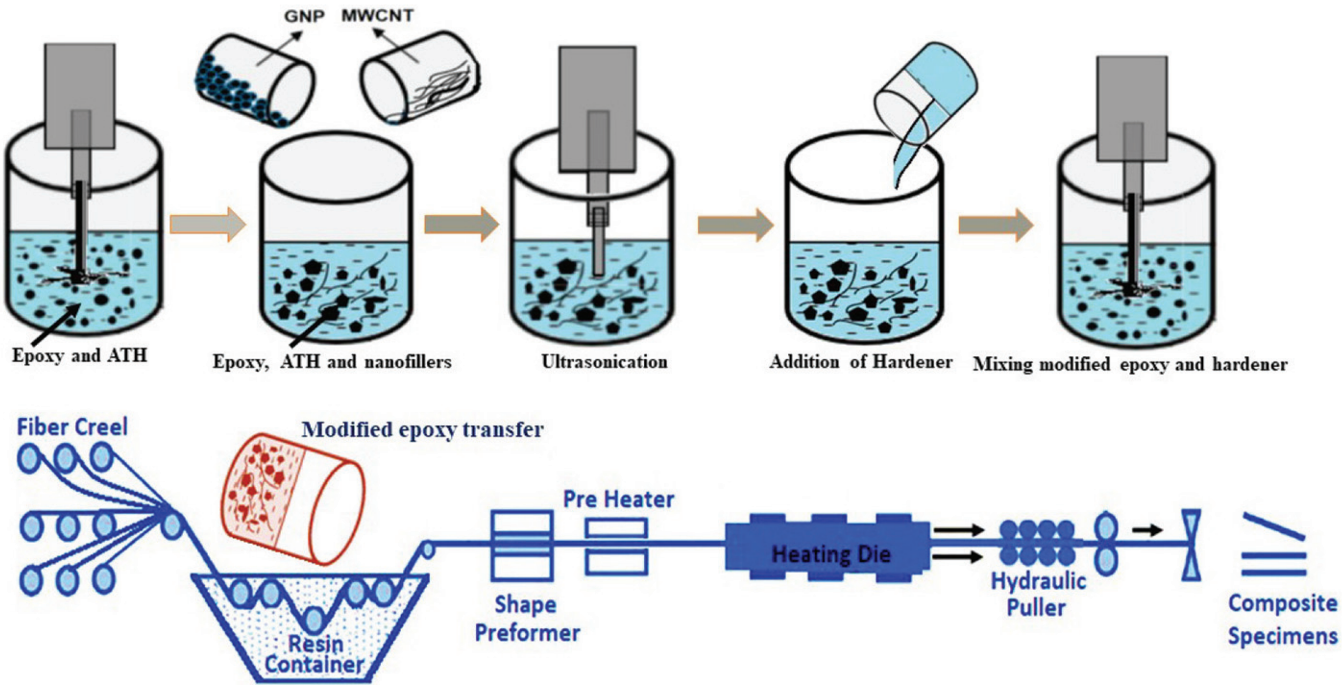

Figure 1: Process of fillers inclusion and fabrication of composites using pultrusion

Table 1: Composites and composition

	Composites	Constituents	Constitutents of composites (wt.%)				
			Glass fiber	Epoxy	ATH	MWCNT	GNP
1.	EGF	Epoxy+GF	80%	20%	0	0	0
2.	EGFA	Epoxy+GF+ATH		18%	2%	0	0
3.	EGFM	Epoxy+GF+ATH+ MWCNT		17.6%	2%	0.4%	0
4.	EGFG	Epoxy+GF+ATH+GNP		17.8%	2%	0	0.2%
5.	EGFH	Epoxy+GF+ATH+ MWCNT+GNP		17.2%	2%	0.2%	0.6%

matrix fibral has been sheared, causing these fibres to fracture. The top view of a shattered specimen in Figure 1(b) reveals glass fibres fully covered by matrix. Few glass fibres are intact, and even fewer are debonded from the matrix, resulting in elongated spaces generated by cavitation. Figure 1(c) is a magnified version of Figure 1(a), showing the matrix undergoing extreme plastic deformation during fracture, which is only achievable with excellent glass fiber-matrix adhesion.

