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

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Comparative study on the effect of aluminium trihydrate and carbon nanofillers on thermal properties of glass fiber reinforced epoxy composites

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ABSTRACT

High-performance glass fiber reinforced epoxy composites are in greater demand in several industrial applications, from civil structures to the aerospace industry. Epoxy is a high-performance polymer due to its highly cross-linked nature. Further, nanomaterials such as multi-walled carbon nanotubes (MWCNT), graphene nanoplatelets (GNP) and aluminium trihydrate (ATH) fillers are being explored to improve the thermal properties of composites. Graphene is the most popular 3D nanofiller for epoxy composites. GNP and MWCNT fillers possess a high aspect ratio and a high specific surface area contributing thermal properties of composites. In spite of that, the challenges associated with these nanomaterials, such as dispersion and interaction. The fabricated nanocomposites are based on glass fiber and modified epoxy resin by adding GNP, MWCNT and ATH fillers using pultrusion assisted by ultrasonication. For comparison, composites containing only MWCNT, GNP and ATH were also tested. X-ray diffraction, and scanning electron microscopy, were used to evaluate the filler dispersion characterization. The thermogravimetric analysis (TGA) was carried out to find the glass transition temperature of composites and thermal analysis. The analysis found that the MWCNT/GNP-ATH composite has enhanced thermal properties due to the addition of ATH filler.

Keywords: Differential Scanning Calorimetry, Thermal kinetics, High-performance polymer, GFRP composites

1. Introduction

Glass fiber-reinforced polymer (GFRP) composites are widely used in a variety of engineering applications, such as power transmission and distribution, aircraft, infrastructure, and electronics[1]–[4]. Because of 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 touted as promising for improving polymer thermal characteristics. Composite properties are influenced by fillers and manufacturing methods [10]–[12]. Fillers with better mechanical and thermal attributes are required to improve thermal characteristics and overcome the limitations of GFRP composites.

The conventional fire-retardant filler most commonly used in GFRP to enhance thermal and flame characteristics is aluminium trihydride (ATH). Physiochemical properties of nanofillers such as MWCNT, GNP, and their hybrids have drawn considerable attention. In combination with ATH microfiller, MWCNT and GNP carbon nanofillers exhibit outstanding 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 epoxy matrix has been filled with conductive carbon nanofillers to improve the GFRP composites electrical and thermal properties. The strong covalent connections formed between the nanofillers and polymer chains in nanocomposites containing MWCNT and its allotropes give them outstanding thermal characteristics. MWCNT is endowed with higher electrical conductivity ($0.5 Sm^{-1}$), ultimate strength(10-63 GPa), and young's modulus (270-950 GPa)[19]–[22], while GNP has (~$6\times105\ Sm^{-1}$, 130 GPa and 1TPa respectively). The thermal conductivity of GNP is 290-380 $Wm^{-1}K^{-1}$ in comparison to the thermal conductivity 3000-5000 $Wm^{-1}K^{-1}$[29], [30]. Researchers also investigated the thermal stability of epoxy nanocomposites modified with GNP, MWCNT and ATH aiming at elevating thermal stability. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) are widely used to examine the thermal properties of GFRP composites when the composite specimen is subjected to increased thermal loading. Several researchers used DSC and TGA to examine the thermal stability of GFRP composites[25]–[29]. Differential scanning calorimetry (DSC) analyses 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 evaluation of composites containing ATH, MWCNT and GNP is carried and compared with the values reported in literature. The main challenge in combining different fillers is that, tendency for agglomeration of nanofillers and increase in the viscosity of the epoxy matrix due. These could be greatly reduced by using ultrasonication assisted pultrusion process. The synergistic effect of carbon nanofillers improved the glass transition temperature and thermal stability of GFRP composites.

2. Materials and methods

The GFRP composites were fabricated by mixing diglycidylether of bisphenol A type epoxy resin and triethyl tetra amine hardener. plain weave E glass fiber was used in the study and the filament diameter was 15 μm. All these laboratory-grade materials were procured from market. Table 1 shows the important properties of the glass fiber and epoxy resin. The nano-Al2O3 particles, which were used as modifiers, have a diameter of 50 nm and were procured from Sigma Aldrich.

