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Mechanically Improved and Multifunctional CFRP Enabled by Resins with High Concentrations Epoxy-Functionalized Fluorographene Fillers

Junhua Wei

Abstract

To meet the maximum potential of the mechanical properties of carbon fiber reinforced plastics (CFRP), stress transfer between the carbon fibers through the polymer matrix must be improved. A recent promising approach reportedly used reinforcing particles as fillers dispersed in the resin. Carbon based fillers are an excellent candidate for such reinforcing particles due to their intrinsically high mechanical properties, structure and chemical nature similar to carbon fiber and high aspect ratio. They have shown great potential in increasing the strength, elastic modulus and other mechanical properties of interest of CFRPs. However, a percolation threshold of ~1% of the carbon-based particle concentration in the base resin has generally been reported, beyond which the mechanical properties deteriorate due to particle agglomeration. As a result, the potential for further increase of the mechanical properties of CFRPs with carbon-based fillers is limited. We report a significant increase in the strength and elastic modulus of CFRPs, achieved with a novel reinforced thermoset resin that contains high loadings of epoxy-reacted fluorographene (ERFG) fillers. We found that the improvement in mechanical performance of CFRPs was correlated with increase in ERFG loading in the resin. Using a novel thermoset resin containing 10 wt% ERFG filler, CFRPs fabricated by wet layup technique with twill weaves showed a 19.6% and 17.7% increase in the elastic modulus and tensile strength respectively. In addition, because of graphene's high thermal conductivity and high aspect ratio, the novel resin enhanced CFRPs possessed 59.3% higher through-plane thermal conductivity and an 81-fold reduction in the hydrogen permeability. The results of this study demonstrate that high loadings of functionalized particles dispersed in the resin is a viable path towards fabrication of improved, high-performance CFRP parts and systems.

Keywords: CFRP, functionalized graphene, tensile properties, hydrogen permeability, through-plane thermal conductivity

1. Introduction

Carbon Fiber Reinforced Plastics (CFRP) have been widely used as lightweight materials replacing metals because of their superior specific strength, stiffness, and

corrosion resistance [1]. In recent years, their application has been extended from high-end industries, like aerospace, aircraft, sports, and military to cost-sensitive industries, like automotive and energy [2]. This new trend requires reducing the cost of parts made from CFRP. This price reduction can be achieved through two approaches: 1) enhancing mechanical properties of CFRPs resulting in lower usage for same function and 2) eliminating functional parts by enabling CFRPs with these functions.

Improving the stress transfer between the carbon fibers (CF) and improvement of stiffness of polymer matrix are most popular research topics. Besides development of highly efficient CFRP fabrication techniques, low price CF manufacturing and material-saving structure designs, these studies also aim at cost reduction via decrease in CFRP usage. Due to the weak interfacial interaction between the load bearing CFs and the polymer matrix that integrate the structure, delamination is one of the major failure modes for CFRP. One of the key reasons for this failure is that CF has relatively low density of surface functional groups, which result in lesser surface interactions. To address this problem, increasing the interface interaction through sizing, a polymer coating that improves stress transfer through chemical bond and physical interlock, is required as part of the CF manufacturing process [3]. Inspired by the sizing mechanism, rigid particles have been added either into polymer sizing or by spraying on the CFs, to encourage strong physical interlock.

New approach to lower the cost and weight of systems containing CFRPs is to make CFRP a functional part in the system. For example, Type V storage vessels used for hydrogen storage are designed with only a single layer of CFRP which endures the compressed gas pressure and simultaneously acts as an efficient hydrogen barrier. Compared with other tank designs (e.g. Type IV), Type V tank is more cost competitive via process, material, and weight saving through limiting the hydrogen barrier liner. However, to realize this design, a large amount of fillers with good gas barrier properties need to be present into the CFRP to form an effective gas barrier layer.

