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The effect of MWCNT and GNP on the Flame Retardant Properties of Glass Fiber Reinforced Composites

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Abstract

Nanotechnology in engineering is intended for achieving newer materials with immensely improved electrical, thermal and mechanical properties. The effectiveness of different fillers (micro and nanoscale) on the flame retardant behaviour of glass fiber reinforced epoxy composites were studied using cone calorimetry. In the present investigation, the fabrication of epoxy composites with ECR glass fiber reinforcement using the pultrusion method was taken up. The effect of incorporation of micron-sized ATH, carbon nanofillers like multi-walled carbon nanotubes (MWCNT) and Graphene nanoplatelets (GNP) is investigated. With respect to flame retardant properties, the composites with the combination of alumina (ATH) and carbon nanofillers show better results as compared to composites with individual fillers. The results exhibit a good agreement with more compact chars formed on the surface of the charred polymer. However, the cone calorimetry results of glass fibre reinforced composite show no significant improvement with respect to heat release rate. Further, Flame parameters of the composites show minimal deterioration due to the incorporation of the ATH and carbon fillers. Studies on the morphology using FESEM are well correlated with the flame properties.

Keywords: *flame parameters, nanomaterials, cone calorimetry, nanotechnology*

1.0 Introduction

Epoxy composites reinforced with glass fibre (GF) are used in various industries, including aerospace, automotive, power, and electronics, due to their high strength, modulus and resilience to high temperatures and corrosion[1]–[4]. However, once the composites are cured, the epoxy matrix structure becomes brittle, reducing its heat resistance. To enhance thermal capabilities and overcome composites limitations, they need to be strengthened with fillers with higher mechanical and thermal properties[5]–[7]. Alumina (ATH) is the common fire-retardant filler most often used in GFRP composites since it is cost-effective, environmentally friendly and easy to handle[8]–[11]. The fire-retardant mechanism of ATH is based on a single-step endothermic process that releases water vapour at temperatures between 200°C and 300°C, leaving a thermally stable residue of aluminium oxide (Al_2O_3)[12]–[14]. During polymer combustion, the water vapour will act as a diluting agent in the gas phase and decrease the composite temperature while the residue of Al_2O_3 forms a protective layer. Multi-walled carbon nanotubes have a unique hollow tubular shape, while graphene nanoplatelets (GNP) shape have a large surface area and display exceptional thermomechanical properties at the nanoscale. The flame retardant mechanism can be categorized into four zones: flame zone, char layer, molten polymer, and underlying polymer, as shown in Figure 1. The char

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layer is important since it regulates heat and mass movement between the condensed and gaseous stages, while volatile compounds are produced in the thermal breakdown zone and then mitigated in the flame zone. The creation of a char layer on the surface limits heat and mass transfer between the gas stage and the condensed phase by inhibiting combustible volatiles from diffusing and isolating the polymer from air and heat in the condensed phase mechanism. The flame, mechanical and thermal properties of three-phase composites are the focus of recent academic research. However, the flame performance of polymer composites is critical for ensuring inherent safety and expanding their applications. The primary objective of this study is to compare the flame retardant qualities of traditional micro and nano flame retardants for application in GFRP composites. In addition, the flame retardant capabilities of MWCNT-GNP-ATH reinforced GFRP composites were investigated in this research.

Since minimal research is available in the literature on the flame properties of the composites, this investigation is carried out. The ultrasonication followed the pultrusion process in this study to fabricate GF/EP, MWCNT/GF/EP, GNP/GF/EP composites, and ATH. Cone calorimetry and UL-94 tests were used to investigate flame retardancy.

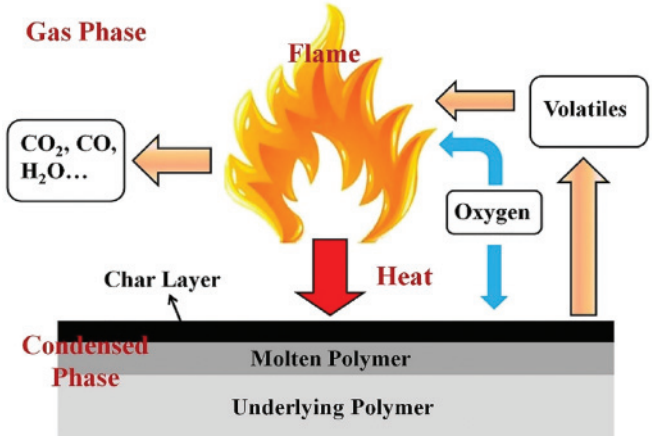


Figure 1: Flame retardant mechanisms in polymer nanocomposites. Reproduced with permission from Ref. [16]. Copyright 2017 Elsevier.