3. Materials and methods

3.1 Materials

Graphene nanoplatelets with an approximate bulk density of 0.03-0.01 g/cm^3 were received in black powder form from Sigma Aldrich. The GNPs had a feature size of average thickness and diameter of 2nm and 15μm, respectively. Multi-walled carbon nanotubes produced by chemical vapor deposition were also 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 10nm and length of 6 to 9μm, respectively. Continuous unidirectional E-glass fiber creels were with an average fiber diameter of 20 μm and M/s Owens-Corning's, India supplied surface density of 0.78 kg/m^2. Diglycidyl ether of bisphenol-A (DGEBA) infusion epoxy resin MY740 and the curing agent HY918 were supplied by M/s Huntsmen India.

3.2 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 quantity of ATH was pre-dispersed in epoxy resin using a mechanical agitator.

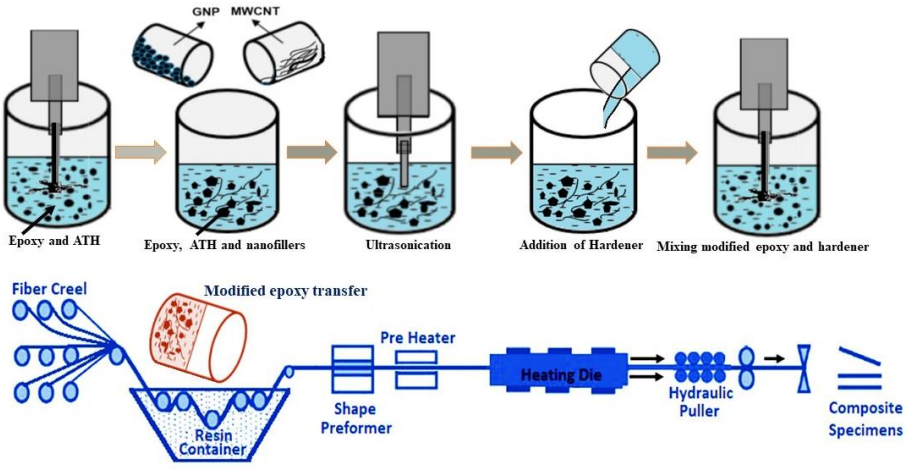

Figure 1. Process of fillers inclusion and fabrication of composites using pultrusion

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.

Table 1. Composites and composition.

Sl. No.	Composites	Constituents	Constituents of composites (wt.%)				
			Glass fiber	Epoxy	ATH	MWCNT	GNP
1.	EGF	Epoxy	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%

3.3 Thermogravimetric analysis

The effect of GNP inclusion on the thermal performance of flax/epoxy composites was studied by a thermogravimetric analyzer (Model: TG/DTA 6200, Seiko Instruments, USA) in compliance with ASTM E1131-03. The composite sample, which had an approximate weight of 10 mg, was put in an alumina crucible. This was heated to 700 °C in a nitrogen medium at a rate of 10 °C min−1. The weight loss of the composites was noted with respect to temperature. For each type of composite, three experimental trials were conducted, and the average values are reported.

4. Results

4.1 Scanning electron microscopy

The fractured surfaces of neat and nanocomposites specimens were analyzed using SEM to examine the dispersion of hybrid MWCNT/GNP and/or ATH fillers in the epoxy matrix as shown in Figure 1(a-d). Figure 1(a) shows a transverse section of a glass fiber wrapped in polymer, demonstrating strong adhesion between the polymer and the glass fibers. The matrix fibral has been sheared, causing these fibers to fracture. The top view of a shattered specimen in Figure 1(b) reveals glass fibers fully covered by matrix. Few glass fibers 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.