Carbon-based materials use in polymer sizing have drawn a lot of attention to this approach because of their superior mechanical properties, chemical structure like that of CFs, and most importantly due to their high aspect ratio. Methods including electrophoretic deposition [4, 5], spray [6, 7], and dip coating [8–12] have been employed to deposit graphene and carbon nanotubes onto CFs surfaces. CFRPs made with these coated CFs show ~20–70% improvement on interlaminar shear strength. Up to 10 wt% of particles laden sizing coated onto CF by such approaches have been demonstrated [8]. However, this approach generally does not improve the tensile or flexural modulus [5, 8, 13]. This is because the polymer matrix is much weaker compared to CF, and as a result, the polymer matrix deforms under stress. To reinforce both the modulus and strength of CFRP, researchers have tried to add carbon-based particulate materials directly into the resin matrix as well, [14–19] but this approach achieved only limited improvement in mechanical properties. The primary limitation is particle aggregation, which prevents high particle loading resins [16, 20]. Typically, CFRP with ~1 wt% of carbon-based fillers in the polymer matrix have shown the best properties. A polymer matrix containing a high loading of dispersed carbon-based materials would therefore be likely to radically increase both, strength and modulus, of CFRPs. Meanwhile, carbon-based materials have been appraised for their excellent properties as electrical and thermal conductors, gas barrier, fire retardant et al. [21, 22]. The advantages of their multifunction can introduce CFRP with special properties to replace other functional part and reduce the device price, when the particle concentrations are high enough.

Fluorographene (FG) is a unique carbon-based material which maintains the excellent mechanical properties of graphene but with excellent chemical, electronic,