2. Materials and methods

2.1. Materials

Graphene nanoplatelets with an approximate bulk density of 0.03-0.01 g/cm^3 in black powder form from Sigma Aldrich were used. The GNP has an average thickness and diameter of 2nm and 15ìm, respectively. Multi-walled carbon nanotubes synthesised by chemical vapour deposition were obtained from IENT, India. The MWCNT had a carbon content of about 98% atomic, and its bulk density was approximately 0.10-0.06 g/cm^3. They featured an average diameter of 10 nm and a length of 6 to 9ìm, respectively. Continuous unidirectional E-glass fiber creels with an average fiber diameter of 20/µm from M/s. Owens-Corning's, India with a density of 0.78/kg/m^2. Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin MY740 and the curing agent HY918 were supplied by M/s. Huntsmen India.

2.2. Fabrication of composites

The process of fillers addition into epoxy resin and fabrication of composites using the pultrusion process is illustrated in Figure 2. Initially, the required quantity of ATH was pre-dispersed 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. The fabricated materials and their identification are shown in Table 1.

2.3. Characterization

Microstructural studies were carried out using SEM instrument JEOL JSM-6390LV model and FESEM instrument JEOL JSM-7100F model. The UL94 is a critical test for the flammability of the polymers, and the method is based on the burning speed, burning time and dripping behaviour, and the ability of the polymer to extinguish the flame after it is ignited. The critical requirement of the UL-94 test method is that no specimen burns with the flame for more than 10 seconds after the test flame is removed, and the total time of burning with flame does not exceed 50 seconds. It should be observed that no specimen produces flaming dripping that ignites the cotton located 12 inches below and does not continue to burn with glowing combustion for more than 30 seconds after the 2nd removal of the test flame.

The UL-94 vertical flame tests have been performed to determine the flame properties. In addition, a cone calorimetry test was conducted to measure the composites flame behaviour as per international standards (ISO 5660). As a result, the parameters such as 'time-to-flame in', 'time-of-flame-out', 'total heat release time', 'peak heat release rate', and 'combustion time' were determined.

