# Graphene Based Hybrid Kevlar/GFRP Nanocomposites for Enhanced Ballistic Protection

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*by*

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# Certificate

It is certified that the work contained in the project titled ***“Graphene Based Hybrid Kevlar/GFRP Nanocomposites for Enhanced Ballistic Protection”*** by following students has been carried out under my/our supervision and that this work has not been submitted elsewhere for a degree.

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# Abstract

Advanced lightweight composite materials provide essential ballistic protection solutions because they balance outstanding specific strength properties with easy processing capabilities and multiple application uses. The ballistic protection domain of defense and aerospace industries uses fiber-reinforced polymer (FRP) composites built with Kevlar and glass fibers to achieve promising results. Epoxy matrices used in traditional applications demonstrate limited resistance to high-speed impacts before they fracture when subjected to tensile forces. Various researchers have proven that incorporating nano fillers improves bonding performance and matrix toughness through graphene nanoplatelets (GNPs) because they enhance both materials properties and ballistic protection assessments. Research evaluates GNP-reinforced Kevlar/GFRP hybrid laminate production and characterization for identifying optimum graphene concentrations suitable in vehicle armour applications.

Graphene nanoplatelets were dispersed in an LY556/HY951 epoxy matrix using ethanol/Triton-X assisted ultrasonication and incorporated into a hybrid Kevlar/glass layup via vacuum-assisted hand layup. The laminates were fabricated with GNP concentrations from 0 to 1 wt.% for mechanical and thermal testing and up to 3 wt.% for ballistic testing. Mechanical characterization included tensile, flexural, ILSS, ±45° shear, and Charpy impact testing as per ASTM standards. The composite containing 0.25 wt.% GNPs showed a 22% improvement in tensile strength, while 0.5 wt.% led to a 28% increase in flexural strength. Charpy impact energy rose from 8.5 J (without graphene) to 13.8 J at 1.0 wt.%. Thermogravimetric analysis revealed a 30°C improvement in thermal degradation onset with GNP addition.

The ballistic test using 9 mm FMJ rounds revealed that the composite with 0.75 wt.% GNP demonstrated maximum energy absorption of 165 J while showing localized delamination which was verified through ultrasonic C-scan. The results show that using 0.25–0.75 wt.% graphene enhances performance at multiple scales through improved transfer of load and deflection of cracks and thermal resistance. Experimental results validate the usefulness of graphene-enhanced hybrid composites as next-generation armour solutions.

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# CHAPTER 1

## Introduction and Organization of the Thesis

### 1. Introduction

Ballistic composites are widely used in the military and nowadays they are used in commercial fields also, mainly because of their protection feature within minimum weight. These materials are used in applications such as soft body armour or hard armours particularly in armoured vehicles. Especially the availability of new high-specific strength and stiffness polymer fibers has opened new possibilities for extensive research in Fiber Reinforced Polymer (FRP) composites. It is now used more frequently in protective and structural forms within military and police vests, vehicle enhancement, and even as part of aircraft and helicopter framework [1], [2].

At its core, a composite material consists of two main components: reinforcement and a matrix system. Reinforcement mostly carries the loads, and the matrix holds the reinforcement together and transfers loads to the fibers. Some of the most often used reinforcement materials consist of metal fibers, ceramic fibers, glass fibers, carbon fibers, aramid polymer fibers and even natural fibers such as basalt, jute, hemp and flax fibers. Of these, aramids and Ultra High Molecular Weight Polyethylene (UHMWPE) have gained wide appreciation for their functionality in ballistic sectors. The most commonly used matrix materials are thermosetting polymers, i.e. epoxies, polyesters, vinyl ester etc are incorporated into these composites as they exhibit good stiffness, heat resistance and ease of processing. Epoxy resins, especially, are known and widely used for their corrosion resistance, thermal characteristics, and high performance which remain stable at higher temperatures. Nonetheless, one demerit of epoxy resins is that they have poor impact resistance, or in other words, they are brittle. Due to their highly crosslinked nature, the fracture energies of these resins are much lower than those of metals or engineering thermoplastics, and as such, impact resistance becomes a key area for its improvement [3]

Over the last few years, use of nano reinforcements like metal oxides, carbon nanotubes, graphene etc have become very common and have given birth to the new class of composites, known as nano fiber reinforced composites. When nanoparticles are incorporated into fiber-reinforced composites, there is enhancement in mechanical properties like increased fracture toughness, interlaminar shear strength and interface shear strength. These improvements, small to significant, greatly rely on how uniformly the nanoparticles are reinforced in the matrix [4].

Despite these advancements, epoxy-based composites suffer from poor resistance under impact loading. Researchers have studied modifications in epoxy matrix systems for improved resistance in low, high and ballistic impact events for many years [5]. The introduction of nanoparticles aims to enhance energy absorption capacity through preventing matrix cracking and delamination failures that occur under impact loading conditions.

Despite these advancements, the development of conventional epoxy composites is still prone to impact damage, especially in high-velocity impact. The two miniature damage modes that emerge include matrix cracking and delamination, both of which hinder the material’s capability in energy absorption. In response to these difficulties, the use of nanoparticles such as graphene and derived materials has been investigated to enhance the impact strength. Graphene, a two-dimensional material made up of a single layer of carbon atoms arranged in a hexagonal lattice, has drawn considerable attention due to its extraordinary mechanical, thermal, and electrical properties [1], [5], [6]. Since its discovery in 2004, graphene has been found to have suitability for application in various fields of industry. Some of the most important opportunities of this material in composites relate to ballistic applications, specifically, the ability to increase energy absorption and reduce internal damage after an impact.

Additionally, the use of graphene increases the fracture toughness and impact strength by greater magnitudes. All these enhancements can be associated with the interaction of the graphene that can turn cracks and dissipate energy in the impact process.

## 1.2 Scope and Aim of the Research

This research project focusses on developing advanced composite materials providing protection against high velocity projectiles as well as fires in armoured vehicles. Graphene reinforced hybrid Kevlar/glass fiber plate were fabricated and tested mechanically and ballistically for their performance along with thermal effects.

## 1.3 Organization of the Thesis

The thesis is divided into six chapters which methodically explore different aspects of the conducted research work:

i. **Chapter 1** discusses about the composites used in ballistic applications and their role in development of vehicular armours along with FST based composite liners. The chapter also stated clearly its scope and aim that follows in this research.
ii. **Chapter 2** provides an extensive review of previous research about fiber-reinforced composites, nano-reinforced composites, phenolic-based systems and their use in ballistic and fire-safe structures. This section emphasizes both the major weaknesses and unexplored research areas discovered in previous investigations.
iii. **Chapter 3** outlines the specific aim and research objectives together with hypothesis along with the detailed methodology used in this research.
iv. **Chapter 4** Presents the mechanical and thermal evaluation of graphene-reinforced Kevlar/GFRP/epoxy composites. The research includes tensile testing and flexural testing and impact testing as well as thermal analysis through TGA and TMA techniques.
v. **Chapter 5** details ballistic performance testing of graphene-reinforced Kevlar and GFRP composites with different graphene weight percentages (up to 3 wt.%). The failure analysis of the composite plates using ultrasonic C scan is also presented in this chapter.
vi. **Chapter 6** Summarizes the essential outcomes together with all research findings.

# CHAPTER NO 2

# LITERATURE REVIEW

## 2.1 Composite Materials

Composite materials represent specially designed materials composed of two or more distinct phases which are arranged properly with a matrix separating them. The characteristics of composite materials exceed what any single component can represent.

Composite materials function according to their matrix, reinforcement, and interface. Composite materials may outperform the performance of their individual components, exhibiting properties do not present in either constituent material alone [7]. This constitutes a considerable benefit of composites. Certain composite properties, including strength and stiffness, can be enhanced through sophisticated designs [8]. Composites generally comprise two categories of constituents: reinforcement and matrix. Composite materials function according to their matrix, reinforcement, and interface.

The matrix stands as a vital structural component of composites because it determines approximately 60% of its properties while maintaining fibre connection and distributing loads between them. The matrix material stands as the main determinant of overall structural properties in composite materials. The composites receive their classification from matrix types and reinforcement types and manufacturing methods. The composites are primarily classified into three categories namely, Polymer matrix composites (PMCs), Ceramic matrix composites (CMCs) and metal matrix composites (MMCs) [9].

### 2.1.1 Polymer Matrices

The main backbone of polymers exists from carbon atoms linked through covalent bonds which form their extended chain-like molecules. The material arrangement exceeds those found in metals and ceramics. Polymers resist chemical attacks more effectively than metals and ceramics because they come at inexpensive processing costs while maintaining ease of processing. The mechanical strength together with stiffness and thermal resistance levels of polymers tend to be lower than other materials. Long-term exposure to ultraviolet radiation together with specific solvent contact leads to degradation of polymer properties. The primary covalent bonds in polymers create materials that are inefficient heat and electricity conductors.

The polymer matrices exist in two main categories which result from either condensation or addition polymerization: Thermosetting and Thermoplastic polymers. The molecular structure of thermosetting and thermoplastic polymers shows crosslinking as illustrated in figure 1. The curing reaction of thermosetting polymers creates cross-linking chains through their normal chemical transformation. The curing reaction requires chemical initiations known as hardeners together with heat and pressure or electron beam radiation for initiation. The property of thermoplastics enables them to become malleable when heated under pressure so they can assume the shape of their mould or laminate. The material turns soft during heating but returns to its hardened state when it reaches room temperature. This two-matrix system displays different behaviours because their molecular structure along with their shape and size and bond classification between Vanderwall and covalent bonds [10]. The development of fibre reinforced polymer composites uses thermosetting and thermoplastic polymers as matrix materials because they effectively transmit loads between the reinforcing fibers.

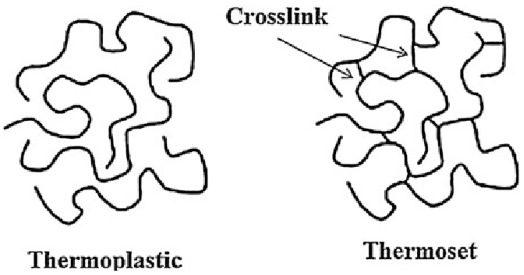


**Figure 1: Crosslinked structure of thermosetting and thermoplastic polymers** *[11]*.

Thermoplastic polymer matrices offer distinguished advantages over thermosetting polymers like having high fracture and impact resistance resulting in improved damage tolerance in composite structures. The plastic behaviour of these matrices may result in shorter processing times, ease of handling and recycling[10], [12], [13]. However, fabrication of composites using these materials as compared to thermosetting polymers are often more complicated because of the higher pressure and temperature requirements for impregnation of fibers, which is usually above its melting point, making it a costly option. Properties of a few thermoplastic polymers are shown in Table 1.

**Table 1: Properties of typical thermosetting and thermoplastic polymers.**

| Polymer Type | Material | Density ($g/cm^3$) | Tensile Modulus (GPa) | Elongation at Break (%) | Flexural Strength (MPa) | Flexural Modulus (GPa) | Fracture Energy ($kJ/m^2$) |
|---|---|---|---|---|---|---|---|
| Thermoset | Epoxy Resin (EP) | 1.1–1.4 | 2.5–3.5 | 1–5 | 90–130 | 2.5–3.0 | 0.5–1.5 |
| Thermoset | Phenolic Resin (PF) | 1.2–1.4 | 3.0–4.5 | 1–2 | 80–100 | 3.0–4.0 | 0.3–0.7 |
| Thermoset | Polyester Resin (UP) | 1.1–1.3 | 2.0–3.5 | 2–5 | 70–100 | 2.0–3.0 | 0.8–1.2 |
| Thermoplastic | Polyether ether ketone (PEEK) | 1.3 | 3.6 | 20–40 | 170 | 4 | 4 |
| Thermoplastic | Polypropylene (PP) | 0.9 | 1.0–1.5 | 200–600 | 30–40 | 1.0–1.5 | 3.0–6.0 |
| Thermoplastic | Polycarbonate (PC) | 1.2 | 2.0–2.4 | 50–120 | 90–100 | 2.0–2.4 | 2.5–3.5 |

The thermoplastic polymers are normally glassy and rigid due to the densely cross-linked three dimensional structures and usually demonstrates high thermoplastic behaviour due to high amount of cross-linking [13]. On the other hand, the thermosetting polymers have shown many advantages for their heavy industrial applications [12], [13]. Thermosetting polymers often retain their original shape and size at relatively higher temperatures, resulting in good resistance against heat, corrosion and other environmental factors. They also have low viscosity which results in good fiber impregnation, which is of vital importance for obtaining good mechanical and thermal behaviour. Properties of a few thermosetting polymers are shown in Table 1.

As evident from Table 1, epoxy resins are of the majorly used thermosetting matrix materials, which are a polymer consisting of epoxide groups (one oxygen atom and two carbon atoms) in its atomic structure.  By far, these epoxies are the most versatile and important materials used for industrial applications such as adhesives, casting, composite structures and surface coatings [18-20]. Rapid growth of epoxy resins in industrial sectors like aerospace, defense, shipping, automobiles etc. is because of their exceptional mechanical and electrical properties along with good resistance to chemicals and solvents [18,19].