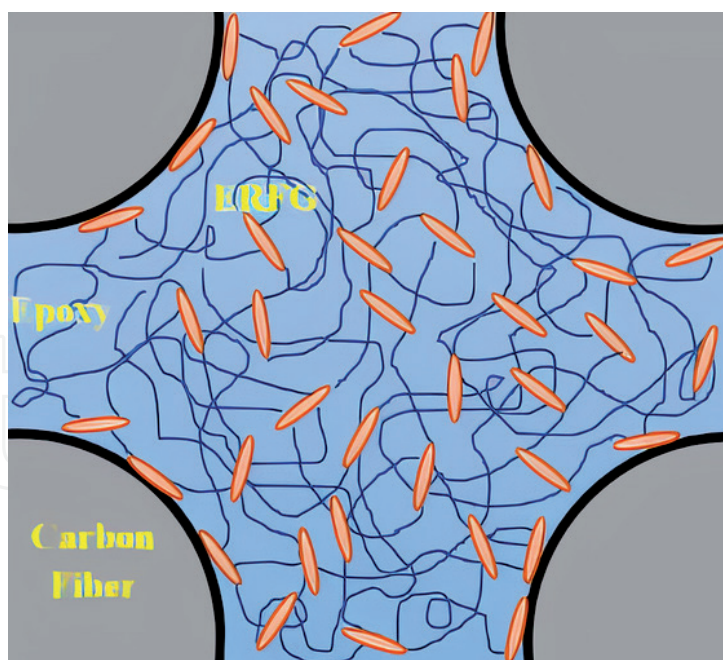


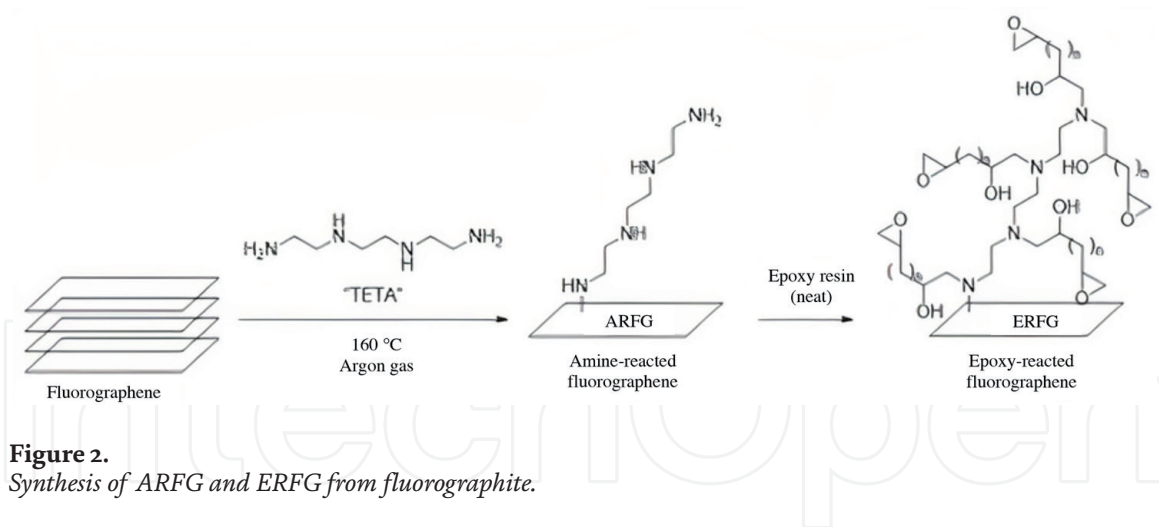
Figure 1.
 Illustration of CFRP containing a high loading of epoxy-reacted fluorographene (ERFG, orange ovals) in the polymer matrix.

tribological, and hydrophobic properties, due to the presence of fluorine atoms [23]. One distinctive advantage of FG is that it easily forms dispersion and exfoliates because fluorination disrupts the van der Waals forces between FG sheets [24]. Other researchers have studied the electrical, thermal and mechanical properties of FG-reinforced polyimide [25–27]. We have previously reported on dispersing epoxy-monomer-functionalized FG in epoxy with 30 wt% loading, which achieved ~90%, ~60%, and ~170% improvement in the tensile strength, modulus, and toughness respectively [28]. In this work, resin containing ERFG was used to make CFRP by wet lay-up method. The high particle loading in the polymer matrix improves stress transfer between the CF, both by physically interlocking with the CFs to improve strength, and by chemical linkage within the polymer matrix to improve modulus (**Figure 1**). Additionally, the high particle loading also enables the CFRP to exhibit properties of FG present within the CFRP, such as low gas permeability, high thermal conductivity, et al. This mechanically improved and multifunctional CFRP is a very competitive composite for cost sensitive CFRP applications.

2. Experimentation

2.1 Materials

Graphite fluoride (FG, also called fluorographite), triethylenetetramine (TETA), and acetone were bought from Sigma Aldrich. Bisphenol A based epoxy resins (EPON 826) with 178 g/mol EEQ (Epoxy Equivalent Weight [29]) was purchased from Miller-Stephenson Chemical Co., Inc. Fibre Glast 2000 (Epoxy), Fibre Glast 2060 (Hardener), 2 K 2 × 2 twill weave carbon fiber fabrics and all the materials for wet layup were from Fibre Glast. Toray T700 12 K 2 × 2 plain weave fabrics and T300 3 K 2 × 2 plain weave fabrics were purchased from Composite Envisions. T800S 12 K 2 × 2 twill weave fabrics and M55JB 6 K 2 × 2 plain weave fabrics were supplied by Rock West Composites. MGS L285 (epoxy) and H287 (hardener) were purchased from Aircraft Spruce & Specialty Co.



2.2 ERFG particle synthesis

ERFG particles were synthesized using the same experimental procedure as in our earlier published work [28, 30], and is presented in **Figure 2**. Briefly, fluorographite was dispersed and solvent exfoliated in TETA, then the C-F bonds on the fluorographite were substituted with amine groups from TETA at high temperature under argon gas protection, thereby producing amine-reacted fluorographene (ARFG). The ARFG particles were recovered from the TETA via filtration, washed, and then dispersed into epoxy resin (EPON 826), to synthesize epoxy-monomer-reacted fluorographene (ERFG).