The presence of MWCNT attached to the surface of glass fibre is shown in Figure 1(d). Because epoxy is remarkably brittle, the surface of glass fibre features wave-like patterns. Figure 1 also indicates that the nanofillers are compatible with the epoxy matrix. Because there are no evident filler clusters, the interactions contribute to produce a network-like structure that improves dispersion, resulting in an overall improvement in composite performance. These findings confirm the hypothesis that the characteristics of nanocomposites are significantly better than those of virgin epoxy.

3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is used to study the fillers effect of on the thermal stability of GFRP reinforced composites. The thermal stability assessment is based on significant weight loss at certain temperature. The thermogravimetric curves of the composites are shown in Figure 3. The evaporation of moisture and volatiles

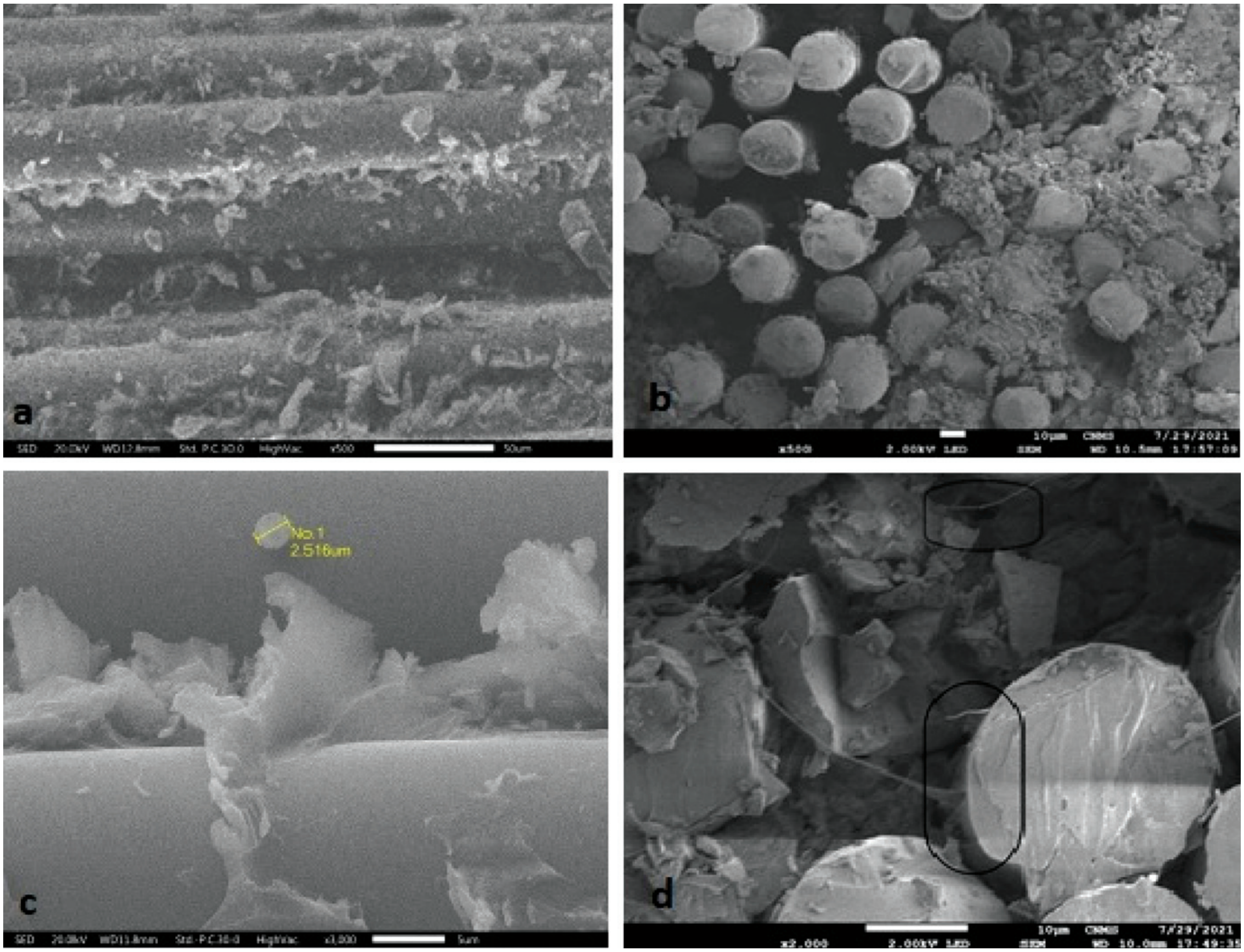

Figure 2: Scanning electron microscope images of specimens

from the composite surfaces causes first weight loss between 90°C and 160°C during initial stage of composite thermal deterioration.

The degradation of the matrix causes weight loss significantlyin the temperature range of 250-450°C. Finally, the progress of char residue was detected when the temperature exceeded 600°C. It was discovered that adding hybrid GNP and MWCNT to GFRP composites improved their thermal stability. This was attributed to the synergistic effect of carbon nanofillers, that prevented evaporation and stimulated the development of char. In the initial stages of thermal degradation, char formation acts as a shield, causing reduced rate of thermal degradation. Char formation also lowers the emission of flammable volatiles, increasing the temperature resistance of the polymer even more. Furthermore, the char acted