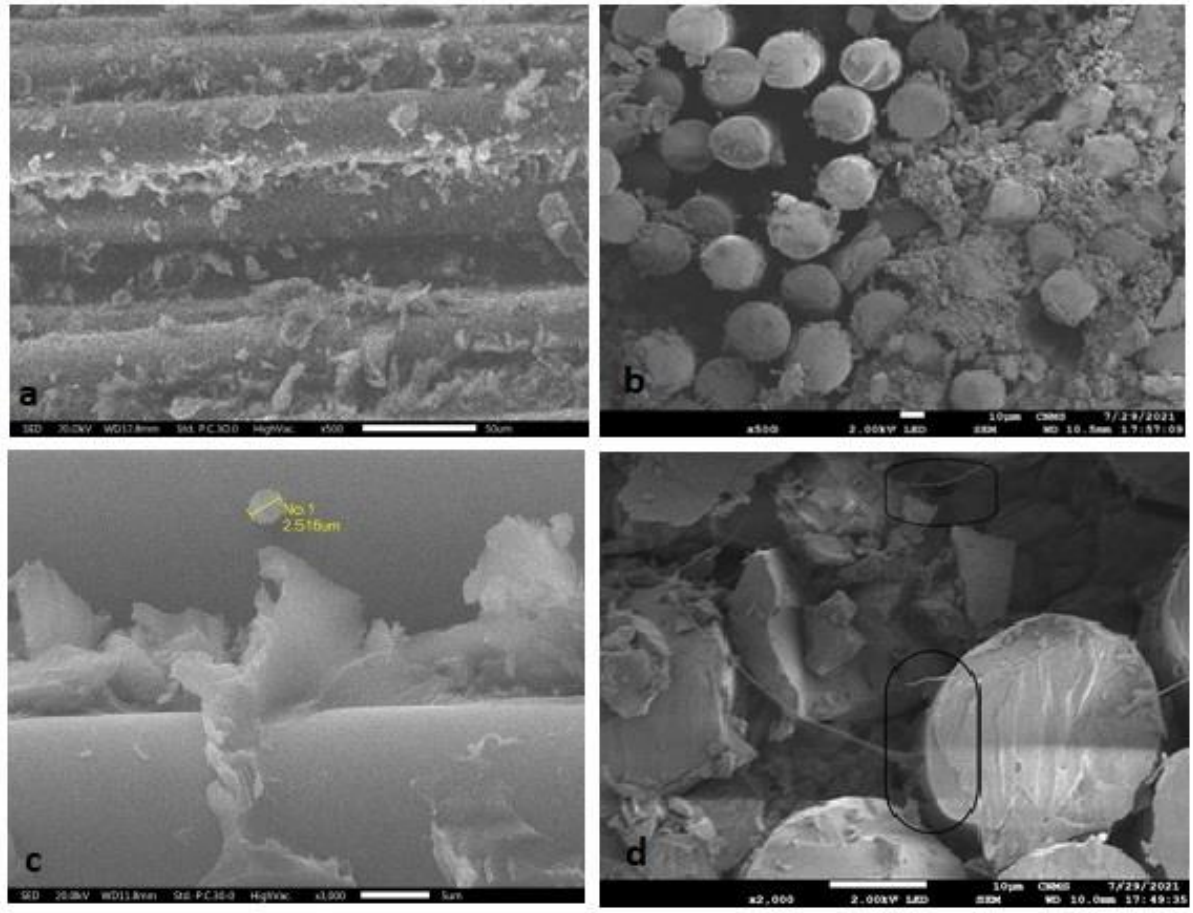

Figure 2. Scanning electron microscope images of specimens

The presence of MWCNT attached to the surface of glass fiber is shown in Figure 1(d). Because epoxy is remarkably brittle, the surface of glass fiber 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.

4.2 Thermogravimetric analysis

The TGA is used to investigate the effect of fillers on the thermal strength of GFRP reinforced composites. The thermal stability assessment is based on significant weight loss at a certain temperature. The thermogravimetric curves of the composites are shown in Figure 3. Initial weight loss occurs between 100°C and 150°C during composite thermal deterioration due to the evaporation of moisture from the composite surfaces.