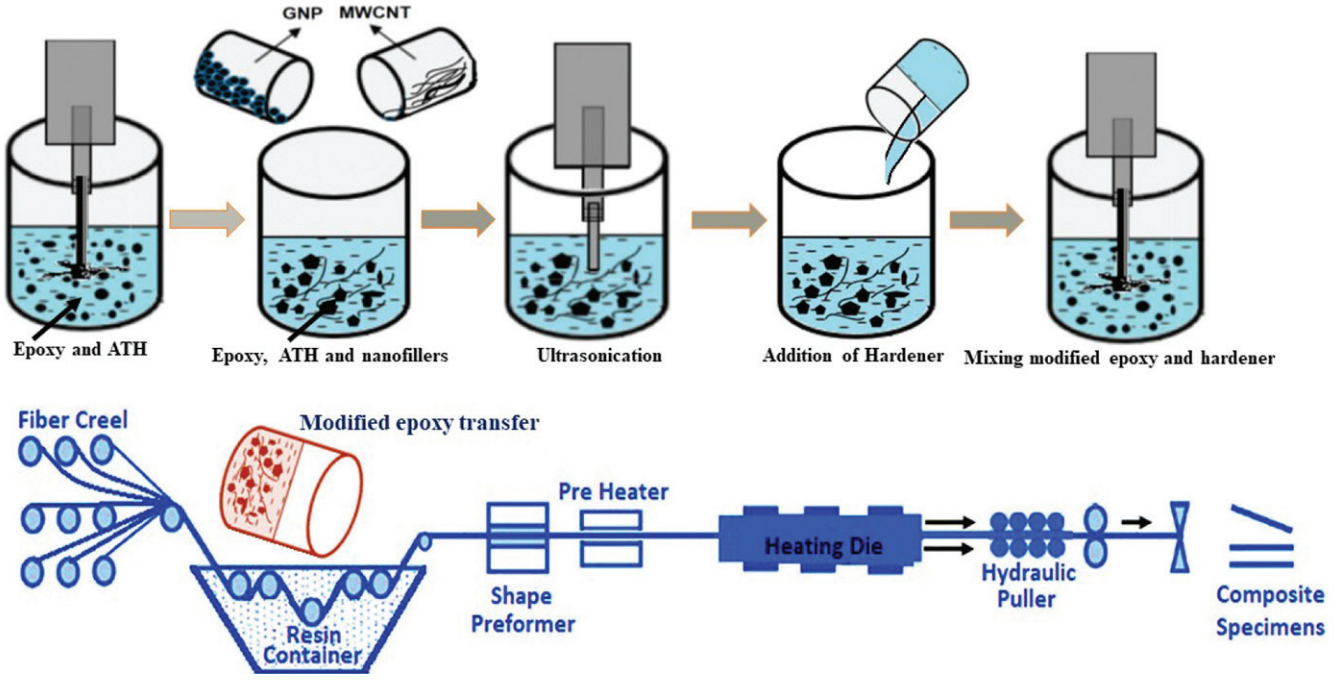


Figure 2: Process of fillers inclusion and fabrication of composites using pultrusion

Table 1: Composites and composition

	Composites	Constituents	Constituents 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		16%	2%	2%	0
4.	EGFG	Epoxy+GF+ATH+GNP		17%	2%	0	1%
5.	EGFH	Epoxy+GF+ATH+ MWCNT+GNP		14%	2%	1%	3%

3.0 Results and discussion

3.1. Scanning Electron Microscopy

The images of the composites were taken using a scanning electron microscope to determine the morphology of the surface of the fractured composites are shown in Figure 3. The SEM images make it possible to visualize a significant quantum of fragmented and deformed epoxy matrix adhering to the glass fibers in the composite. In addition, because of MWCNT, stronger adhesive bonding between glass fiber and epoxy in composite has been established. As a result, bare glass fibres with very little epoxy can be seen in composites. Furthermore, consistent spacing between the fibres and the creation of layers of fillers in the epoxy matrix resulted in an increase in thermal conductivity in the thickness direction of the composite. On the other hand, the region of space between the fibers, which has regions of epoxy, shows little evidence of the distribution of fillers. This is because the graphene nanoplatelets show orientation angles pointing in the fiber direction.

3.2. Flame Retardancy

Composites were subjected to a UL-94 vertical flame test and found that all composite's performance was well within the acceptable range, and hence they belong to the UL-94 V-0 class. As a result, the fillers had no effect on the V0 categorization of the base epoxy