as a barrier to the flammable gases produced by polymer breakdown, preventing oxygen from entering the composite. While comparing the EGFA and EGFH composites to the EGF composite, it is noticeable that the char residue formed for the EGFA and EGFH composites in increased. Further, GNP and MWCNT were added to EGFG and EGFM composites, the initial degradation temperature was raised to 160°C. The development of the breakdown products was inhibited by a well-distributed GNP and MWCNT. This also delayed the temperature of degradation, improving thermal stability. In addition, adding GNP and MWCNT to the EGFG and EGFM composites reduced the temperatures of degradation. This was attributed to the composites greater aggregation of GNP, that let them to degrade faster.

3.3 Derivative thermogravimetry

The impact of GNP on the glass fiber reinforced epoxy was investigated using a derivative thermo-

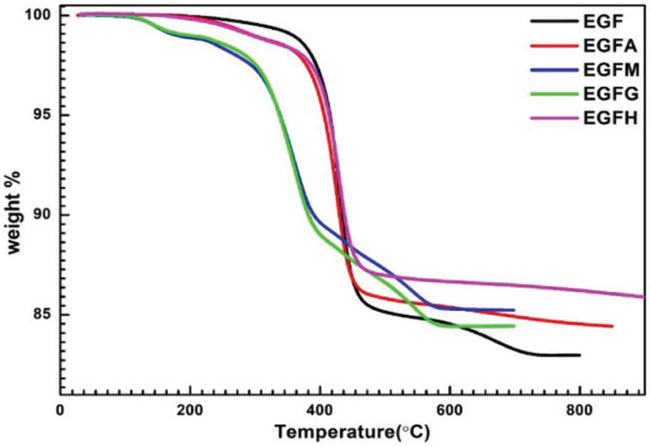

Figure 3: Thermogravimetric curves of composites

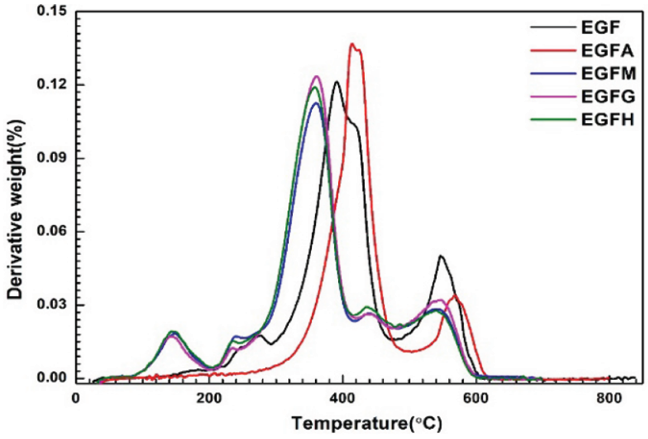

Figure 4: Derivative thermograms

gravimetric (DTG) technique and the results presented in Figure 4. Two promimnet peaks were noticed for EGF and EGFA composites, while three promimnet peaks were observed for composites with carbon fillers. The first smaller peak revealed the presence of water molecules in the composites as well as the voids generated during composite fabrication. The second highest peaks indicated that EGF,EGFA composites decompose at greater temperatures than EGFM, EGFG, and EGFH composites. The use of carbon nanofillers lowered the composites' derivative weight loss. The EGFA composites had a higher derivative weight loss than the other composites. The EGF and EGFA composites showed a two-step breakdown mechanism. Decomposition took place at temperatures of around 400°C and 530°C, corresponding to highest decomposition.