### 2.1.2 Fiber Reinforcements

Fibers are the main principal constituents in fiber reinforced composites because of the certain advantages it offers. These fibers have small diameters in terms of their grain size or other microstructural unit, allowing them to attain a higher fraction of mechanical strength as compared to its bulk form [10] [11,21]. A huge amount of load can be transferred to these fibers via matrix with higher aspect ratios (length to diameter ratio, l/d ratio). Moreover, the flexible behaviour of these fibers allows a variety of fabrication techniques for having different composite materials [1], [2].

Since fibers are the primary load-bearing elements in composite materials, the choice of fiber type, orientation, and volume fraction plays a critical role in designing composites for aerospace and defense applications. Several material characteristics—such as density, tensile and compressive strength, elastic modulus, fatigue resistance, and failure mechanisms including fiber pull-out, elongation, rupture, and delamination—collectively determine composite performance. These factors must be carefully optimized based on the intended application. Among the various fiber types available, high-performance reinforcements such as aramid fibers (e.g., Kevlar), glass fibers (GFRP), carbon fibers (CFRP), and ultra-high molecular weight polyethylene (UHMWPE) are widely adopted in ballistic and structural systems. While natural fibers, boron fibers, and ceramic fibers are occasionally used, their application is more limited. The key physical and mechanical properties of select high-performance fibers are presented in Table 2.

**Table 2: Properties of few high-performance fibers [22].**

| **Fiber Material** | **Density ($g/cm^3$)** | **Tensile Strength (GPa)** | **Tensile Modulus (GPa)** | **Elongation at Break (%)** | **Compression Strength (GPa)** | **Fatigue Resistance** | **Typical Applications** |
|---|---|---|---|---|---|---|---|
| **Nylon 66 (Polyamide)** | 1.14 | 0.8–1.0 | 2.0–3.0 | 18–25 | ~0.1–0.2 | Moderate | Textiles, flexible armor, lightweight structures |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Kevlar 29 (Aramid)** | 1.44 | 3.0–3.6 | 70–83 | 2.5–4.4 | ~0.2–0.3 | Excellent | Ballistic protection, aerospace components |
| **Kevlar 49 (Aramid)** | 1.44 | 3.4–3.6 | 120–130 | 2.0–2.8 | ~0.2–0.3 | Very Good | Aerospace structures, defense armor |
| **Kevlar 129 (Aramid)** | 1.44 | 3.6–4.0 | 95–100 | 3.0–4.0 | ~0.2–0.3 | Excellent | High-performance ballistic vests, helmets |
| **Kevlar KM2 (Aramid)** | 1.44 | 3.6–4.1 | 90–100 | 3.2–4.0 | ~0.2–0.3 | Excellent | Military helmets, advanced armor panels |
| **E-Glass (GFRP)** | 2.55 | 3.4–3.5 | 72–76 | 4.8–5.5 | ~0.8–1.0 | Good | Aircraft panels, radar domes |
| **Carbon Fiber (T300)** | 1.76 | 3.5–3.7 | 230–240 | 1.5–2.0 | ~0.8–1.0 | Excellent | Aerospace structures, defense equipment |
| **Carbon Fiber (IM7)** | 1.78 | 5.5–5.7 | 280–290 | 1.8–2.1 | ~1.0–1.2 | Very High | Military aircraft, UAVs |
| **UHMWPE (Spectra/Dyneema)** | 0.97 | 2.4–3.0 | 80–120 | 2.7–3.8 | ~0.1–0.2 | Very Good | Personal armor, vehicle armor panels |
| **Boron Fiber** | 2.6 | 3.4–3.8 | 380–400 | 0.8–1.2 | ~1.0 | High | Space structures, high-stiffness panels |
| **Basalt Fiber** | 2.7 | 2.8–3.1 | 85–90 | 2.7–3.1 | ~0.5–0.6 | Good | Fire protection, ballistic structures |

Table 2 summarizes the key mechanical properties of various high-performance fibers commonly utilized in defense and aerospace applications. These include multiple grades of aramid fibers (such as Kevlar 29, 49, 129, and KM2), carbon fibers (T300, IM7), E-glass, ultra-high molecular weight polyethylene (UHMWPE), basalt, boron fibers, and engineered polyamides like Nylon 66. Each fiber offers distinct advantages: carbon fibers exhibit exceptional stiffness-to-weight ratios, though at the cost of higher density; aramid and UHMWPE fibers excel in energy absorption and tensile ductility, making them ideal for impact and blast resistance; meanwhile, basalt and boron fibers contribute enhanced thermal resistance and compressive strength. In practice, composite designers often integrate different fiber types within a single laminate to exploit the synergistic benefits of their respective properties. This strategic blending of reinforcement materials lays the groundwork for the next sections, which focus on how nanoscale matrix enhancements and hybrid lay-up architectures can further improve the multifunctional performance of advanced vehicle armour systems.

### 2.1.3 Nanocomposites Based on Epoxies

Epoxy resins find extensive application in fiber-reinforced composites because they demonstrate excellent thermal stability along with resistance to chemicals and superior strength per weight among other properties. The extensively cross-linked molecular arrangement of epoxy resins leads to material brittleness together with reduced damage tolerance which limits their application for dynamic and impact-loaded systems [14]. Nanomaterials have emerged as a transformative approach to improve epoxy systems because researchers have increasingly studied their integration into these systems. The mechanical and thermal properties and dielectric behaviour of epoxy resins have been enhanced by research into carbon nanotubes and graphene and nanosilica and nanoclays as nanofillers [15], [16]. Nanofiller dispersion along with improved interfacial bonding allows researchers to obtain major advancements in both stiffness and endurance strength together with glass transition temperature and fracture toughness. The next part examines how epoxy matrices are modified through nanoparticle incorporation specifically for aerospace and defense applications which use fiber-reinforced composite systems.

Nanoparticles added to epoxy resins create materials with enhanced properties which include extended glass transition temperatures and mild increases in glassy modulus and low dielectric constant and substantial improvements in mechanical properties [7]. Research during the past decades demonstrates that nano and micro-scale particles have the potential to enhance both properties and performance characteristics of fiber reinforced polymer matrix materials. Researchers have dedicated substantial work to creating and processing fiber-reinforced epoxy nanocomposites. Research on nanocomposites primarily focuses on two-phase systems, for example carbon nanotubes dispersed in epoxy but various researchers expect nanofiller addition to polymers will enhance three-phase composite mechanical properties including fracture toughness and compression strength (for instance glass/carbon fiber reinforced epoxy with carbon nanotubes) as Figure 2-3 demonstrates [4]. For example, Haque et al. [28] achieved substantial improvements in mechanical properties for S2-glass fiber laminates through vacuum assisted resin infusion (VARI) method with minimal layered silicate content. The researchers achieved results by distributing 1 wt. % nano silicates throughout the material.

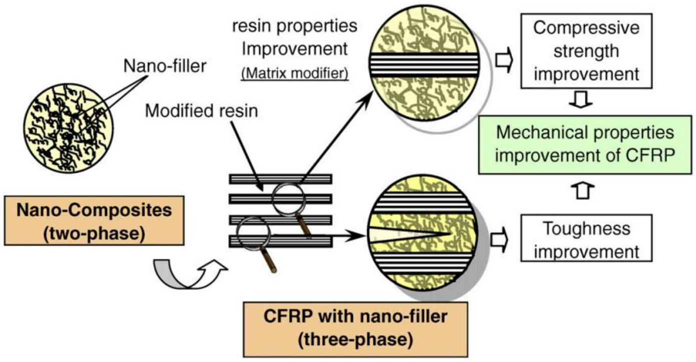


**Figure 2: Scenario of mechanical properties improvement of CFRP by incorporation of CFRP by incorporation of nanofillers [4].**

## 2.2 Graphene Reinforced Nanocomposites

As discussed earlier, various researchers and scientists have developed new advanced materials through nanoparticle utilization because it enables them to create materials with enhanced and desired properties. Epoxy resin becomes stronger in mechanical, thermal and electrical properties when nanoparticles are added to it. The use of graphene along with its derivatives presents itself as a suitable material choice for fibre reinforced composites.

### 2.2.1 Introduction to Graphene

Graphene stands out as a 2D material formed from a single layer of carbon atoms bonded through $sp^2$ bonds which shows great promise for enhancing the impact resistance and toughness of FRP laminates because of its excellent mechanical and thermal and electrical characteristics. The performance of FRP composites depends on how well these nanomaterials disperse and what dimensions they have. The discovery of monolayer $sp^2$-bonded carbon material graphene through graphite mechanical exfoliation happened in 2004, two decades after scientists found carbon nanotubes (CNTs) [17]. This discovery started a new paradigm in materials science because graphene enables impressive capabilities such as enhanced mechanical qualities along with exceptional electron transport abilities and improved thermal properties [18], [19]. The Young's modulus value of approximately 1 TPa makes graphene one of the most robust materials ever discovered. In recent years, with increasing scientific and technological impetus, many research studies have been conducted focussing on the unique properties of graphene. For example, graphene as a conductive material finds its applications in printing electronics. The research by Yang et al. [20] resulted in the development of a supercapacitor with capacitance within the range of 200-300 F/g. The use of graphene as a transparent electrode allowed Kim et al. [21] to develop an organic photovoltaic device.

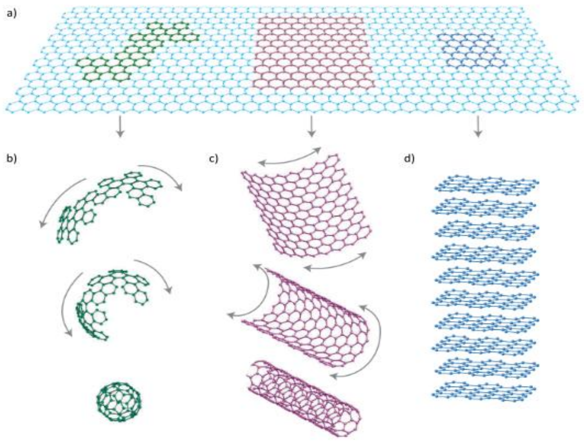


**Figure 3: Graphene is a 2D material for carbon materials of all other dimensionalities [40].**

### 2.2.2 Graphene Oxide and Functionalized Graphene

The compound known as Graphene oxide (GO) represents a derivative of graphene which contains various ratios of oxygen, carbon and hydrogen elements. The production of GO occurs through extensive graphite oxidation followed by its exfoliation process. The Hummers [22] method uses $KMnO_4$ and $H_2SO_4$ as strong mineral acids and oxidising agents for treating graphite while the Staudenmaier [23] [43] method employs $HNO_3$ and $KCLO_3$ as such agents. Scientists have not established any definitive model to explain GO structure because there exists no single analytical method to precisely analyse this compound. Research shows that carboxylic groups (-COOH) exist mostly at GO edges yet hydroxyl (-OH), epoxide and other functional groups reach their highest concentration in the graphene basal plane. The illustration in Figure 4 demonstrates this type of representation.

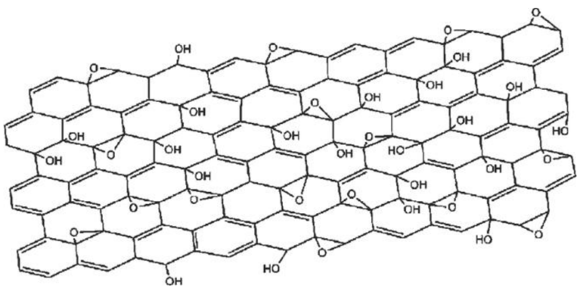


**Figure 4: Schematic of GO structure** *[24]*.

The tendency of graphene to agglomerate in epoxy matrices makes pristine graphene ineffective for intercalating large species such as polymer chains [25]. Research on other nanofillers demonstrates that matrix improvements occur when nanofillers maintain homogeneous dispersion throughout the matrix material [26]. Thus, the performance of graphene nanocomposites depends heavily on both the dispersion state and the strong bond formation between graphene and various matrices [27].