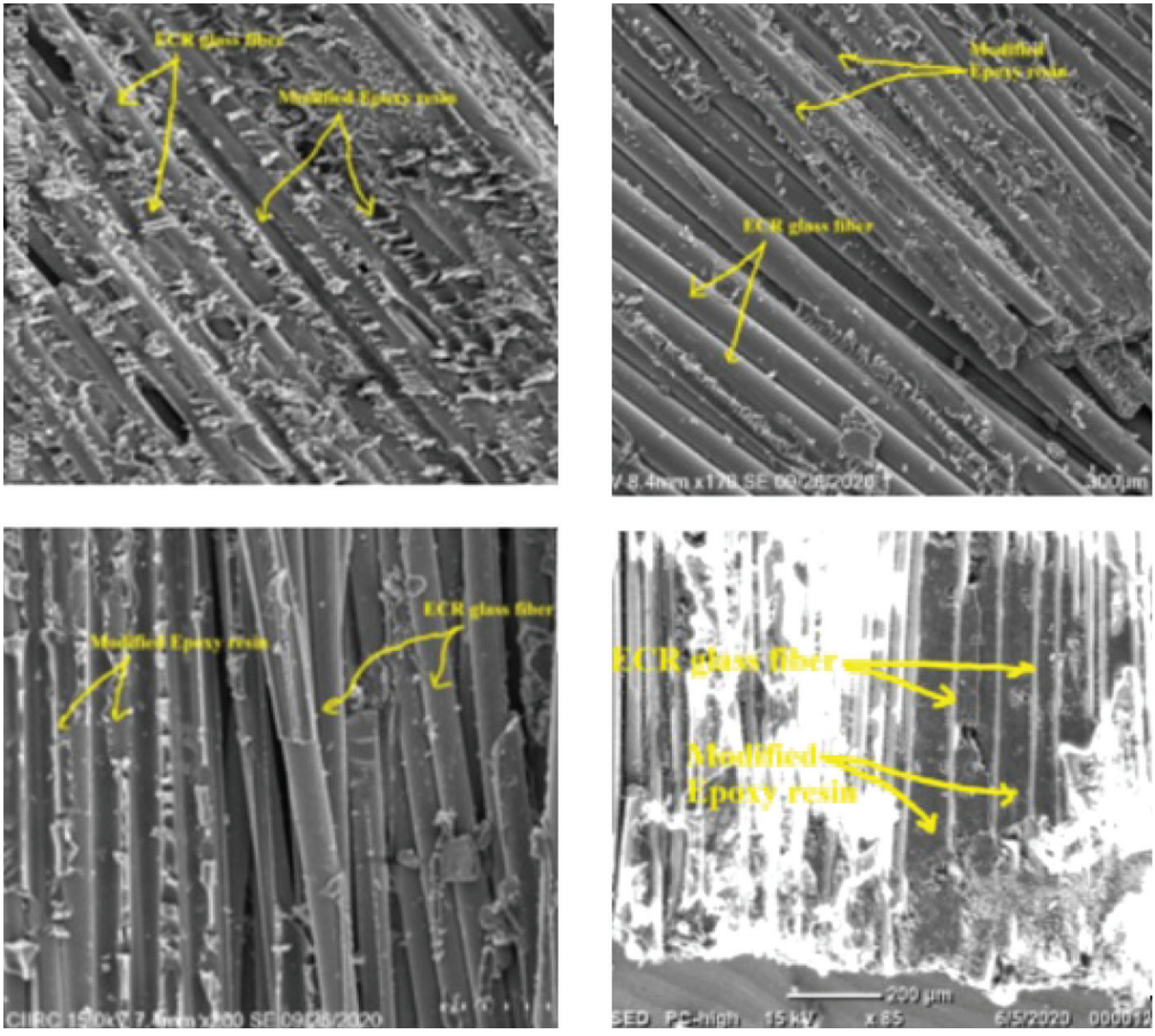


Figure 3: SEM images of the fractured surface of composites

composites EGF and the composites with carbon and ATH fillers. A cone calorimeter was used to determine the time to ignition and the temperature at which combustion begins to further assess the effect of the fillers on the flame attributes. With a steady heat flux of 35 kW/m^2, the time to ignition in EGF was 81 seconds, while in EGFA, it was 97 seconds. As a result, including ATH into composites helps to extend the period of ignition. Carbon fillers have been found to have an effect on flame characteristics, owing to their increased thermal conductivity.

The role of carbon nanofillers in flame retardant polymer composites has been widely discussed [15]–[17]. Though many reports [18] attribute improvements in flame properties due to the presence of carbon fillers, it is well-known that the high thermal conductivity of the carbon nanofillers reduces the flame performance of nanocomposites. Decrease of flame characteristics depends on both the quantity and distribution of fillers in a polymer matrix. Despite this, carbon nanofillers negate ATH performance in the composite flame properties.

Figure 3 shows the characteristic curve of the EGFH composite (heat release rate-HRR) from a cone