From DTG graphs small peaks are observed between 180°C to 250°C in EGFM, EGFG and EGFH composites. This small peaks observed is due to the presence of the carbonaceous fillers. In comparison to virgin epoxy resin, adding carbon fillers in epoxy increases stability. As a result, when MWCNT and GNP are added to the nanocomposites, their thermal stability improves, and these nanofillers function as adjourning representative in epoxy deterioration. This is mainly due to the carbanecous fillers ability to thermally reserve the polymer matrix and preventing the movement of degrading explosives through the matrix by forming a circuitous path[34].

4.0 Conclusions

The thermal decomposition mechanism involved with the incorporation of micron and nanofillers is studied. Some of the important conclusions is as follows.

- The ultrasonication assisted pultrusion technique aids in the avoidance or minimization of carbon nanofiller agglomeration, resulting in improved filler dispersion.
- The incorporation of ATH significantly improves the thermal stability of the composites, while the carbon fillers reduces the ATH improvement slightly.
- The considerable synergistic effect of the two carbon fillers in the thermal characteristics of the composites is due to the high aspect ratio of GNP.
- The use of multiscale hybrid fillers further improves the thermal stability of the composites.

5.0 Acknowledgements

The authors would like to express their gratitude to the Department of Electrical and Electronics Engineering at Siddaganga Institute of Technology in Tumakuru for permitting them to conduct a research study by providing all of the necessary facilities and encouragement.

6.0 References

[1] D. K. Rajak, D. D. Pagar, P. L. Menezes, and E. Linul, "Fiber-reinforced polymer composites: Manufacturing, properties, and applications," *Polymers* (Basel)., vol.11, no.10, 2019, doi: 10.3390/polym11101667.

[2] M. M. Zagho, E. A. Hussein, and A. A. Elzatahry, "Recent overviews in functional polymer composites for biomedical applications,"

Polymers (Basel)., vol. 10, no. 7, 2018, doi: 10.3390/polym10070739.

[3] M. Hesami, R. Bagheri, and M. Masoomi, “Combination effects of carbon nanotubes, MMT and phosphorus flame retardant on fire and thermal resistance of fiber-reinforced epoxy composites,” Iran. *Polym. J.* (English Ed., vol. 23, no. 6, pp. 469–476, 2014, doi: 10.1007/s13726-014-0241-z.

[4] K. P. Matabola, A. R. De Vries, F. S. Moolman, and A. S. Luyt, “Single polymer composites: A review,” *J. Mater. Sci*., vol. 44, no. 23, pp. 6213–6222, 2009, doi: 10.1007/s10853-009-3792-1.

[5] K. Y. Chan, B. Jia, H. Lin, N. Hameed, J.-H. Lee, and K.-T. Lau, “A critical review on multifunctional composites as structural capacitors for energy storage,” *Compos. Struct.*, vol. 188, pp. 126–142, 2018, doi: https://doi.org/10.1016/j.compstruct.2017.12.072.

[6] S. Das, S. Sharma, T. Yokozeki, and S. Dhakate, “Conductive layer-based multifunctional structural composites for electromagnetic interference shielding,” *Compos. Struct*., vol. 261, p. 113293, 2021, doi: https://doi.org/10.1016/j.compstruct.2020.113293.

[7] T. J. Adam et al., “Multifunctional composites for future energy storage in aerospace structures,” *Energies*, vol. 11, no. 2, 2018, doi: 10.3390/en11020335.