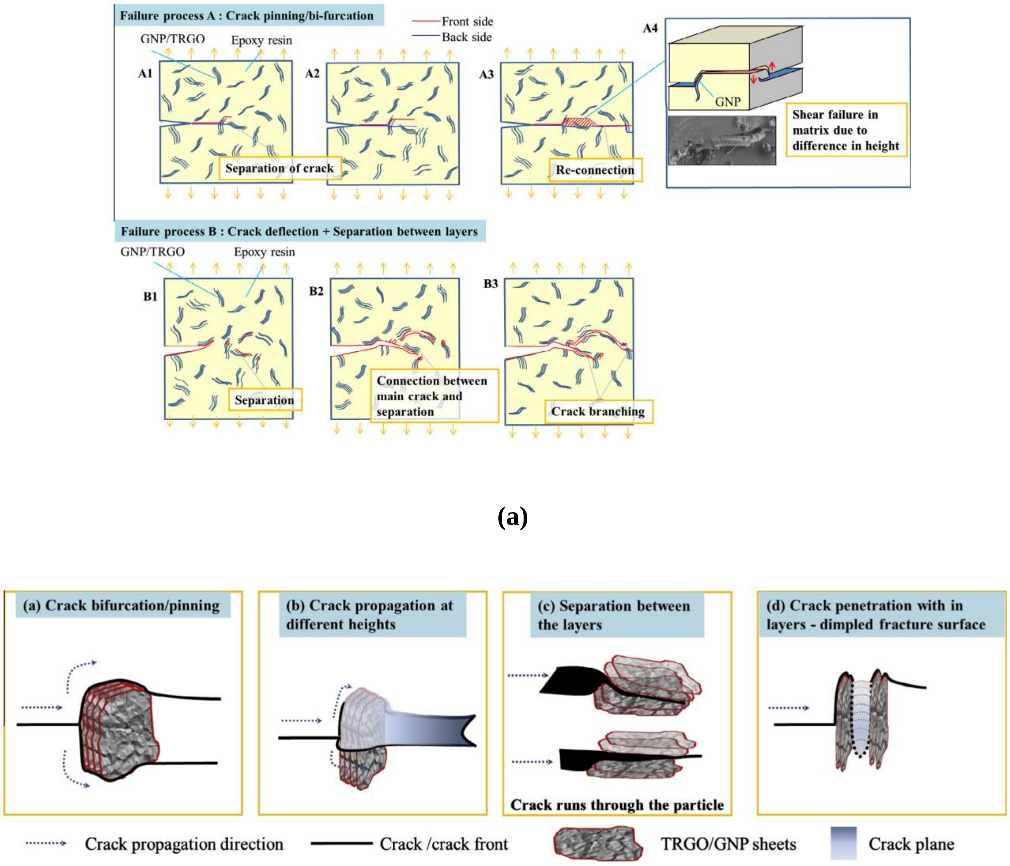
The agglomeration problem of graphene can be solved by chemical functionalization and its if utmost interest because not only it improves the dispersion in the epoxy but also enhances the interactions with organic polymer molecules. Various functionalization methods have been developed and consists of small molecules or long polymer chains [28] or long polymer chains [29]. The functionalization of graphene is normally classified into covalent and noncovalent functionalization. More details can be found in [28], [30], [31].

## 2.3 Mechanical Properties of Graphene-Epoxy Nanocomposites

Graphene has got excellent mechanical properties like, Young's modulus, high tensile strength together with high fracture toughness [32]. These unique traits of graphene make it perfectly suitable as a nanofiller in the development of high-performance composites. Research on epoxy/graphene nanocomposites focuses mainly on leveraging graphene's exceptional mechanical properties while adding enhanced electrical conductivity and thermal stability [33], [34].

As presented above, graphene has excellent mechanical properties, particularly Young’s modulus, high tensile strength, fracture toughness, etc. [32]. These exceptional properties make graphene an ideal candidate as a nanofiller for high performance nanocomposites. Most of the work conducted on epoxy/graphene nanocomposites is aimed at exploiting the remarkable mechanical enhancement effect of this graphene coupled with the possibility to introduce further functionalities, such as electrical conductivity [33], and thermal stability [34].

Chandrasekaran et al. [35] investigated the effect of the addition of three different carbon nanofillers on fracture toughness ($K_{IC}$) and the failure mechanism of epoxy-based polymer nanocomposites. At 0.5 wt.% pf filler, a significant rise of 40% in fracture toughness have been observed due to the toughening effect of thermally reduced graphene oxide. An improvement of 25% in toughness using graphene in epoxy has also been observed along with 8% improvement with Multiwalled Carbon nanotubes (MWCNT). Evidence of crack deflection, crack pinning at the edges of the sheets were also observed using SEM fractography. Some of the crack propagation mechanisms with graphene nanoplatelets/TRGO particles are shown in Figure 5 below.



**(a)**

**(b)**

**Figure 5: Schematics of (a) Crack propagation mechanisms in TRGO/Graphene epoxy composite, (b) Interaction of crack front from Graphene/TRGO particles** *[35]*.

In one of the studies by Mishra et al. [36], the authors studies the influence of graphene (0%, 1%, 2%, and 3% by weight) on the mechanical performance of glass fiber-reinforced epoxy composites fabricated using hand lay-up method. The researchers tested two different lay-up arrangements (0/90 and (0/90/±45) to evaluate their impact on tensile and flexural and impact properties. The addition of graphene at 2 wt.% produced the most significant enhancements to all mechanical properties in bi-directional glass/epoxy composites. The tensile strength increased by up to 58% while flexural strength increased by up to 80% in both lay-ups when compared to the unmodified composite. The mechanical properties of the composite decreased after 2 wt.% graphene because the graphene particles started to clump together. SEM imaging revealed optimal performance at 2 wt.% graphene concentration because it enhanced the bond strength between fibres and matrix while improving crack bridging.

Tang et al. [37] have presented the enhancement in the electrical and thermal properties of epoxy nanocomposites using RGO. The researchers created epoxy composites with RGO using ball milling and without it to propose that 0.2 wt.% RGO dispersion enhanced fracture toughness by 52% while raising Tg by 11$^{0}$C and significantly improving electrical conductivity. The tensile and flexural moduli values, however, did not change during the experiments. Qiu et al [20] employed thermotropic liquid epoxy to modify graphene. The fabricated nanocomposite displayed improved tensile strength from 55.43 MPa to 78.96 MPa at 1wt% while Charpy tests reported 100% improvement in impact strength. Liu et al. [38] modified the epoxy resin by using 0.5% silane functionalized graphene through an ultrasonication and mechanical stirring process. The elastic modulus increased by 20% while tensile strength improved by 16% compared to neat epoxy samples due to this method. Rafiee et al. [39] have reported a similar enhancement in Young's modulus at 0.1 wt.% graphene ratio prepared through shear mixing and ultrasonication. Izzuddin et al. [40] observed good adhesion between graphene and matrix. The polyoxyalkyleneamine functionalized graphene in epoxy resin achieved a strong interface through ultrasonication followed by mechanical stirring. The fracture toughness of resin samples increased by 224% when the sample contained 0.489% vol.

## 2.4 Ballistic Impact Response of Composites

The speed at which an impact occurs determines the entire response of composites during such events. When impact velocity changes the energy transfer mechanisms between projectile and composite panel along with the damage progression patterns and energy dissipation methods will vary [5]. Composite panels subjected to high-velocity impacts develop various failure mechanisms which include surface indentation and matrix cracking and interlaminar delamination and shear plugging and fiber tensile rupture [1]. Ballistic impacts describe the situation where projectiles or lightweight fragments hit composite or soft armour materials at velocities ranging from 100 to 1000 m/s [41], [42], [43].

The ballistic resistance of composites depends strongly on four main factors which include reinforcing fibre mechanical properties and fabric weave design and polymer matrix performance and fibre–matrix interface strength. The performance results during ballistic testing significantly depend on both projectile shape and testing boundary conditions [13]. A deep through understanding of the ballistic impact mechanisms still needed to be understood despite having numerous experimental and simulation-based studies.

### 2.4.1 Ballistic Local and Global Impact

Composite panels experience are subjected to dual effects of global response and local response during impact events [44]. The area directly impacted by the impactor shows local response behaviour whereas global response describes the behaviour of the remaining composite area [44] [83]. The projectile velocity stands as the primary factor for determining both target types of response. Robinson and Davies [45] defined the velocity threshold between high and low-velocity impacts by using the ratio of impactor velocity to the speed of sound in the plate's thickness direction. A high-velocity impact occurs when the impact ratio exceeds the failure strain of the target material. The schematic Figure 6 demonstrates the responses of composites under high and low velocity impacts [46] . The velocity classification appears in Figure 7 to show the boundaries between high velocity and low velocity [6] .

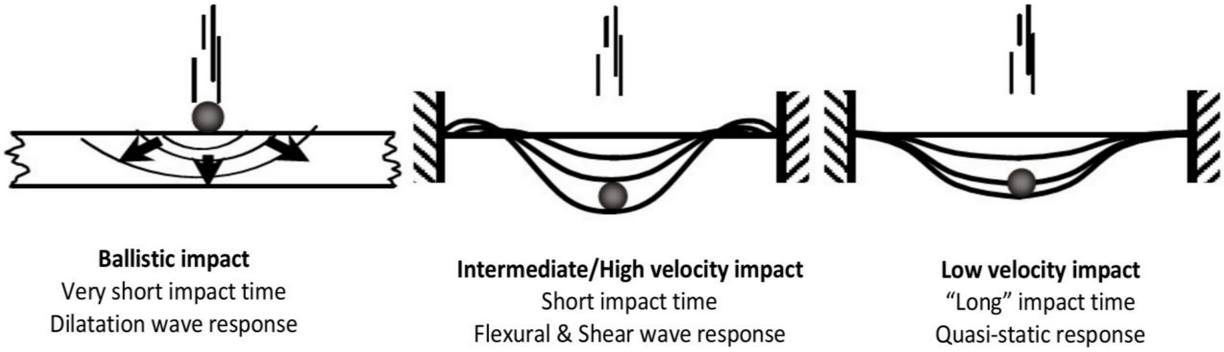


**Figure 6: Low and high velocity impact response of composites** *[47]*.

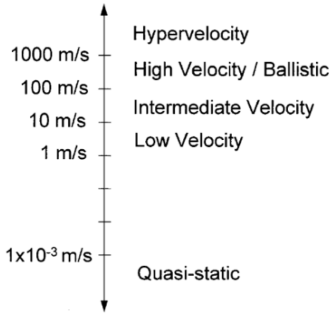


**Figure 7: Velocity classification for various impacts** *[47]*.

Rodriguez et al. [47] performed a study to analyse CFRP responses under low and high velocity impacts. The authors established that local damage dominates the energy absorption process when impacts occur at high velocities, but plate deflection becomes more important at lower velocities. The research demonstrated that higher impact energy led to expanding delamination area.

Olsson [48], [48] demonstrated that target dimensional characteristics together with boundary conditions show minimal impact on response behaviour during small mass ballistic events. The ratio of local contact frequency to structural frequency of the target at 40 serves as another classification criterion according to Bucinell et al. [49]. The engineering of composites requires a thorough investigation of ballistic impact failure mechanisms.

## 2.5 Energy Dissipation Mechanisms in Different Impacts

The energy absorption capacity is one of the key parameters affecting the ballistic performance of composites [5], [50]. The overall kinetic energy of the projectile is converted into several other energy forms during the impact on composites in ballistic events. The most dominant failure in composite materials are the yarn failure in tension, matrix cracking, delamination's, fiber pull outs etc[5], [51]. Composites mainly absorb energy not only by deformation but also by matrix cracking as well as rupture of the fibers.

The energy absorption characteristics of composite material subjected to ballistic loading, according to Cunniff [52] have been classified into material parameters, construction parameters and Impact conditions to which the materials are subjected. Material parameters include failure criteria for different materials, and the constitutive properties, i.e. Stress-strain relationship, constructions parameters include classification of fabrics, armour thicknesses, areal density etc. and impact conditions include projectile mass, striking velocity, striking obliquity, and projectile geometry, like nose shape, design etc.

Two types of matrix cracks have been proposed by various researchers that normally occurs during ballistic impact. These developed cracks serve as an initiation point for intra/inter delamination in composites. Figure 8 shows the typical transverse shear and bending cracks. Transverse cracks usually develop slightly away from an impact point at approximately 45° due to the superposition of interlaminar shear stress and transverse stress. On the other hand, bending cracks appears at the bottom of the laminate when they are subjected to high magnitude in-plane tensile stresses.  Increase bending beyond delamination ultimately results in fiber elongation at the back face of the panel [51].

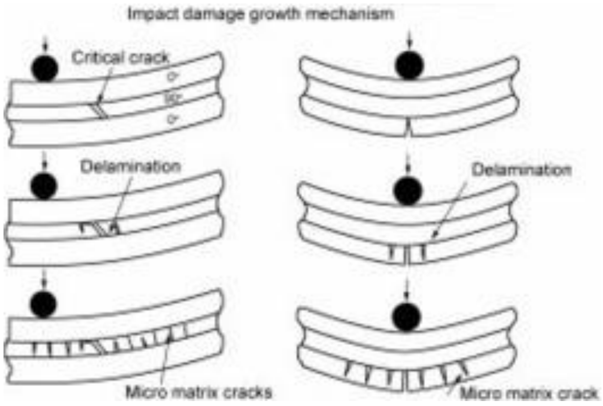


**Figure 8: Impact damage growth mechanism**[53].

In case of high velocity impacts, the projectile normally perforates the first few layers of the composite laminate, commonly known as shear plugging. Shear plugging is commonly associated with projectiles having sharp edges, or the initial strain if fibers exceed their failure threshold, i.e. Figure 9. The subsequent layers of the laminates are stretched and absorb the energy through membrane behaviour [54].