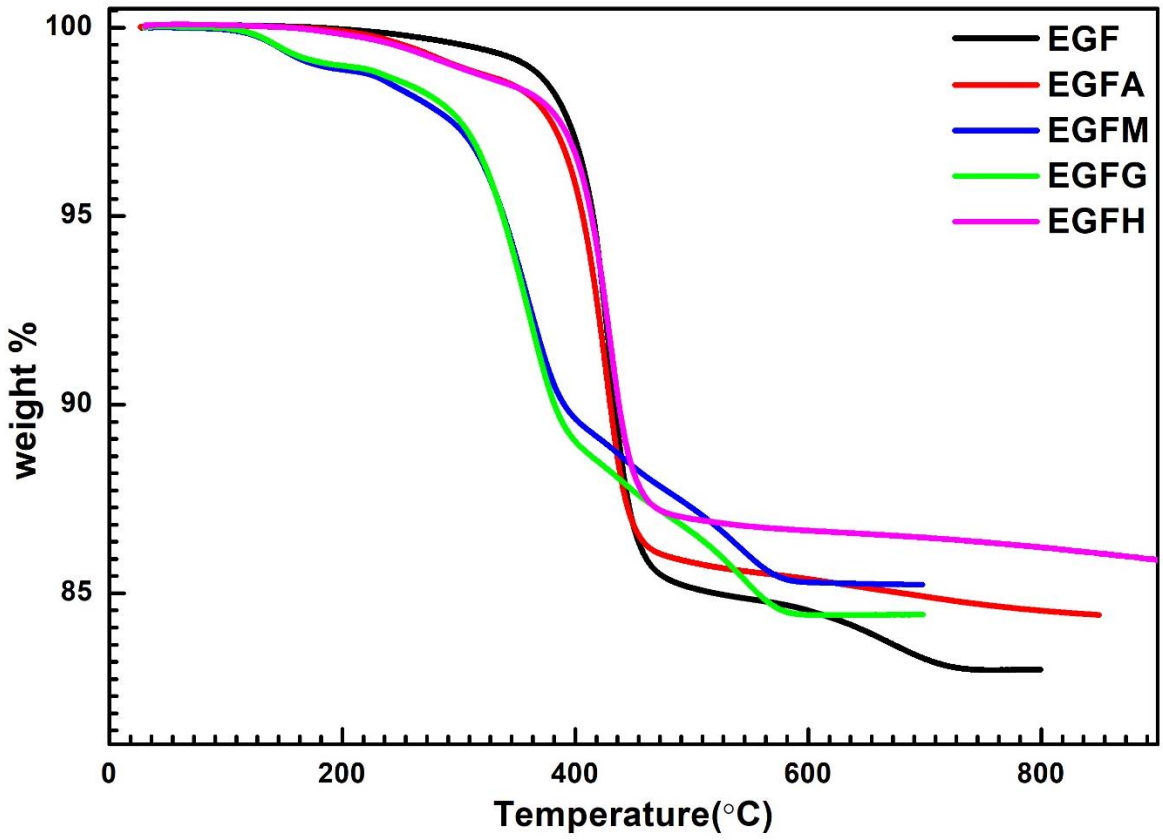

Figure 3. Thermogravimetric curves of composites.

The degradation of the matrix caused significant weight loss in the temperature range of 250–450°C. Finally, the development 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 early stages of thermal degradation, char formation acted as a shield, causing greater thermal degradation. Char development also lowered the mass 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 of the EGFA and EGFH composites was enhanced. When 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 and the char residue level. This was attributed to the composites greater aggregation of GNP, that let they to degrade faster.