[8] M. Rafiee, F. Nitzsche, J. Laliberte, S. Hind, F. Robitaille, and M. R. Labrosse, “Thermal properties of doubly reinforced fiberglass/epoxy composites with graphene nanoplatelets, graphene oxide and reduced-graphene oxide,” *Compos*. Part B Eng., vol. 164, pp. 1–9, 2019, doi: 10.1016/j.compositesb.2018.11.051.

[9] S. Kopsidas and G. B. Olowojoba, “Multifunctional epoxy composites modified with a graphene nanoplatelet/carbon nanotube hybrid,” *J. Appl. Polym*. Sci., vol. 138, no. 35, pp. 1–19, 2021, doi: 10.1002/app.50890.

[10] L. Schlagenhauf, Y. Y. Kuo, Y. K. Bahk, F. Nüesch, and J. Wang, “Decomposition and particle release of a carbon nanotube/epoxy nanocomposite at elevated temperatures,” *J. Nanoparticle Res*., vol. 17, no. 11, 2015, doi: 10.1007/s11051-015-3245-5.

[11] Y. M. Yun et al., “Pyrolysis characteristics of GFRP (Glass Fiber Reinforced Plastic) under non-isothermal conditions,” *Fuel*, vol. 137, pp. 321–327, 2014, doi: 10.1016/j.fuel.2014.08.001.

[12] J. W. Zha, T. X. Zhu, Y. H. Wu, S. J. Wang, R. K. Y. Li, and Z. M. Dang, “Tuning of thermal and dielectric properties for epoxy composites filled with electrospun alumina fibers and graphene nanoplatelets through hybridization,” *J. Mater. Chem. C*, vol. 3, no. 27, pp. 7195–7202, 2015, doi: 10.1039/c5tc01552a.

[13] S. Mondal and D. Khastgir, “Elastomer reinforcement by graphene nanoplatelets and synergistic improvements of electrical and mechanical properties of composites by hybrid nano fillers of graphene-carbon black & graphene-MWCNT,” *Compos. Part A Appl. Sci. Manuf.*, vol. 102, pp. 154–165, 2017, doi: 10.1016/j.compositesa.2017.08.003.

[14] L. Yue, G. Pircheraghi, S. A. Monemian, and I. Manas-Zloczower, “Epoxy composites with carbon nanotubes and graphene nanoplatelets - Dispersion and synergy effects,” *Carbon N. Y.*, vol. 78, pp. 268–278, 2014, doi: 10.1016/j.carbon.2014.07.003.

[15] Y. Perets, L. Aleksandrovych, M. Melnychenko, O. Lazarenko, L. Vovchenko, and L. Matzui, “The Electrical Properties of Hybrid Composites Based on Multiwall Carbon Nanotubes with Graphite Nanoplatelets,” *Nanoscale Res. Lett*., vol. 12, 2017, doi: 10.1186/s11671-017-2168-8.

[16] L. C. Tang et al., “The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites,” *Carbon N. Y.*, vol. 60, pp. 16–27, 2013, doi: 10.1016/j.carbon.2013.03.050.

[17] G. Mittal, V. Dhand, K. Y. Rhee, S. J. Park, and W. R. Lee, “A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites,” *J. Ind. Eng. Chem*., vol. 21, pp. 11–25, 2015, doi: 10.1016/j.jiec.2014.03.022.

[18] M. R. Mansor, S. H. S. M. Fadzullah, N. A. B. Masripan, G. Omar, and M. Z. Akop, Comparison Between Functionalized Graphene and Carbon Nanotubes. Elsevier Inc., 2019.

[19] M. Trihotri, U. K. Dwivedi, and M. M. Malik, “Study of low weight percentage filler on dielectric properties of MWCNT-epoxy nanocomposites,” vol. 6, no. 3, pp. 1–9, 2016, doi: 10.1142/S2010135X16500247.

[20] C. C. Teng et al., “Preparation and characterization of nano-inorganic materials coated multi-walled carbon nanotubes/epoxy composites for thermal interface materials,” IMPACT Conf. 2009 Int. 3D IC Conf. - Proc., pp. 469–472, 2009, doi: 10.1109/IMPACT.2009.5382220.