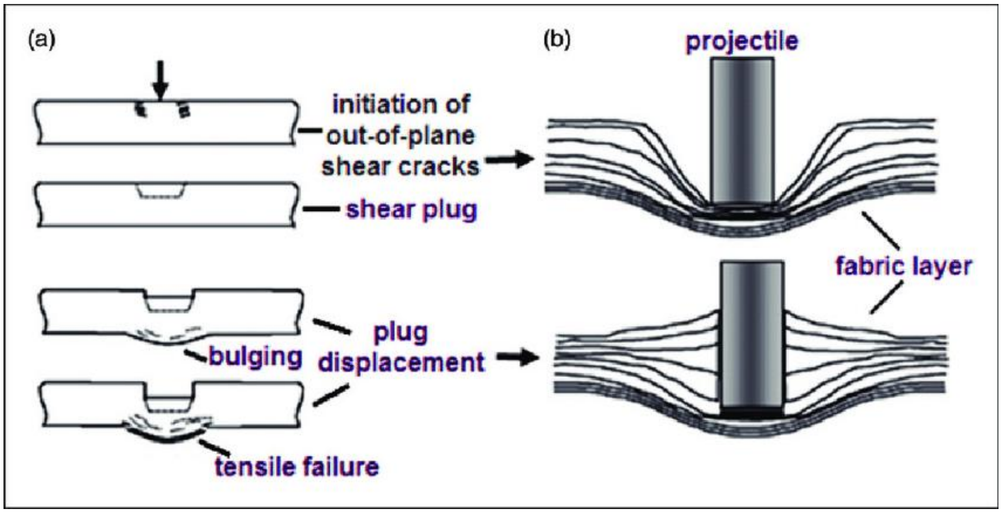


**Figure 9: penetration into compliant laminates (a) with shear plug formation and (b) with compaction and spring back *[55]*.**

## 2.6 Nanoparticles effect on the ballistic performance of composites

As presented in the previous section, different failure mechanisms are involved in the ballistic impact event including matrix cracking and delamination’s. Researchers across the globe have put a variety of efforts to increase/improve the energy absorption of laminates by using different nanoparticles [56]. Much experimental research has proven that certain type of nanoparticles can improve the mechanical, thermal, impact and electrical properties of laminate that are critical for ballistic resistant composites. The impact energy absorption capacity of nanocomposite depends upon the type of fiber, matrix and particle, interfacial properties of the components, volume fraction, dispersion of nanoparticles in resins and their method [57].

Avila et al. [58] examined how nanoclay and nano graphite affect ballistic impact performance in glass/epoxy composites. The researchers found that glass/epoxy laminated composites attained better high velocity impact resistance after nanoclay and graphene nanosheet integration, yet this addition caused substantial changes to their failure process. The desired properties in nanocomposites emerge from the specific constituents along with the nanoparticle weight fraction and their distribution state within the matrix. Miyagawa et al. [59] reported the increase in fracture toughness and critical energy release rate of carbon/epoxy by adding 5 wt.% nanoclay. While Pol et al. [60] studies experimentally the effect of nanoclay on the ballistic behaviour of woven fabric composites fabricated by vacuum assisted resin transfer moulding (VARTM). A 5% improvement was also observed in the energy absorption capability at impact velocity which is higher than its ballistic limit. Gibson [61] in his work, has presented various armour composite panels consisting of Kevlar K-29 fiber in an epoxy resin with MWCNT. A 6.5 % improvement in ballistic limit was found at 1.65 wt.% of MWCNT.

The ballistic mechanical properties of epoxy nanocomposites improve when graphene and its substitutes act as fillers because they enhance stiffness and tensile strength along with fracture toughness. Few studies exist which explore how graphene and its derivatives affect the ballistic properties of composite materials.

## 2.7 Limitations

**Dispersion Challenges:** The main obstacle for achieving uniform dispersion of graphene or its derivatives including graphene oxide or TRGO exists within epoxy matrices. The mechanical performance suffers due to stress concentrators when graphene agglomerates because of inadequate dispersion.

**Limited Studies on Ballistic Performances**: Research on ballistic performance of graphene-epoxy composites remains scarce despite extensive investigation of tensile, flexural and impact properties for these materials.

**Interfacial Bonding Issues:** The strength of mechanical enhancement relies entirely on how well graphene bonds with the matrix material. The ability of composites to transfer stresses is negatively impacted by both poorly functionalized and weak graphene-matrix interfacing.

# Chapter 3

## Aim, Objective and Methodology

### 3.1 Aim of the Study

To create lightweight hybrid laminates using Kevlar reinforced with Glass-epoxy and graphene while measuring how different weights of graphene (0–3 wt %) affect mechanical and ballistic properties for armour applications.

### 3.2 Specific Research Objectives

The objectives of this research are summarized as follows:

- To create graphene-reinforced hybrid Kevlar/glass fibre epoxy composites through the addition of graphene nanoplatelets up to 1.0 wt.% for mechanical and thermal testing and up to 3.0 wt.% for ballistic testing.
- Evaluation of graphene nanoplatelets and fabricated composites structural and thermal properties will be achieved through SEM, XRD, FTIR, Raman spectroscopy, and TGA techniques.
- To investigate mechanical and impact properties for the composites will be performed through tensile, flexural, interlaminar shear strength (ILSS), ±45° in-plane shear, and Charpy impact testing using ASTM standards.
- To investigate ballistic response, post-impact damage of composites through high-velocity impact testing with C-scan analysis for determining the best graphene concentration level to enhance both energy absorption and structural integrity.

### 3.3 Methodology to Achieve the Objectives

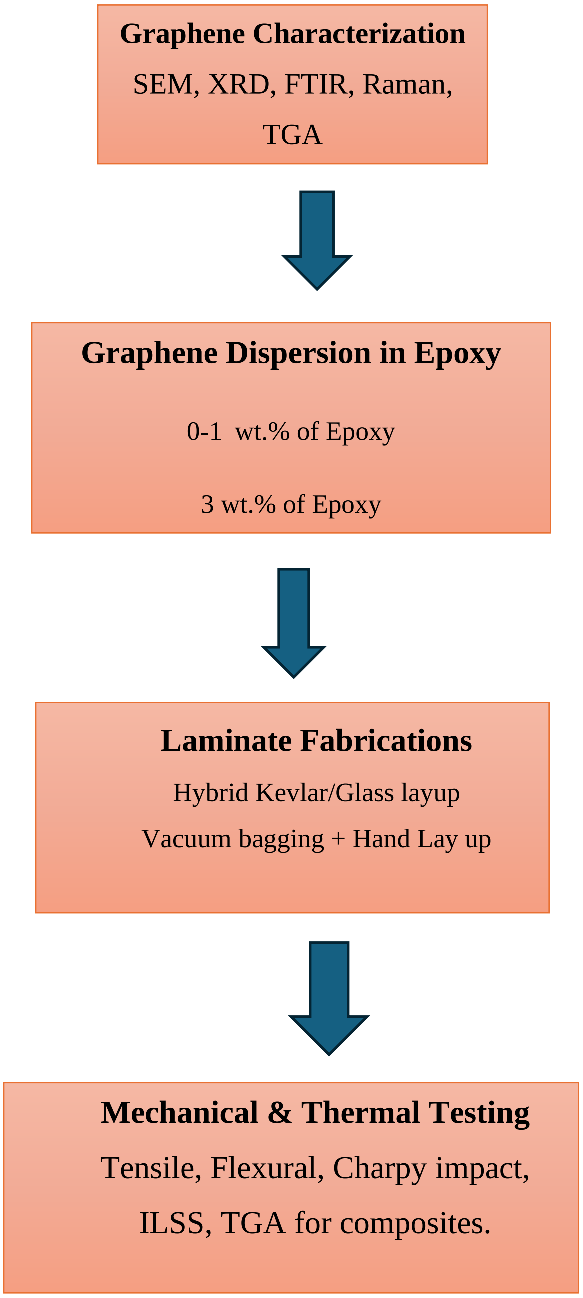
### 3.4.1 Materials

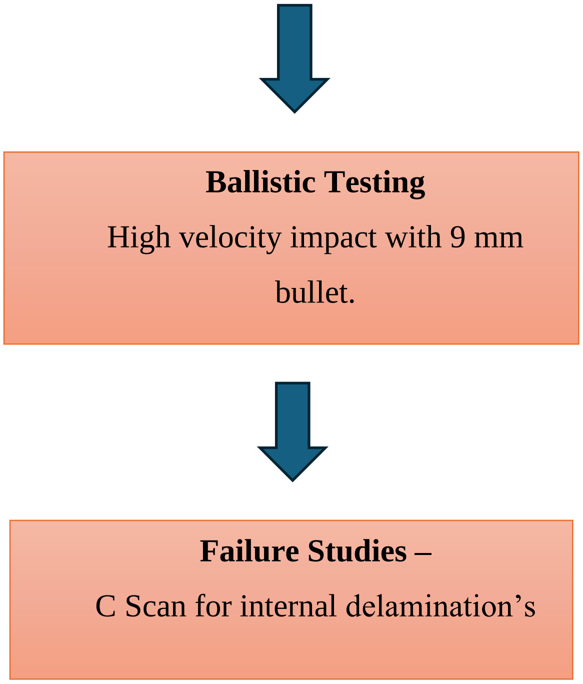
| Component | Specification | Supplier | Purpose |
|---|---|---|---|
| Graphene nanoplatelets | 3–8 nm thick, 5 µm lateral, purity > 99 % | Ad-Nano, IN | Nano-reinforcement |
| Kevlar® 29 plain-weave | 200 g $m^{-2}$ | DuPont | Ballistic fiber |

| | | | |
|---|---|---|---|
| E-Glass plain-weave | 200 g $m^{-2}$ | Carbon black Composites Pvt Ltd. | Stiffness fiber |
| Epoxy resin | Araldite LY 556 + HY951(10:1) | Huntsman | Matrix |

### 3.4.2 Process Flow Chart

The following flow chart shown below outlines the methodology and steps of the research conducted in this work.





## 3.4 Hypothesis

It is hypothesized that the optimal incorporation level of graphene nanoplatelets at 1.0 wt.% should enhance all mechanical performance measures and impact strength as well as thermal properties through improved load transfer capabilities and better crack-bridging mechanisms in hybrid Kevlar/glass fiber epoxy composites. The ballistic resistance of these composites should improve with rising graphene content up to 3.0 wt.% weight percentage because this will decrease both back-face deformation and internal delamination. The addition of graphene beyond its optimal concentration leads to deterioration of properties through stress concentration and poor dispersion because of agglomeration.

## 3.5 Summary

The research will follow this systematic framework that begins with graphene characterization then moves to laminate fabrication and extends to multi-scale testing and ballistic evaluation and ends with statistical analysis to confirm the hypotheses and meet research goals.

# Chapter 4

# Mechanical, Thermal and Impact Characterization of Graphene Reinforced Kevlar/GFRP Hybrid Composites

## 4.1 Introduction

This chapter presents the experimental research on graphene-reinforced hybrid Kevlar/glass fiber epoxy composites on the effect of graphene on their mechanical properties as well as thermal behaviour and impact resistance. The first part of this chapter shows X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and Raman spectroscopy results to verify the structural quality and shape of graphene nanoplatelets. The fabricated composite laminates with different graphene levels undergo tensile testing and three-point bending and interlaminar shear strength (ILSS) and ±45° in-plane shear and Charpy impact testing according to ASTM standards. Thermal behaviour assessment of the composites is conducted through thermogravimetric analysis (TGA) to evaluate how graphene affects their thermal stability.

## 4.2 Material and Methods

### 4.2.1 Materials used

The hybrid composite laminates consisted of plain-weave Kevlar® fabric and E-glass fibre as reinforcements together with a diglycidyl ether of bisphenol-A (DGEBA)-based epoxy resin system as the matrix. The researchers employed GNPs as nanofillers to improve both mechanical characteristics and ballistic properties of their composites. The epoxy matrix received GNPs at different weight ratios starting from 0.1% up to 1.0% for mechanical testing and extending to 3.0% for ballistic testing. The details of the resin and graphene used are enlisted below.

**Table 3: Graphene (ADG-X) Composite Grade Specification.**

| Property | Details |
|---|---|
| **Product Name** | Graphene X (ADG-X) |
| **Type** | Few-Layer Graphene, Composite Grade |
| **Purity** | > 99% |

| | |
|---|---|
| **Particle Size (D50)** | < 20 µm |
| **Thickness** | 5–10 nm |
| **Bulk Density** | ~0.11 g/cm³ |
| **Surface Area** | ~70–120 m²/g |
| **Form** | Powder |
| **Color** | Black |
| **CAS Number** | 1034343-98-0 |
| **Applications** | Composites, automotive parts, electronics, thermoplastics, thermosets |

**Table 4: Epoxy Resin and Hardener Details**

| Property | Details |
|---|---|
| Resin Type | Epoxy (Bisphenol-A type) |
| Resin Name | Araldite LY556 |
| Hardener Name | HY951 |
| Mixing Ratio (Resin: Hardener) | 100:10 |
| Viscosity (at 25°C) | 12–20 Pa·s |
| Pot Life | 45–60 minutes |
| Curing Schedule | 30°C for 24 h → 120°C for 2 h → post-cure at 150°C for 1 h |

### 4.2.2 Graphene Dispersion and Resin Preparation

The dispersion of graphene was carried out in two stages namely:

**Stage 1 - Preparation of graphene suspension:** A mixture of ethanol and Triton X-100 served as solvent to break down agglomerates in graphene nanoplatelets. The suspension underwent magnetic stirring at 500–700 rpm for 30 minutes. A Branson ultrasonic bath operated for 180 minutes exposed the mixture to ultrasonic treatment which produced better exfoliation and uniformity results. Figure 10 shows the steps of preparing graphene suspension.