2.3 CFRP fabrication

The formulation was prepared by a two-step procedure. Firstly, ERFG particles were added into an epoxy resin by centrifugal mixing. Immediately before use for CFRP fabrication, the epoxy resin containing ERFG particles was mixed with a hardener. The optimum weight ratio between the epoxy/ERFG mixture to the hardener was determined by a dynamic DSC screening for the maximum curing enthalpy. The CFRP panels were fabricated according to literature [31]. Next, the formulation consisting of epoxy with ERFG particles and hardener was spread onto each layer of CF fabric. After piling and spreading, accessories like the vacuum bagging were added. The impregnated CF fabrics were cured at room temperature for 5 hr. under vacuum, and then post-cured at 100°C for another 5 hr. The cured CFRP was removed from vacuum and bagging and was then cut into specific shapes according to ASTM D3039 by a water-cooled diamond saw for tensile testing.

2.4 Characterization

The chemical functionalization of the particles was characterized by an ATR FT-IR (Perkin Elmer). The morphology of the ERFG particles was imaged by a TEM (Jeol 1200).

The mechanical properties of CFRP were measured according to ASTM 3039 using a universal tester (AGS-X, Shimadzu). The through-plane thermal conductivity was measured as per ASTM D7984 using a thermal conductivity analyzer (TCi, C-Therm). Hydrogen permeability tests were performed by a professional testing lab (Versaperm Ltd.) in accordance with ASTM G148.

3. Results

3.1 Particle characterization

The mechanism of attaching molecular amine groups to fluorographene through substitution of surface fluorine atoms has been previously reported [32]. In this work, TETA served both as solvent to exfoliate fluorographite and as a reagent for introduction of amino functional groups onto the exfoliated fluorographene to produce Amine Reacted Florographene (ARFG) particles. The color of fluorographite changed from white to black during this substitution reaction. In the second step, the amine groups on ARFG were capped with EPON 826, a low molecular weight diglycidyl epoxy resin derived from bisphenol A. FT-IR spectroscopy was used to identify the chemical groups present on the particles during each step of synthesis. In **Figure 3a**, a prominent feature at 1260 cm^{-1} characteristic of covalent C-F stretching of fluorographite was detected [33]. There are three identifying absorptions peaks for TETA: $1050\text{--}1200\text{ cm}^{-1}$, 1450 cm^{-1} , 1600 cm^{-1} representing C-N stretching, C-H bending, and N-H bending, respectively [34, 35]. In the ARFG FTIR spectrum, a broad absorption peak appears from 1000 cm^{-1} to 1200 cm^{-1} as a result of C-N stretching appeared in place of C-F stretching. The C-F stretching absorption peak at 1260 cm^{-1} is greatly diminished in comparison to the starting material, fluorographite. The 1580 cm^{-1} absorption on the ARFG is inherited from TETA representing N-H bending. In the FTIR spectrum of ERFG, the epoxy functionality display a large number of additional absorptions peaks: 1034 cm^{-1} , 1184 cm^{-1} and 1241 cm^{-1} , 1300 cm^{-1} , 1509 cm^{-1} representing C-O-C ether stretching, C-C-O-C stretching, stretching of cyclic ether, and C-C stretching of aromatic ring, respectively [36, 37]. In ERFG, the C-O-C absorptions extended the broad feature seen in ARFG (1000 cm^{-1} to 1200 cm^{-1}) to a broader range (1000 cm^{-1} to 1300 cm^{-1}), which indicates the presence of epoxy groups onto the ERFG particles. The high aspect ratio, single-digit micro-sized, and few-layer sheet [38] ERFG was shown in the TEM micrographs of ERFG particles (**Figure 3b**).