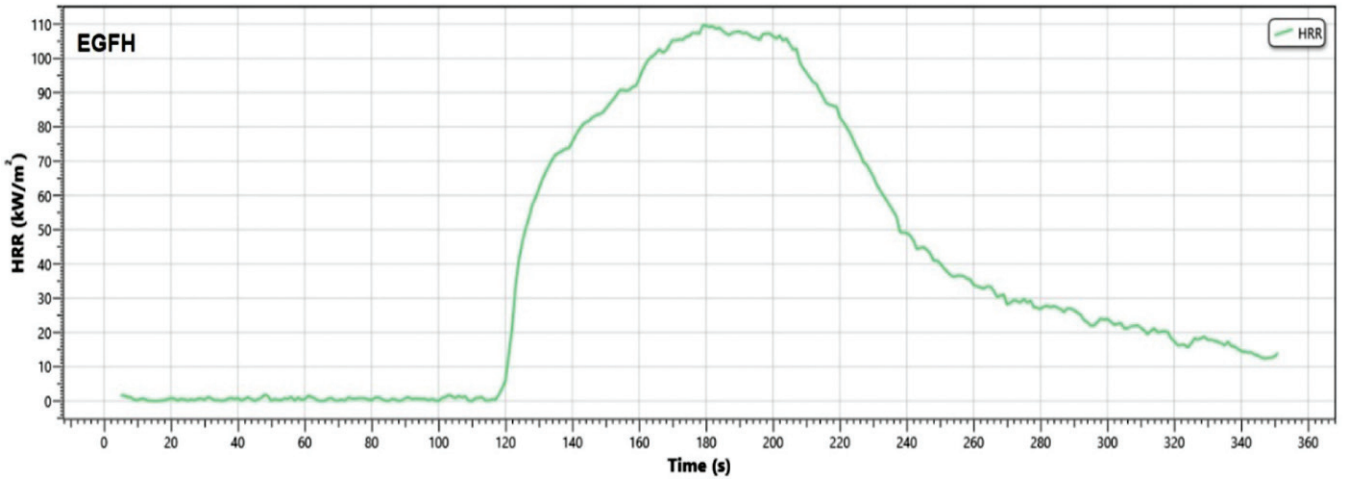


Figure 4: The heat release rate Vs. Time for EGFH composite.

Table 2: Flame properties of composites

Samples	Time to Flame-in	Time to Flame-out	PHRR (kW/m^2)	Time taken for PHRR (s)	Combustion time(s)	Total heat release (MJ/m^2)
EGF	81	360	86.4	180	257	21.2
EGFA	97	401	97.8	232	306	19.4
EGFM	80	394	92.6	210	314	16.1
EGFG	71	383	92.8	206	306	14.7
EGFH	75	347	109.7	195	250	13.1

calorimeter test. Table 2 lists the collected data after the cone calorimeter test. From Table 2, the Time to Flame-in of the EGFH composite was 75±3 s, which was comparatively shorter than that of the pure EGF composite (81±3 s). The HRR peak of pure EGF was broad and low (PHRR was 86.4 kW/m^2), whereas the HRR peak of the EGFH nanocomposite was high and sharp (PHRR was 109.7 kW/m^2). The addition of carbon nanofillers increases the flame propagation (increase HRR) of EGFH, though the THR value of the nanocomposite decreases. This phenomenon in the cone calorimeter test's heat release rate differed from nanocomposites literature data [19] of the nanocomposites. In the EGFH nanocomposite, the increased flame propagation (increased HRR) was induced by the accelerated thermal decomposition of the matrix owing to the addition of carbon nanofillers. As a result, the mass-loss rate of the EGFH nanocomposite was faster than that of EGF during the developed flame zone. With the presence of ATH filler during polymer combustion, the water vapour formed will act as a diluting agent in the gas phase and decreases the composite temperature while the residue of Al_2O_3 builds up to create a shielding layer. In the coming years, the demand for ATH is likely to outpace the need for other flame retardant materials, especially when environmentally friendly flame retardant technology is gaining ground. However, the high loading requirement of ATH for acceptable flame retardance is a persistent issue with the usage of ATH in polymers. A high level of ATH might increase processing viscosity, decrease performance and processability, and increase the density.

Another critical issue is the thermal stability of ATH, which is the essential factor in evaluating its effectiveness in polymers. ATH starts to decompose at relatively lower temperatures than some polymers, which require high processing temperature and thermally stable thermosets.

The MWCNT have formed a thin film covering the composite. With MWCNT/GNP capacity to transport heat along the tubes and its heat resistance within, this tube is dense and intricate despite its very low thickness. When the char layer protects the composites

from flame, oxidising chemicals have difficulty penetrating and aiding in their fire resistance. A char layer will be formed though out if MWCNT and GNP fillers are well distributed in the matrix. This barrier will also reduce the risk of fire and oxygen exposure. The flame cannot expand or fade since the potential to rekindle is greatly diminished. The compact design further enhances the composites fire resistance.

The oxygen transport is slowed and combustible chemicals are prevented from burning in the material by using nanofillers to build a multilayer heat-resistant and heat-retaining barrier. As a result, the heat transfer process reduces the time it takes for a material to burn. In addition, the creation of a uniform layer of silicate ash on the nanocomposite surface has prevented the flame penetration from aiding in extinguishing the combustion process.

4. Conclusions

Carbon nanofillers are widely used in polymer composite fabrication. Unlike traditional flame retardants, carbon nanofillers can improve the flame retardancy of polymers, which is a desirable characteristic for building high-performance polymer nanocomposites. As a result, a substantial reduction in PHRR and Time to Flame-in was seen in MWCNT/GNP/polymer nanocomposites.

The reduction in PHRR follows the order: EGF < EGFM < EGFG < EGFA < EGFH. The high flame retardant efficiency of hybrid filler containing ATH/MWCNT/GNP is attributed to a well-exfoliated layered morphology favourable over spherical particles, tubes and platelets.

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