4.3 Derivative thermogravimetry

The derivative thermogravimetric (DTG) analysis was performed to explore the impact of GNP on the glass fiber strengthened epoxy. The results are shown in Figure 4. Two prominent peaks were noticed for EGF and EGFA composites, while three prominent peaks were observed for composites with carbon fillers. The first smaller peak showed evidence of water molecules in the composites and the continuance of voids, which formed in the course of composite manufacturing. The second highest peaks suggested a decomposition of EGF, EGFA composites at higher temperatures relative to EGFM, EGFG and EGFH composites. The addition of carbon nanofillers have reduced the derivative weight loss of the composites. The derivative weight loss for EGFA composites was relatively higher than remaining composites. The EGFM composite revealed a minimal derivative weight loss. The EGF and EGFA composites displayed a two-step process of decomposition. Here, the decomposition occurred at around 400°C and 530°C, which corresponded to the maximum decomposition rates.

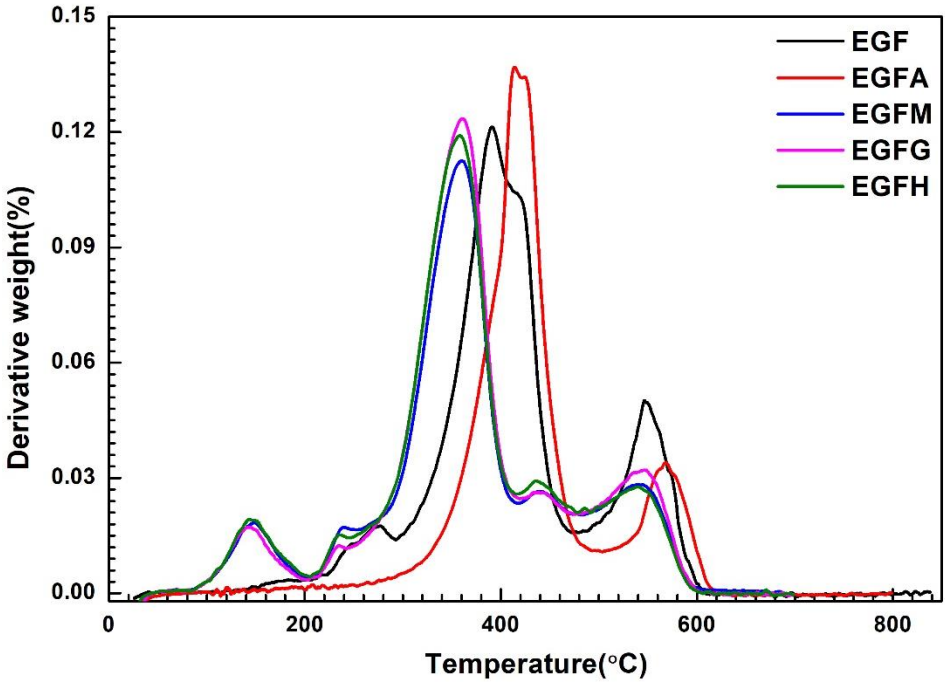

Figure 4. Derivative thermograms of the composites.

From DTG graphs small peaks are observed between 180ºC to 250 ºC in EGFM, EGFG and EGFH composites due to the presence of the carbon nanofillers. The addition of hybrid nanofillers to the epoxy matrix causes higher thermal resistance as compared to the virgin epoxy resin. Therefore, the thermal stability of the nanocomposites increases when the

MWCNT and GNP are incorporated, and these nanofillers can act as a delaying agent for the degradation of the epoxy. This can be ascribed to the ability of the carbon-based fillers to thermally protect the polymer matrix and hinder the transport of degradation volatiles through the matrix by the formation of a tortuous path [34].

5. Conclusions

Thermal analysis of the GFRP composites was carried out using TGA to understand the mechanisms involved in the thermal decomposition when micron and nanofillers are incorporated. Some of the important conclusions of the study can be summarized as follows.

- The ultrasonication assisted pultrusion technique aids in the avoidance or minimization of carbon nanofiller agglomeration, resulting in improved filler dispersion.
- 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 and the extra linkages given by MWCNT to GNP.
- The use of multiscale hybrid fillers further improves the thermal stability of the composites.

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