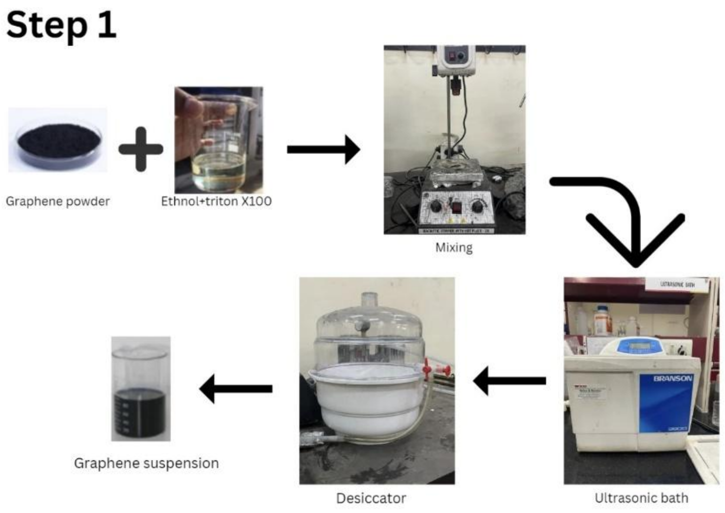


**Figure 10: Dispersion of graphene in ethanol–Triton X-100 using magnetic stirring and ultrasonication.**

**Step 2 – Mixing of graphene suspension in epoxy resin:** The prepared graphene suspension were then dropwise using plastic dropper into LY556 epoxy resin under mechanical stirring for achieving homogeneity. A desiccator received the mixture after complete mixing to extract trapped air bubbles. The mixture reached uniform consistency after which the hardener could be added for composite manufacturing. Figure 11 shows the step 2 of this method.

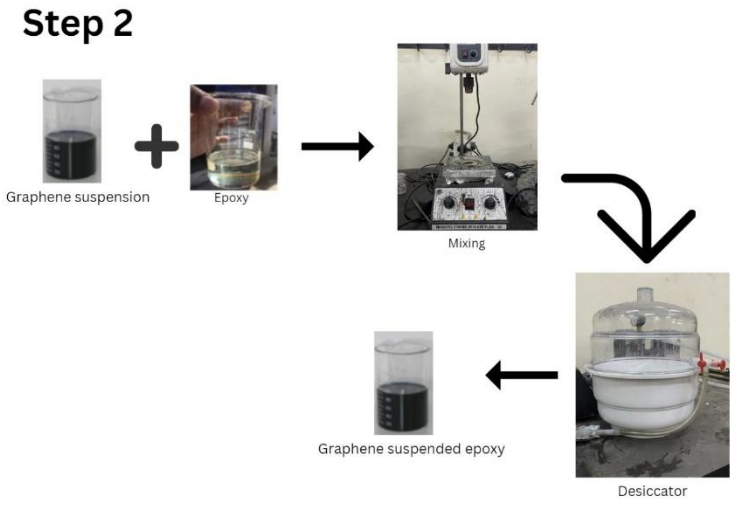


**Figure 11: Mixing of graphene suspension in epoxy with desiccation.**

### 4.2.3 Preparation of Composite Laminates

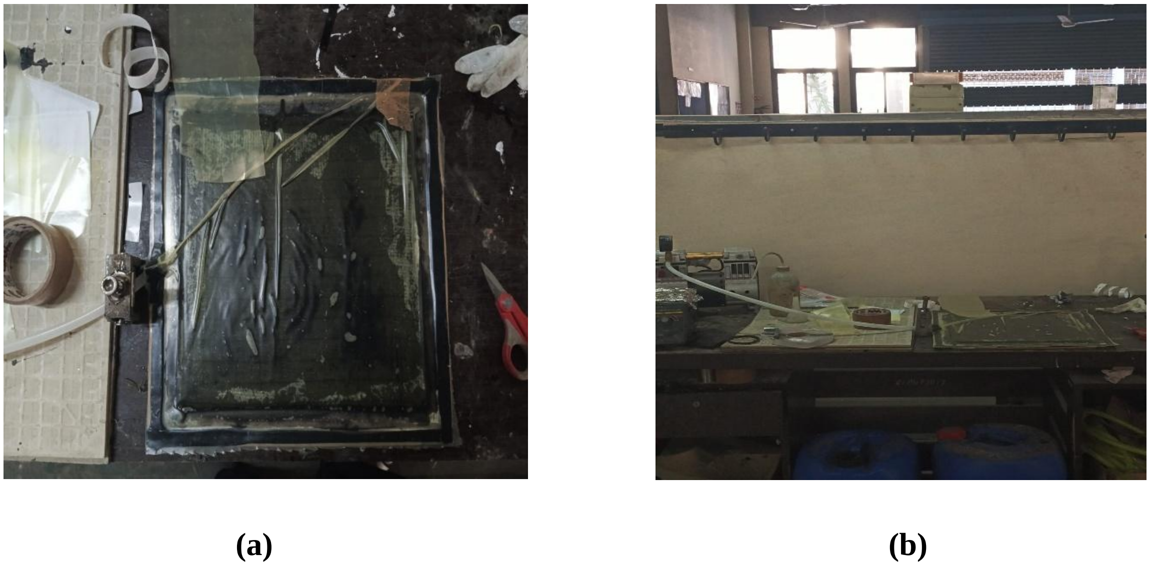
The hybrid Kevlar/GFRP composite laminates were fabricated using hand lay-up technique followed by vacuum bagging to achieve uniform resin impregnation and minimize void content. A mixture of graphene and epoxy obtained through ultrasonic dispersion served as the matrix material.

Each composite laminate consists of the layers of Kevlar fiber and GFRP in this specific order: The laminate starts with four Kevlar layers as its base followed by three E-glass layers and then two Kevlar layers, one E-glass layer, and finishes with three Kevlar layers on top.

The hand lay-up process required fabric layers to be placed on thick glass plates after applying a release agent coating. A roller was then applied to the graphene-reinforced epoxy material with uniform distribution between all laminate layers. A vacuum bag sealed the fabric stack which contained peel ply and mesh on top of the fabric layers. The assembly underwent vacuum pressure of 0.6 bar through a vacuum pump connection to remove air and achieve laminate consolidation. The vacuum setup shown in Figure 12 while Figure 13 displays the schematic of the lay-up system.

A 24-hour room temperature cure followed vacuum consolidation before the laminates underwent a post-curing process at 80°C for 2 hours and 120°C for 2 hours and 150°C for 1 hour to achieve full crosslinking. The laminates were then cut into necessary specimen dimensions through a water-jet cutter before performing mechanical, thermal, and impact tests. The final laminates weighed approximately 200 grammes while their thickness remained between 3-4 mm.

Figure 12: Schematic of vacuum assisted hand layup process.


(a) (b)

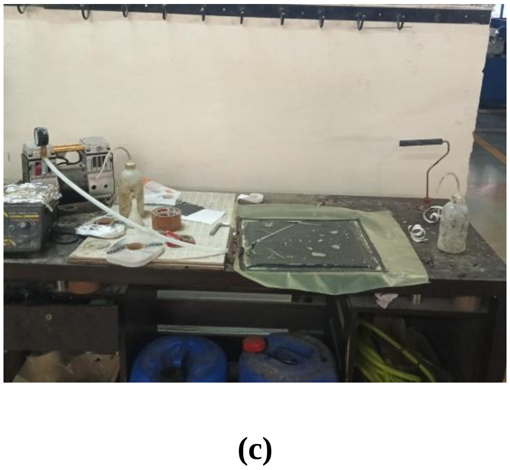

(c)

Figure 13: Prepared graphene reinforced composite laminates.

### 4.2.4 Synthesis of Acquired Graphene

Graphene acquired for this work were synthesized using XRD, FTIR, Raman Spectroscopy and SEM.

### 4.2.5 Mechanical and Thermal Characterizations

The following mechanical tests were conducted according to the relevant ASTM standards with the measured properties as shown below. Thermogravimetric analysis (TGA) was used to perform the thermal analysis of the composite samples.

**Table 5; Mechanical tests performed on Laminates**

| Test | Standard | Crosshead Speed | No. of Samples | Parameters Measured |
|---|---|---|---|---|
| Tensile Strength and Modulus | ASTM D3039 | 1 mm/min | 5 | Tensile strength, tensile modulus, strain at break |
| Flexural Test (3-Point) | ASTM D790 | 1.5 mm/min | 5 | Flexural strength, flexural modulus |
| Interlaminar Shear Strength | ASTM D2344 | 1 mm/min | 5 | Short-beam shear strength (ILSS) |
| In-Plane Shear Test (±45°) | ASTM D7078 | 1 mm/min | 5 | Shear strength, shear strain, shear modulus |
| Charpy Impact Test | ASTM D6110 | Impact pendulum | 5 | Impact energy absorbed |

## 4.3 Results and Discussions

### 4.3.1 Graphene Synthesis

XRD, FTIR, SEM, and Raman spectroscopy to study graphene morphology and crystallinity and functional groups and thermal stability before composite laminate reinforcement. The analysis confirmed the reinforcement quality of the graphene material.

#### 4.3.1.1 XRD

Figure 14 shows a typical XRD curve obtained for acquired graphene powder. The XRD pattern of synthesized graphene nanoplatelets displayed a strong peak at 26° (2θ) which indicated the (002) plane of graphitic carbon. The peak's narrow width together with its high intensity demonstrates both excellent crystallinity and proper layer stacking in graphene. The XRD pattern reveals the material's high purity and low structural defects which make it suitable for composite reinforcement.

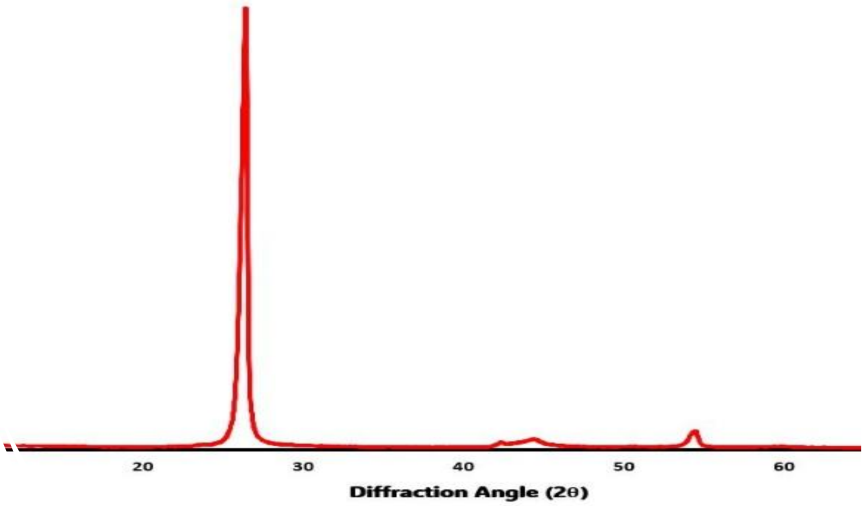


**Figure 14: XRD of Graphene ADG-X composite grade.**

#### 4.3.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

The surface composition of graphene was analyzed by FTIR which showed distinctive absorption peaks:

- The spectrum shows a wide peak at 3430 cm$^{-1}$ which indicates hydroxyl (–OH) groups exist in small amounts.
- The peaks at 2922 cm$^{-1}$ and 2852 cm$^{-1}$ indicate very small amounts of organic solvent residues or hydrocarbons attached to the graphene surface.
- The FTIR spectrum showed a peak at 1630 cm$^{-1}$ which was assigned to either C=C stretching or carbonyl-related functional groups. The peak at 1384 cm$^{-1}$ indicates slight oxidation through epoxide or carboxylic groups.

The FTIR spectrum analysis confirms the existence of pure few-layer graphene with low oxidation levels and high quality.

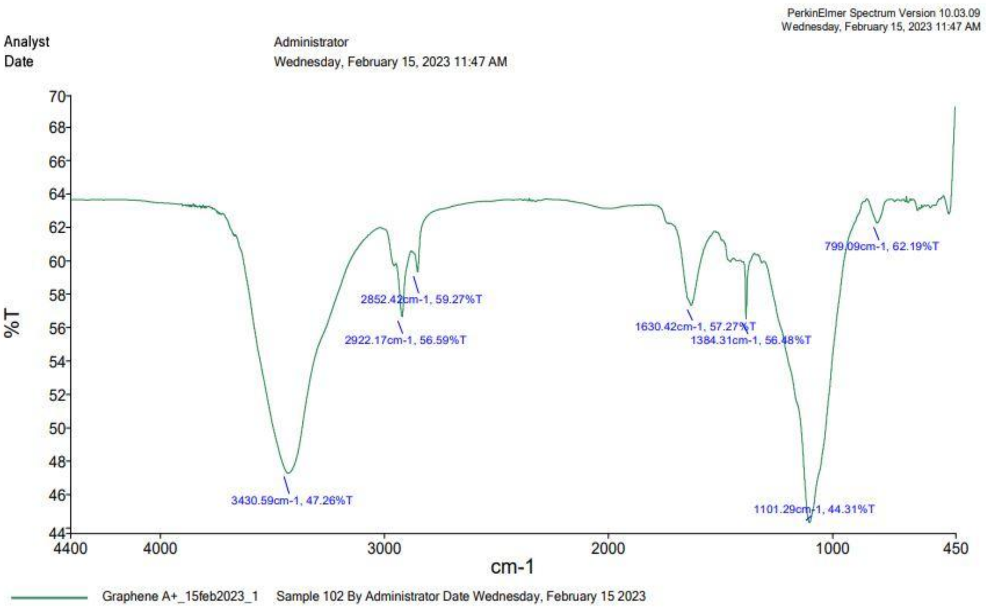


**Figure 15: FTIR of graphene ADG-X.**

### 4.3.1.3 Raman Spectroscopy

Raman spectroscopy confirmed both the multilayer nature of graphene and its structural quality through analysis. Three main bands appeared in the spectrum.