3.2 CFRP characterization

CFRPs were fabricated with Fibre Glast CF fabrics and Fibre Glast 2000/2060 resin base with different weight loadings of ERFG according to the procedure

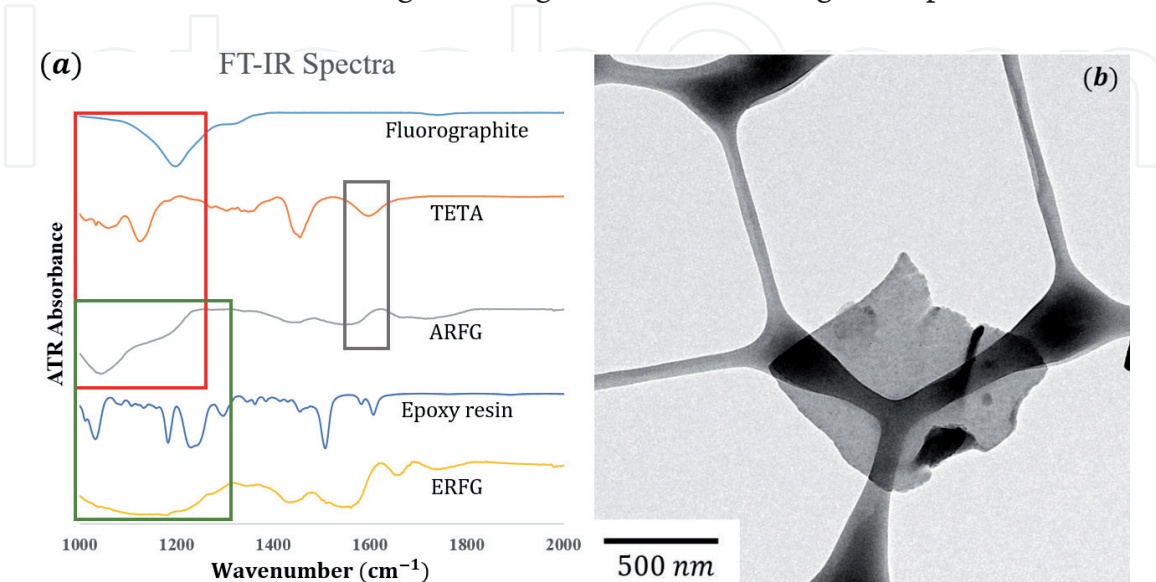


Figure 3. FT-IR spectra of ERFG and its synthetic precursors (a), and TEM image of an ERFG particle (b).

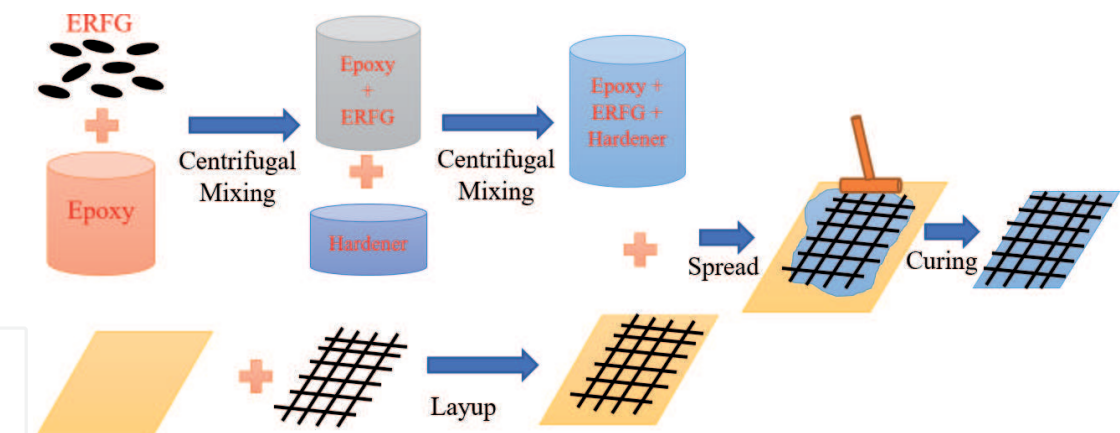


Figure 4.
Fabrication of CFRP using wet layup method.