[21] K. M. F. Shahil and A. A. Balandin, "Thermal properties of graphene and multilayer graphene: Applications in thermal interface materials," *Solid State Commun*., vol. 152, no. 15, pp. 1331–1340, 2012, doi: 10.1016/j.ssc.2012.04.034.

[22] N. Platelets, Y. Jen, and J. Huang, "Synergistic Effect on the Thermomechanical and Electrical Properties of Epoxy Composites with the Enhancement of Carbon Nanotubes and Graphene," doi: 10.3390/ma12020255.

[23] S. Gantayat, D. Rout, and S. K. Swain, "Carbon Nanomaterial–Reinforced Epoxy Composites: A Review," Polym. - *Plast. Technol. Eng*., vol. 57, no.1, pp. 1–16, 2018, doi: 10.1080/03602559.2017.1298802.

[24] R. Atif, I. Shyha, and F. Inam, "Mechanical, thermal, and electrical properties of graphene-epoxy nanocomposites-A review," *Polymers* (Basel)., vol. 8, no. 8, 2016, doi: 10.3390/polym8080281.

[25] I. Kranauskaitë et al., "Enhancing electrical conductivity of multiwalled carbon nanotube/epoxy composites by graphene nanoplatelets," *Lith. J. Phys*., vol. 57, no. 4, pp. 232–242, 2017, doi: 10.3952/physics.v57i4.3602.

[26] M. R. Ayatollahi, M. M. Shokrieh, S. Shadlou, A. R. Kefayati, and M. Chitsazzadeh, "Mechanical and Electrical Properties of Epoxy/ Multi-walled Carbon Nanotube/Nanoclay Nanocomposites," vol. c, no. 10, pp. 835–843, 2011.

[27] A. Mani, P. Tambe, and A. Rahaman, "Flexural properties of multiscale nanocomposites containing multiwalled carbon nanotubes coated glass fabric in epoxy/graphene matrix," *Compos. Interfaces,* vol. 26, no. 11, pp. 935–962, 2019, doi: 10.1080/09276440.2019.1569396.

[28] S. Gupta and A. Rahaman, "Effect of Carbon Nanotube on Thermo-Mechanical Properties of Glass Fiber / *Epoxy Laminated Nanocomposites,*" vol. 5, no. 2, pp. 1–5, 2015.

[29] A. Moosa, A. Ramazani, A. A. Moosa, and M. N. Ibrahim, "Mechanical and Electrical Properties of Graphene Nanoplates and Carbon-Nanotubes Hybrid Epoxy Nanocomposites," Am. *J. Mater. Sci.*, vol. 6, no. 6, pp. 157–165, 2016, doi: 10.5923/j.materials.20160606.03.

[30] A. Krivda et al., "Characterization of epoxy microcomposite and nanocomposite materials for power engineering applications," *IEEE Electr. Insul. Mag*., vol. 28, no. 2, pp. 38–51, 2012, doi: 10.1109/MEI.2012.6159180.

[31] G. Iyer, R. Gorur, R. Richert, A. Krivda, and L. Schmidt, "Dielectric Properties of Epoxy Based Nanocomposites for High Voltage Insulation," *IEEE Trans. Dielectr. Electr. Insul*., vol. 18, no. 3, pp. 659–666, 2011, doi: 10.1109/TDEI.2011.5931050.

[32] I. Pleºa, P. V. Noþingher, S. Schlögl, C. Sumereder, and M. Muhr, "Properties of polymer composites used in high-voltage applications," *Polymers* (Basel)., vol. 8, no. 5, 2016, doi: 10.3390/polym8050173.

[33] N. R. Paluvai, S. Mohanty, and S. K. Nayak, "Synthesis and Modifications of Epoxy Resins and Their Composites: A Review," *Polym. - Plast. Technol. Eng*., vol. 53, no. 16, pp. 1723–1758, 2014, doi: 10.1080/03602559.2014.919658.

[34] A. Leszczyñska, J. Njuguna, K. Pielichowski, and J. R. Banerjee, "Polymer/montmorillonite nanocomposites with improved thermal properties. Part I. Factors influencing thermal stability and mechanisms of thermal stability improvement," *Thermochim. Acta*, vol. 453, no. 2, pp. 75–96, 2007, doi: 10.1016/j.tca.2006.11.002.