- The D band at ~1350 $cm^{-1}$ indicates structural disorder in the material.
- The Raman spectrum revealed two main bands at 1580 $cm^{-1}$ which represents in-plane vibrations of $sp^2$ carbon atoms.
- The broad asymmetrical 2D band at ~2700 $cm^{-1}$ proved the existence of few-layer graphene.
- The intensity ratio (I_D/I_G) indicated a moderate defect level that commonly occurs in functionalized or partially reduced graphene nanoplatelets thus improving composite interfacial bonding.

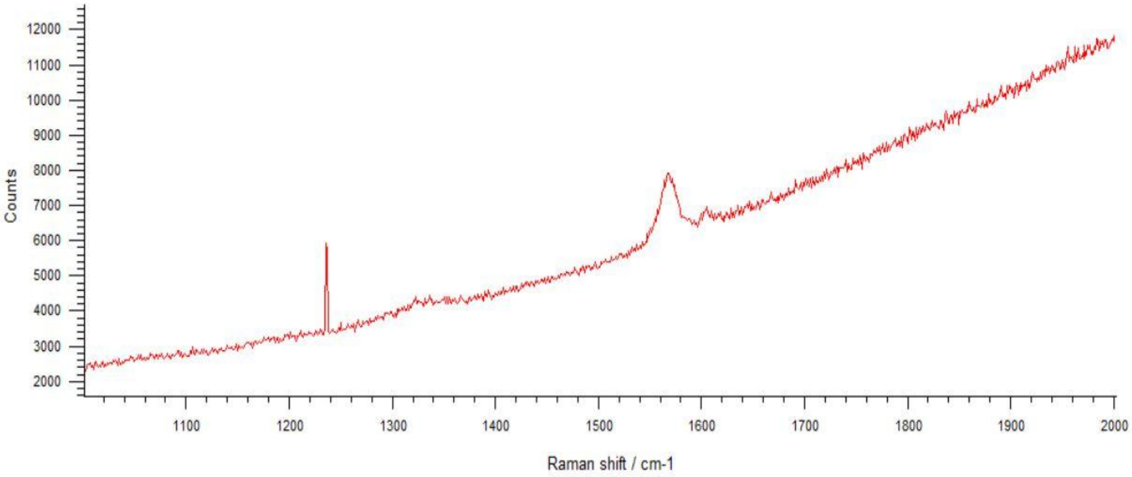
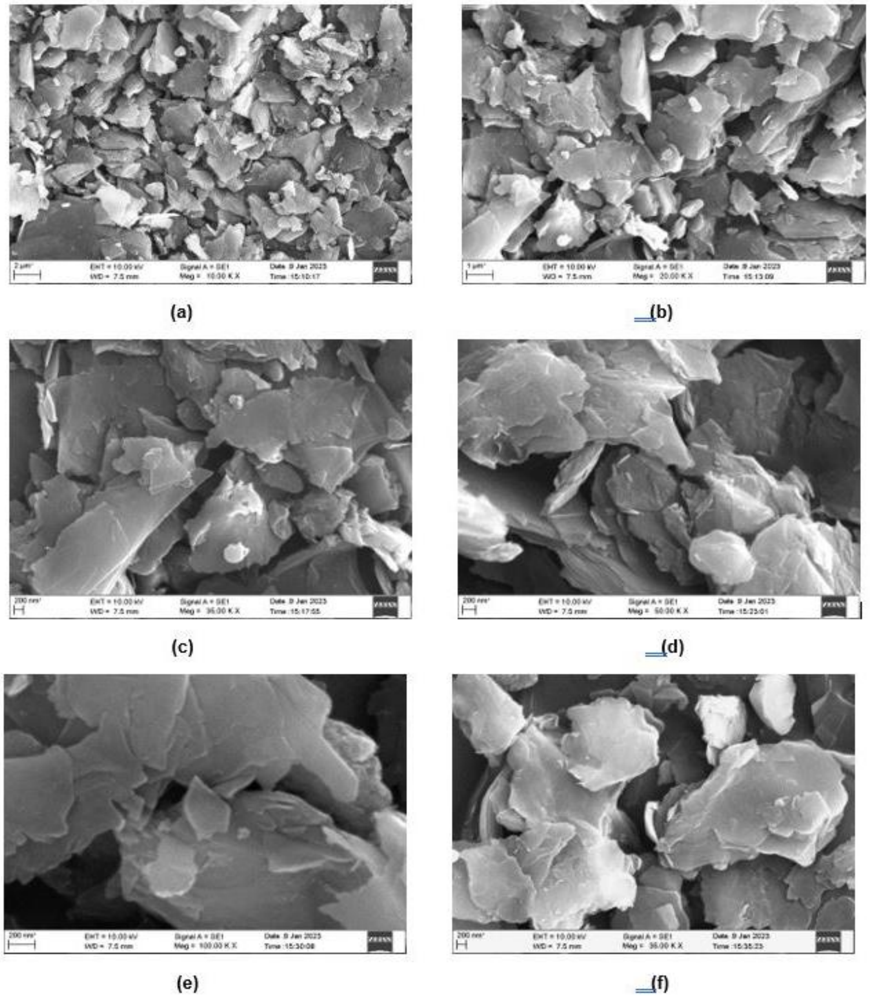


**Figure 16: Raman Spectroscopy curve of Graphene ADG-X.**

#### 4.3.1.4 SEM Analysis

The SEM images displayed graphene structures that were thin and wrinkled and had micrometre-scale dimensions and nanometer-scale thicknesses according to vendor data. Good exfoliation and lateral connectivity emerge from the surface morphology of the material because they enable better stress transfer when embedded in polymers. The dispersion technique used for preparing composites appears suitable because no significant agglomerates formed during this stage.



(a) (b)

(c) (d)

(e) (f)

Figure 17: SEM images of graphene.

### 4.3.2 Mechanical Characterization

The mechanical response of fabricated hybrid Kevlar/GFRP composite laminates containing different weights of graphene nanoplatelets (0%, 0.1%, 0.25%, 0.5%, and 1.0%) is discussed in this section. The experimental tests were conducted as per ASTM standards for strength and stiffness measurements.

#### 4.3.2.1 Tensile Tests

The tensile tests were conducted as per ASTM D3039. Each tensile curve of graphene composition demonstrated that graphene incorporation substantially impacted the tensile strength and modulus values. The tensile strength of the composite containing 0.25 wt.% graphene achieved the maximum improvement by reaching 22% above the base sample. The tensile performance showed a minor decrease at 1.0 wt.% because graphene particles might be aggregating. The enhanced tensile properties at low graphene concentrations result from enhanced load transfer mechanisms and effective crack-bridging capabilities alongside decreased brittle matrix behaviour.

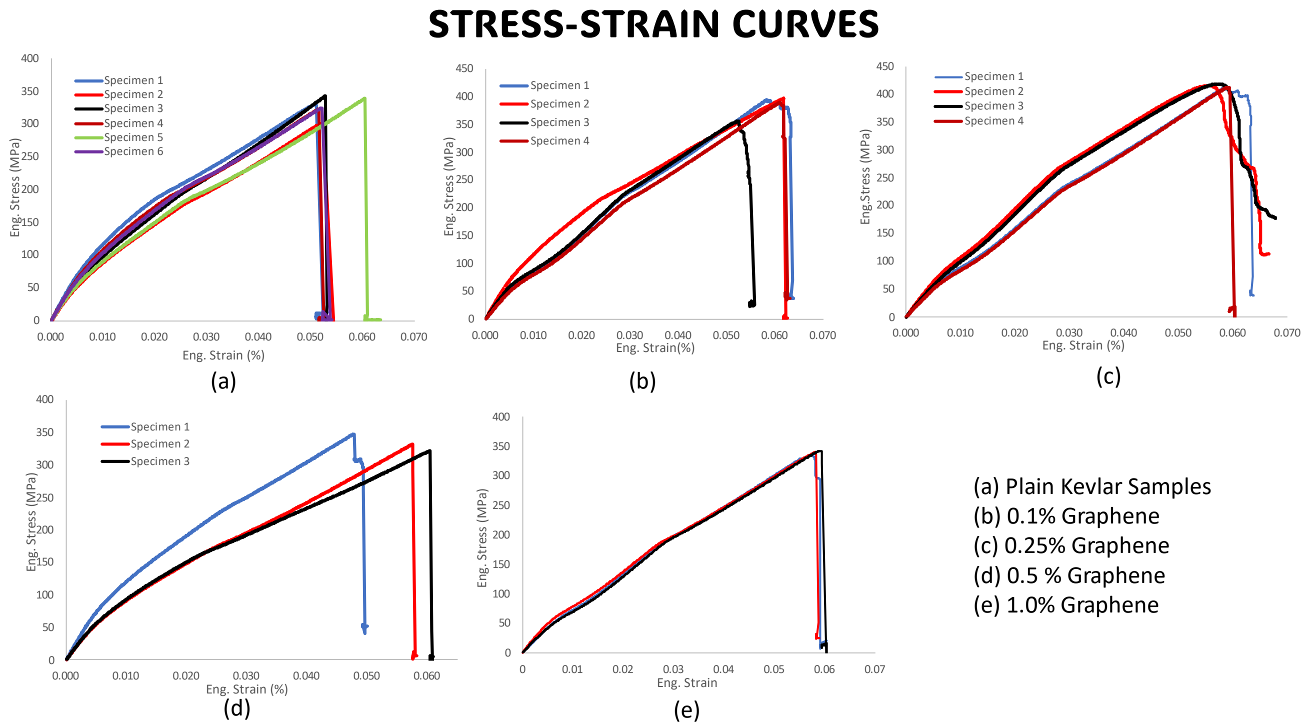


**Figure 18: Tensile stress-strain curves at different graphene ratios.**

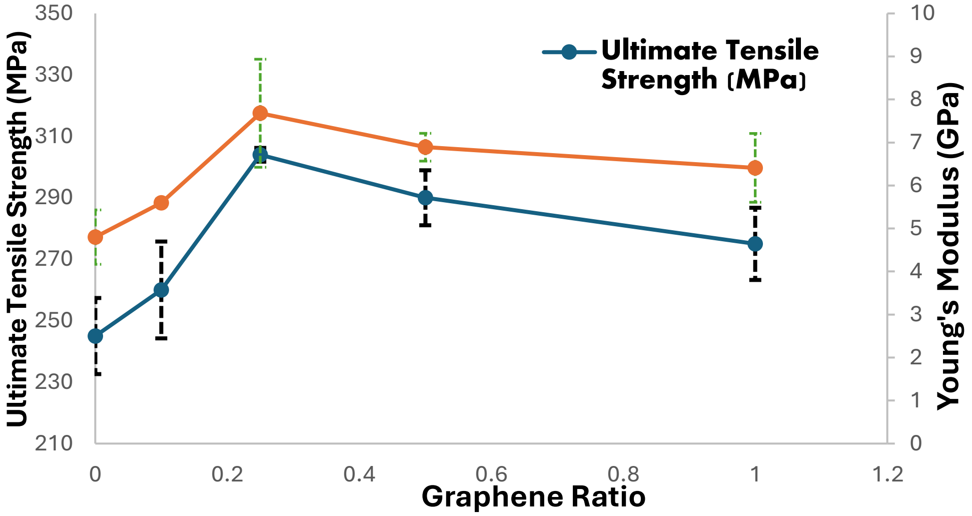
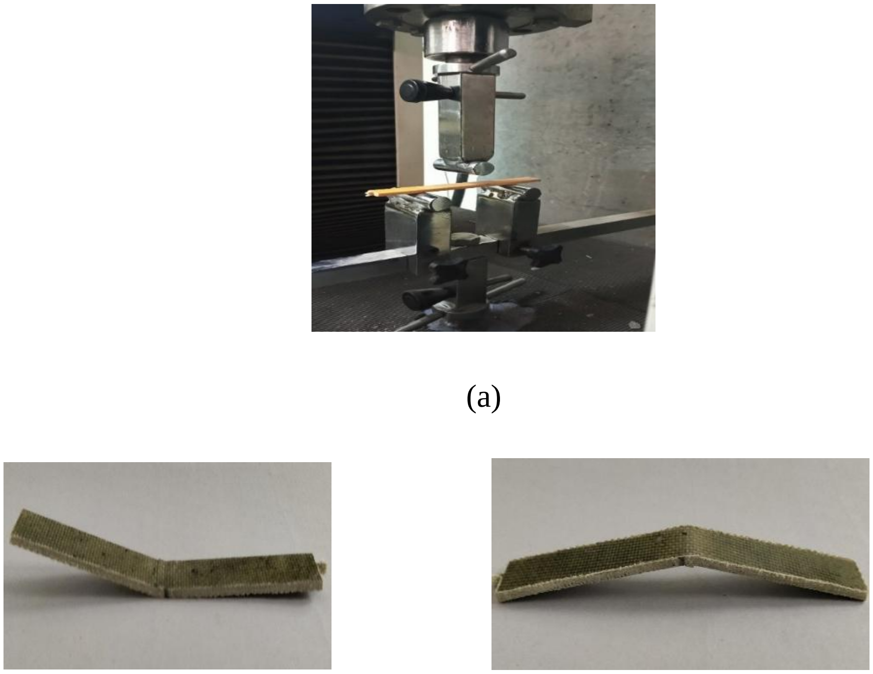


**Figure 19: Variation of Elastic Modulus and Tensile modulus with different graphene ratios.**

#### 4.3.2.2 Flexural and ILSS Tests

The flexural testing followed the protocols of ASTM D790. The incorporation of graphene improved the flexural strength and stiffness values of the composites. The flexural strength reached its peak value of ~28% in the composite that contained 0.5 wt.% graphene compared to the control sample (Figure 21(a)). The high aspect ratio and planar orientation of graphene are thought to enhance bending load stress distribution. The interfacial bonding strength between fibre and matrix improved when graphene was added according to ILSS testing (ASTM D2344). The 0.25 wt.% graphene sample achieved the maximum ILSS value which resulted in a 20% increase (Figure 21(b). The strength remained steady or decreased slightly at loadings above 1.0 wt.% because of inadequate dispersion or stress concentration sites caused by graphene clusters. The load-elongation curves of Flexural Tests and ILSS tests are given in Appendix A.