Sample	Pure (0 wt% ERFG)	5 wt% ERFG	10 wt% ERFG	15 wt% ERFG
Elastic Modulus (GPa)	51.5 (1.3)	55.1 (7.6)	61.6 (4.4)	63.9 (3.1)
Tensile Strength (MPa)	500.7 (15.6)	536.3 (14.9)	608.9 (22.8)	583.9 (22.0)
Thermal conductivity (W/(m × k))	0.425 (0.005)	0.578 (0.001)	0.677 (0.006)	NA
Hydrogen permeability (mol/ (m × s × Pa))	1.79E-14 (0.01)	NA	2.20E-16 (0.02)	NA

Note: the carbon fibers take 37 vol% to 42 vol% in the tested CFRPs.

Table 1.
Mechanical properties, through-plane thermal conductivity, and hydrogen permeability of CFRP made by Fibre Glast CF fabrics and Fibre Glast 2000/2060 resin with different wt% of ERFG (standard deviation).

shown in **Figure 4**. The mechanical, thermal, and gas barrier properties of these samples were investigated and are summarized in **Table 1**.

Unlike the carbon fiber surface particle coating from previous reports, adding particles to the polymer matrix increased both the elastic modulus and the tensile strength. The increase of the elastic modulus of the CFRP made by ERFG resin correlated well with the increase of the ERFG loading below 15 wt%. However, the tensile strength decreased for CFRP with 15 wt% ERFG. There are two possible explanation for this phenomenon. First, the viscosity of resin with ERFG particles increased when adding more particles. For highly viscous resin, higher vacuum pressure and elevated temperature are required for uniform wetting. Second, 15 wt% of particles in the resin can form aggregates or liquid crystal domains. Both these structures prevent the uniform distribution of the particles through the CF fabric. Since the enhanced interfacial interaction between CFs and polymer matrix is based on the premise of attachment of the ERFG present in the polymer matrix to the surface of CF to form a physical interlock. The formation of aggregates or liquid crystal domains decreases the density of ERFG coated onto the CF surface and causes less effective stress transfer and results in decrease of CFRP’s overall tensile strength. Further investigations are underway to reveal which mechanism dominates at higher particle loading CFRPs.

The in-plane thermal conductivity of C FRP can reach ~1000 W/(m × K) due to the continuous nature of the carbon fibers [39]. In contrast, the through-plane thermal conductivity of CFRP is in the 0.2–0.5 W/(m × K) range [40] because the polymer matrix separates the carbon fiber tows. Historically reported approaches

Material	Hydrogen permeability 10E-16 mol/(m × s × Pa)	Ref.
ERFG-enhanced CFRPs	2.20	This work
HDPE	11.20–8.09	[44, 45]
LDPE	24.50	[45]
PA	6.69–2.23	[45]
PTFE	36.20	[46]

Table 2.
Hydrogen permeability of conventional polymer liner for COPV tanks [43].

added highly thermally conductive particles like graphene [40] or diamond [41] into the polymer matrix to increase the through-plane conductivity, but this compromises the other properties of CFRP, mainly mechanical properties. In this work, a significant improvement in the through-plane conductivity is achieved. The ERFG particles serve as bridges to facilitate the conduction of heat between individual carbon fibers. A 60% improvement in the through-plane thermal conductivity was realized in this way (**Table 1**). This significant improvement on the through-plane thermal conductivity can improve the CFRP’s stability under thermal cycling and will enable the replacement of metal built electronic box in weight essential applications [42].

The 2D structure and high aspect ratio of the ERFG particles dispersed within the cured epoxy matrix were efficient in blocking the through-plane permeation of hydrogen gas. The hydrogen permeability of CFRP made with 10 wt% ERFG was 81 times lower than that of CFRP made with pure, unfilled epoxy resin (**Table 2**). These results make ERFG-enhanced CFRPs as state-of-the-art hydrogen barrier materials, far exceeding the properties of conventional polymer liner used in COPV (Composite Overwrapped Pressure Vessels) tanks [43, 47, 48]. The decreased hydrogen permeation is a huge benefit for building COPV tanks for hydrogen or natural gas storage. Additionally, use of ERFG-enhanced CFRPs eliminates one manufacturing step – polymer liner pre-molding – required to manufacture the current Type IV COPV tanks. This multifunctional CFRP is very promising for direct manufacturing of liner-less Type V COPV tanks.