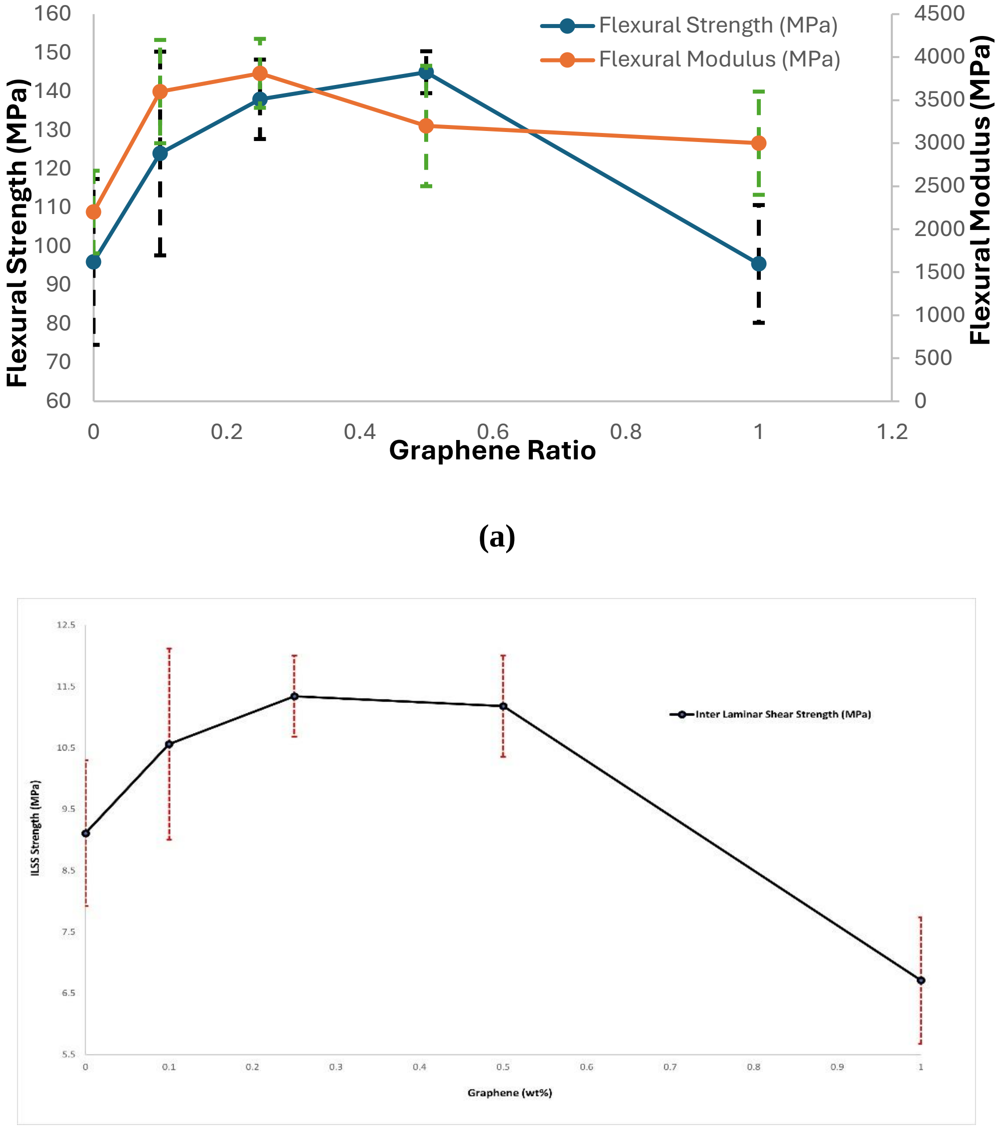


(a)

(b)

(c)

**Figure 20: Experimental pictures of flexural tests and failed samples (a-c).**



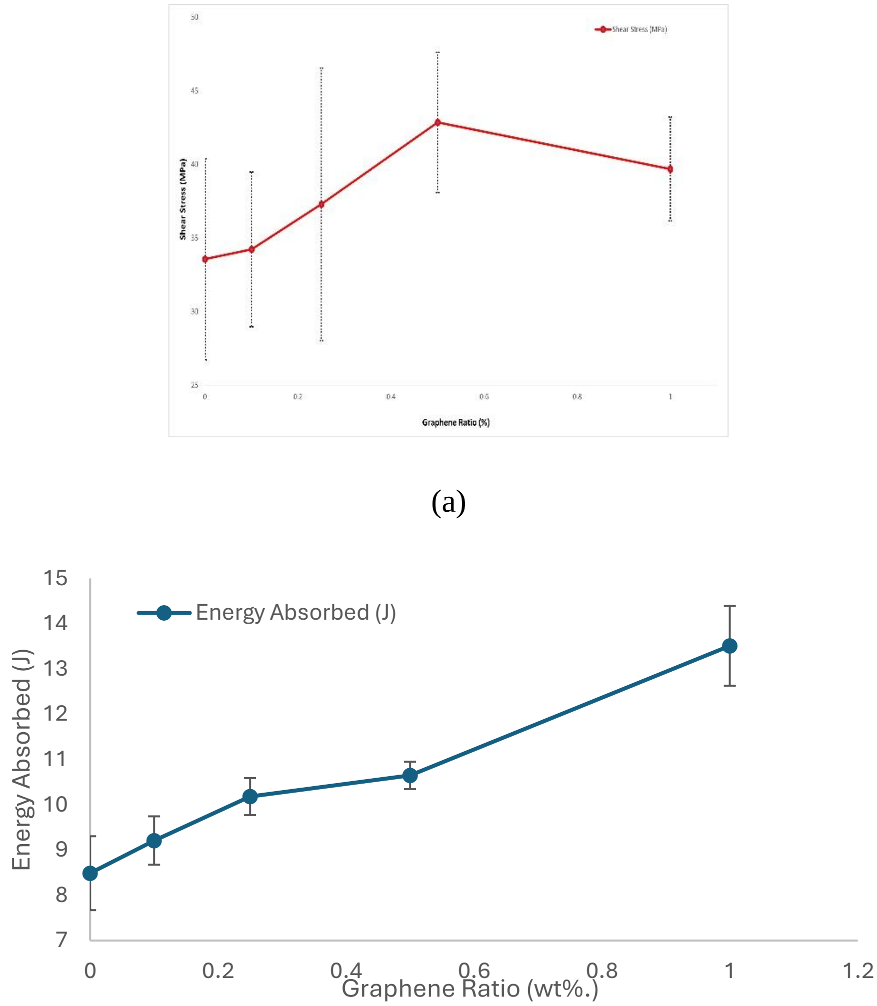
**(a)**

**(b)**

**Figure 21: Variation of (a) Flexural Tests and (b) ILSS Tests parameters with different graphene ratios.**

### 4.3.2.3 Shear and Charpy Impact Tests

The in-plane shear characteristics of the laminates was studied in accordance with ASTM D7078 . The laminates showed improved shear load capacity with delayed failure initiation because of the graphene incorporation. The samples with 0.25 wt.% and 0.5 wt.% demonstrated the best results by showing enhanced energy absorption until the failure point. Whereas the Charpy impact tests was based on ASTM D6110, which measured the impact resistance of the samples. The data from the tests (figure 22) reveals that energy absorption of the laminates increased steadily until reaching 1% graphene ratio. The plane sample absorbed 8.5 J of impact energy but the sample containing 1wt.% graphene reached 13.8 J.



(a)

(b)

**Figure 22: Variation of (a) Shear strength, (b) Energy absorbed in Charpy impact tests of composites.**

### 4.3.3 Thermal Gravimetric Analysis (TGA)

The thermal stability of Kevlar/GFRP composite laminates reinforced with graphene was investigated using Thermogravimetric Analysis (TGA). The weight loss data (%) and derivative weight data (%) are shown in in Figure 23 for plane and hybrid samples containing 0.1 wt.%, 0.25 wt.%, 0.5 wt.%, and 1.0 wt.% graphene.

Three separate degradation phases appear in TGA curves given as follows:

- ➢ The initial weight loss below 150°C results from both moisture evaporation and volatile substance removal.
- ➢ The second significant weight reduction happens between 300°C and 600°C because it represents both epoxy matrix decomposition and fibre breakdown initiation.
- ➢ Beyond 600°C the third degradation stage occurs because Kevlar backbone breaks down and carbon residues stabilize.

The Figure 23 demonstrates that graphene-reinforced samples experience delayed degradation onset temperatures and demonstrate reduced total weight loss than the plain Kevlar control. The thermal stability of the 1.0 wt.% graphene composite reaches its maximum level because degradation begins later by ~25–30°C and produces more char residue at 800–900°C. The barrier function of graphene nanoplatelets creates two benefits: they slow down degradation product diffusion and help produce more char material. The derivative TGA (DTG) curves demonstrate that higher temperatures characterise the degradation peak shift as graphene content increases in the composites due to enhanced thermal resistance.

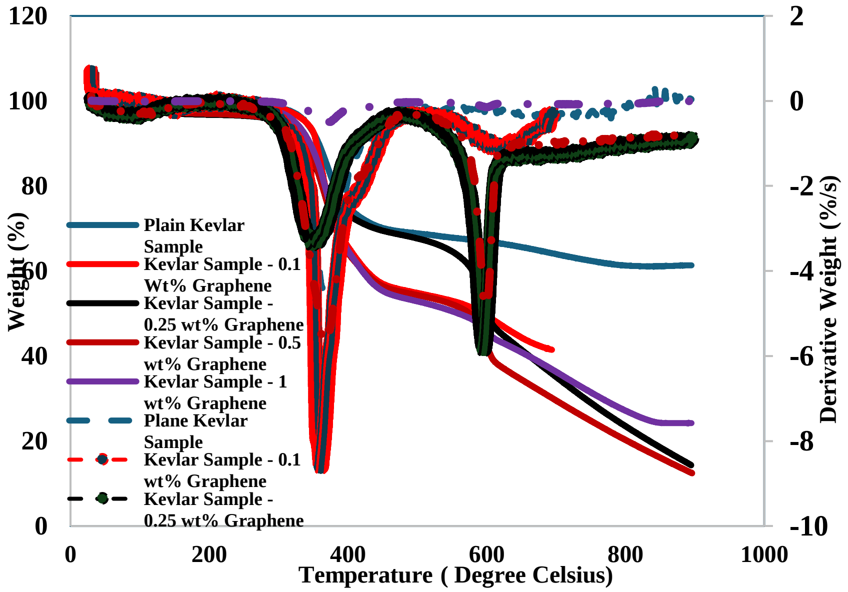


Figure 23: TGA of Kevlar/GFRP composites.

# Chapter 5

## Ballistic Testing of Graphene Reinforced Kevlar/GFRP Composites

### 5.1 Introduction

The defence and vehicular armour systems depend heavily on ballistic protection as an essential performance criterion for composites. Unlike static mechanical tests, ballistics tests involve high velocity projectiles of different shapes and sizes, that induces localized damage with delamination, matrix cracking and shear plugging. Gaining deep knowledge of advanced hybrid composite performance in extreme conditions enables better optimization of their structural designs and material configurations.

This chapter presents the evaluation of ballistic performance of the fabricated graphene reinforced Kevlar/GFRP hybrid composites. Composite panels with different graphene wt.% percentages ( 0-3%) were tested ballistically at Defense Metallurgical Research Laboratory (DMRL), Hyderabad using 9 mm Fully Metal Jacket Bullet (FMJ) Key ballistic parameters such as energy absorption, ballistic limit ($V_{50}$), and post impact analysis using C-Scan, compared and presented. The objective of this work is to assess the effect of graphene addition on ballistic resistance of composite laminates and to identify the most optimum graphene concentration for maximum energy absorption and structural integrity.