4. Discussion

In this work, the idea of adding high loadings of graphene derivative into the polymer matrix to increase both the elastic modulus and tensile strength of CFRP has been achieved with Fibre Glast fabrics and 2000/2060 resin. To further demonstrate the universality of this idea, we tested the tensile properties of CFRP made with another widely used resin system, MGS 285/287, and with different classes of CFs. To maintain consistency, all CF fabrics used were made with Toray CF. In these carbon fibers, T300 and T700 represent the standard modulus CF. T300 is primarily used for automotive parts and sports products, and T700 is used in gas tanks. The T800 represents the intermediate modulus carbon fiber used in aircraft applications. The M55 is a high modulus carbon fiber mainly used in spacecraft. MGS resin systems have been widely used in CFRP wet layup fabrication with applications in aircraft. By testing CFRP made using widely popular commercial resin with different grades of CFs, we demonstrated the universality of our idea.

Table 3 summarizes the elastic modulus and tensile strength of CFRPs made with different CF using MGS 285/287 resin with 10 wt% ERFG. the elastic modulus

CF	Elastic Modulus (GPa)		Tensile Strength (MPa)	
	Pure (0 wt% ERFG)	10 wt% ERFG	Pure (0 wt% ERFG)	10 wt% ERFG
T300	45.9 (3.4)	51.5 (0.9)	402.9 (14.2)	432.0 (25.1)
T700	51.9 (3.7)	59.1 (7.1)	586.9 (26.7)	701.8 (48.0)
T800	56.8 (3.1)	65.2 (4.7)	683.7 (45.9)	762.5 (37.3)
M55	94.5 (2.0)	111.8 (2.5)	376.2 (28.7)	427.1 (38.0)

Note: the carbon fibers take 38 vol% to 45 vol% in tested CFRPs.

Table 3.
Mechanical properties of CFRP made by different types of CF fabrics and 10 wt% ERFG MGS resin.

of all the CFRP samples made with ERFG show a 15–20% increase in these mechanical properties, due to formation of highly uniform dispersion of ERFG in the polymer matrix and from stronger interfacial interaction between polymer and ERFG through epoxy monomer functionalization. However, the trend observed in tensile strength is more complex. With T700, T800, and M55 CFRPs, the tensile strength increased by ~15–20% when 10 wt% ERFG was added in the resin. When compared, the strength of CFRPs with T300 CF increased by only ~10%. The variation with use of different carbon fibers could be the result of different sizing used on the carbon fibers and structure of fabrics. The thickness, stiffness, and chemical structure of the sizing radically affects the interface between carbon fiber and the polymer matrix. The addition of ERFG amplifies the effect of sizing on interfacial interactions. Different CF weaving structure and fabric density (gsm) affect the resin penetration through the fabric, which together with the increased resin viscosity due to dispersed ERFG particles, resulted in a non-uniform distribution of the particles across CFRP thickness.

5. Conclusions

In this work, significant improvements to both the elastic modulus and the tensile strength of CFRP were achieved through high ERFG particle loadings in the polymer matrix of CFRP. The low surface tension of C-F groups in the fluorographite precursor material, the epoxy monomer functionalization, and the small size, collectively result in high loading of well-dispersed exfoliated ERFG in epoxy resin. Furthermore, the loading of ERFG is high enough to enhance other properties of CFRP composite. The through-plane thermal conductivity of CFRP was increased by ~60% and the hydrogen permeability of CFRP was decreased by a factor of ~81. This work provides a universal method to reduce the cost of CFRPs by 1) decreasing the weight of CFRP parts through improved mechanical properties, and by 2) reducing system complexity by having CFRP parts multiple desirable properties which would ordinarily require separate parts made from different materials. The approach reported in our work represents a viable strategy for low cost parts made with CFRP for applications in automotive, sporting goods and energy sectors.

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