### 5.2 Ballistic Test-Setup and Procedure

The ballistic evaluation of graphene reinforced hybrid Kevlar/GFRP composites was done using a high velocity impact testing setup at DMRL, DRDO. Testing of these materials occurred as per guidelines specified by NIJ standard 0108.01 using 9 mm FMJ bullet at a velocity of 440 m/s.

#### 5.2.1 Projectile and Firing Conditions

Ballistic tests were performed using 9 mm FMJ bullet with a nominal projectile mass of 7.44 gms and a muzzle velocity of 440 m/s, The test frame supported the composite materials through rigid clamps and the shots were fired from 5 meters away at $0^0$ angle to achieve a perfect normal impact condition. All the ballistics tests were performed at an ambient room temperature. One of such schematic of ballistic setups are shown in figure 24 below.

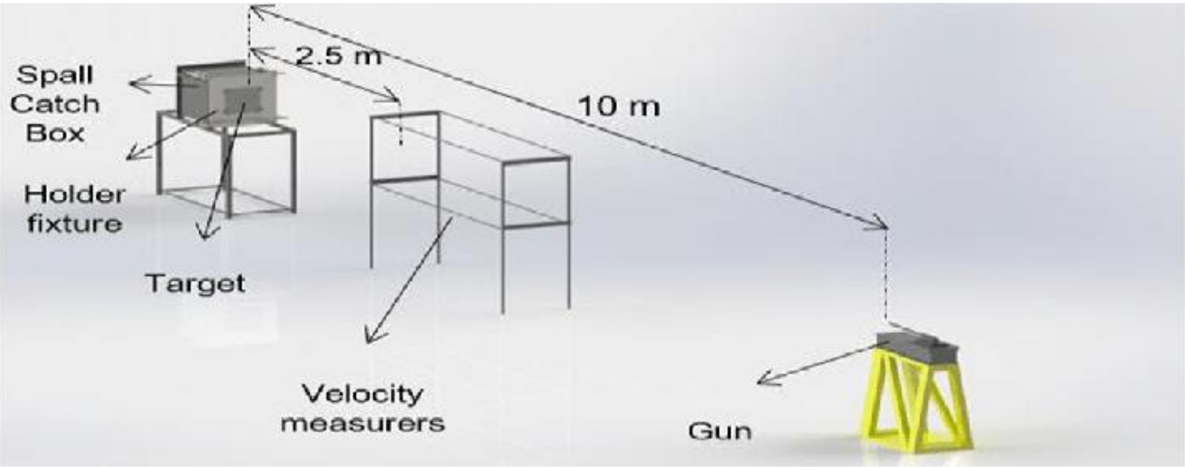


**Figure 24: Typical schematic of a ballistic setup** *[62]*.

### 5.2.2 Composite Panel Configuration

Each composite laminate tested for ballistic loads were integrated by combining Kevlar and E-glass fibers embedded in epoxy matrix system. The configuration has been carefully optimized to improve and maximize the energy absorption, and delay through thickness failure during ballistic impact.

The laminate contained the following layered sequence:

- The bottom section consists of six Kevlar fabric layers with 0.4 mm thickness each (400 GSM) which serves to absorb initial impacts and disperse energy.
- The laminate contains three intermediate E-glass fibre (GFRP) layers (200 GSM) which measure 0.2 mm in thickness to enhance structural stiffness and distribute loads after impact occurs.
- The core layers consist of two Kevlar fabric sheets with reduced thickness (0.25 mm) which serve as impact wave absorbers. Two layers of E-glass fibre (0.2 mm thick) serve as upper reinforcement by deflecting cracks and bridging failures that occur across the mid-thickness of the material.

- The top strike face consists of four Kevlar fabric layers with 0.4 mm thickness which provides superior resistance against projectile entry and stronger delamination resistance.

The composite panel consisted of 17 individual fabric layers, leading to a total laminate thickness of about 6.65 mm, which varied based on the compaction achieved during vacuum-assisted curing. The epoxy matrix utilized for impregnation comprised a graphene-reinforced LY556/HY951 system, with the graphene content varying from 0 to 3.0 wt.% in the various samples evaluated.

## 5.3 Results and Discussions

The DMRL under DRDO performed ballistic impact tests on hybrid Kevlar/GFRP composite plates reinforced with graphene at different weight percentages ranging from 0 to 3.0 wt.%. The tests used 7.44 g 9 mm full metal jacket (FMJ) projectiles to measure inlet velocity and outlet/residual velocity and energy absorption. The testing samples underwent identical manufacturing procedures while receiving identical vacuum-assisted curing treatment to maintain uniformity. The difference between inlet and outlet velocities served to determine the kinetic energy absorption for each panel.

The ballistic performance showed an irregular pattern with the increase in graphene concentration levels. The composite panel containing 0.75 wt.% graphene achieved the maximum energy absorption of 165 J which exceeded all other tested specimens. The energy absorption rate rose progressively from 0 wt.% to 0.75 wt.% graphene before decreasing slightly at 1.0 wt.% then increased again at 3.0 wt.% graphene. The observed trend indicates an optimal reinforcement threshold where graphene agglomeration and poor dispersion start to diminish the energy dissipation mechanisms including fibre pull-out and delamination resistance and matrix toughening. Figure 24 presents the energy absorption variation as a function of graphene content. The composite material with 0.75 wt.% graphene achieved maximum energy absorption which confirmed the existence of an optimal nanoparticle concentration for ballistic resistance.

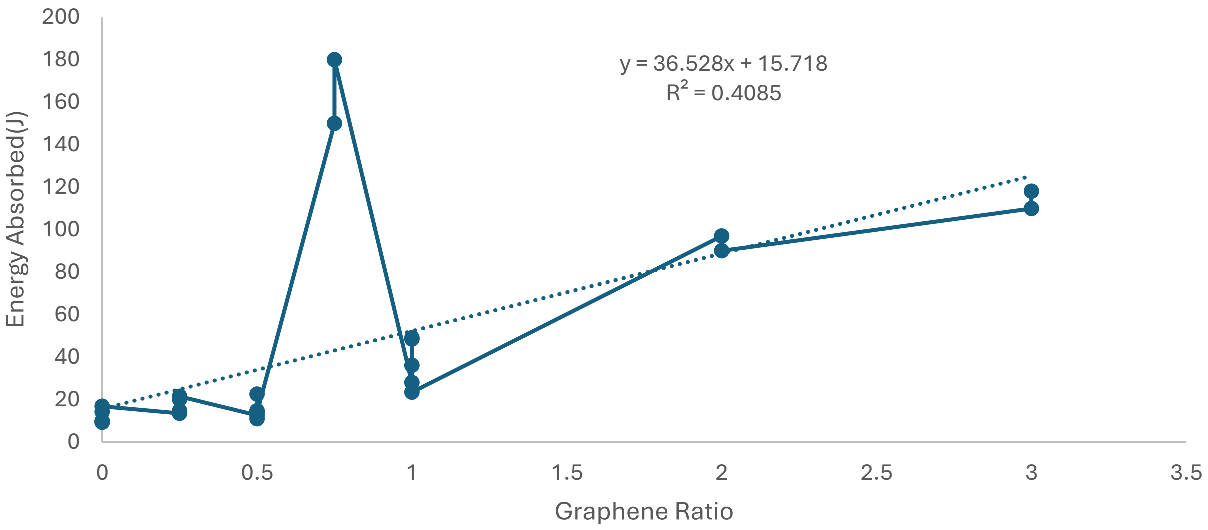
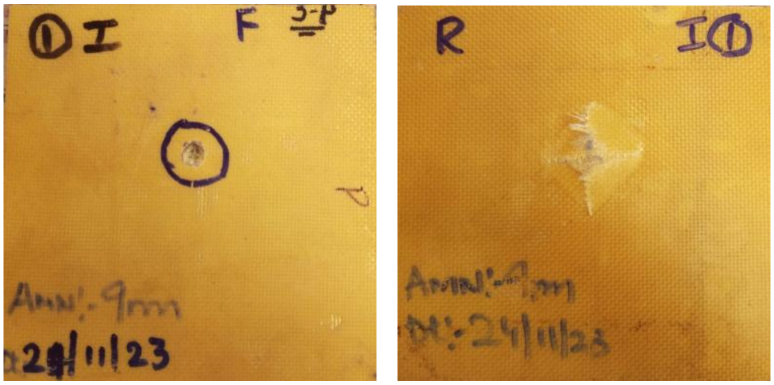


**Figure 25: Energy absorption of composite laminates at different graphene ratios.**

Visual examination of the failed specimens showed major distinctions between the front and rear surface damage patterns. The plain Kevlar/GFRP samples (0 wt.%) demonstrated extensive damage through large entry holes and extensive fibre rupture zones and extensive back-face deformation because of their poor energy absorption and fast through-thickness crack propagation. The panels with graphene reinforcement displayed entry damage that remained confined to a specific area while maintaining better fibre–matrix bonding. The damage zones at 0.75 wt.% graphene showed more confined characteristics because graphene nanoplatelets with good dispersion enabled both stress redistribution and crack arrest through their crack-bridging and deflection capabilities. Few of the failed samples are shown in Figure 26(a-c).

SAMPLE 5– PLANE SAMPLE

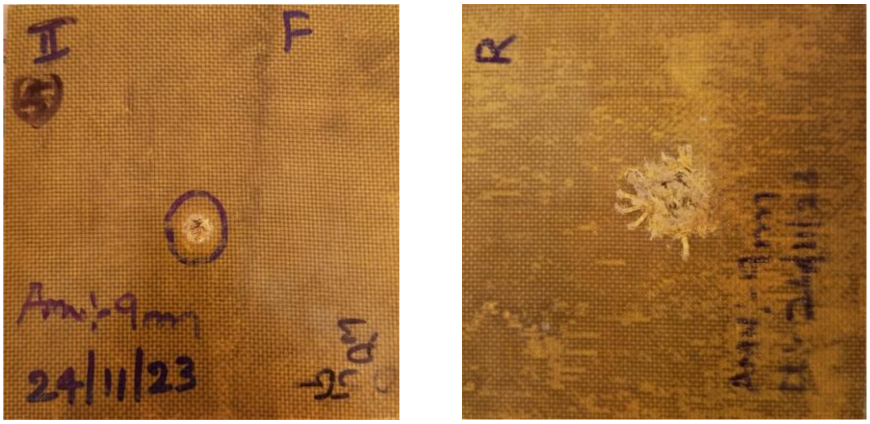


FRONT SIDE

REAR SIDE

(a)

SAMPLE NO 9– 0.25 % GRAPHENE



FRONT SIDE

REAR SIDE

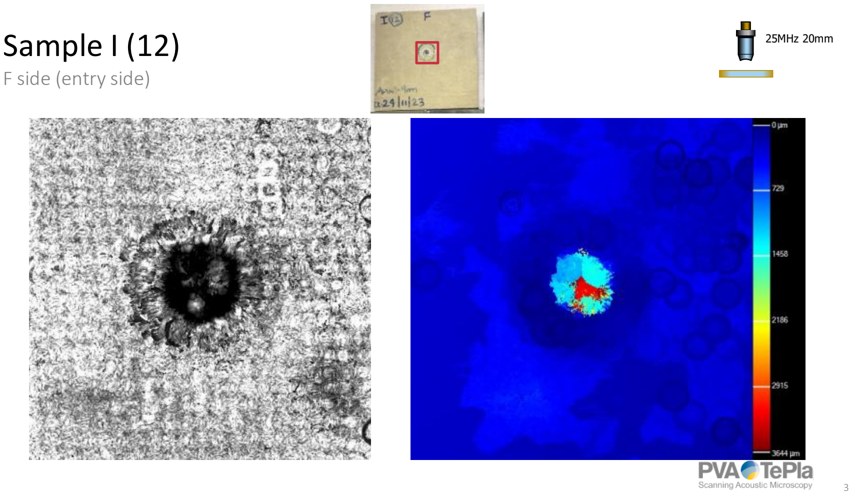
(b)

(c)

**Figure 26: (a-c) Failed samples of plane and graphene reinforced composite laminates.**

The Ultrasonic C-scan and thermography were also conducted on few of the failed samples. The panels containing optimal graphene concentrations exhibited reduced internal delamination zones while showing uniform crack propagation behaviour. The findings from these observations match the earlier presented mechanical and impact data to show that Kevlar-based hybrid composites gain improved ballistic resistance and toughness from moderate graphene incorporation. The results show that graphene provides exceptional reinforcement until it reaches a critical concentration of ~0.75 wt.% but processing issues related to agglomeration start to reduce its effectiveness. To further assess the damage inside the surface of the failed laminate, active infrared thermographic analysis was done after ballistic test. The experimental system used thermal modulation for stimulation while infrared imaging ran in synchronisation. The thermographic images revealed localised hotspots which indicated internal delamination and matrix cracking at the projectile entry points and deformation areas. The combination of temperature distribution plots with matched philtre processing enabled better contrast and depth-based visualisation of thermal anomalies. The correlation peak appeared within a damaged area where heat trapping occurred because of delaminated layers and air gaps. The 3D thermographic sequence showed damage progression through the thickness which matched C-scan results. The non-destructive method functions as an important supplemental detection tool to locate hidden damage which cannot be seen externally after impacts.

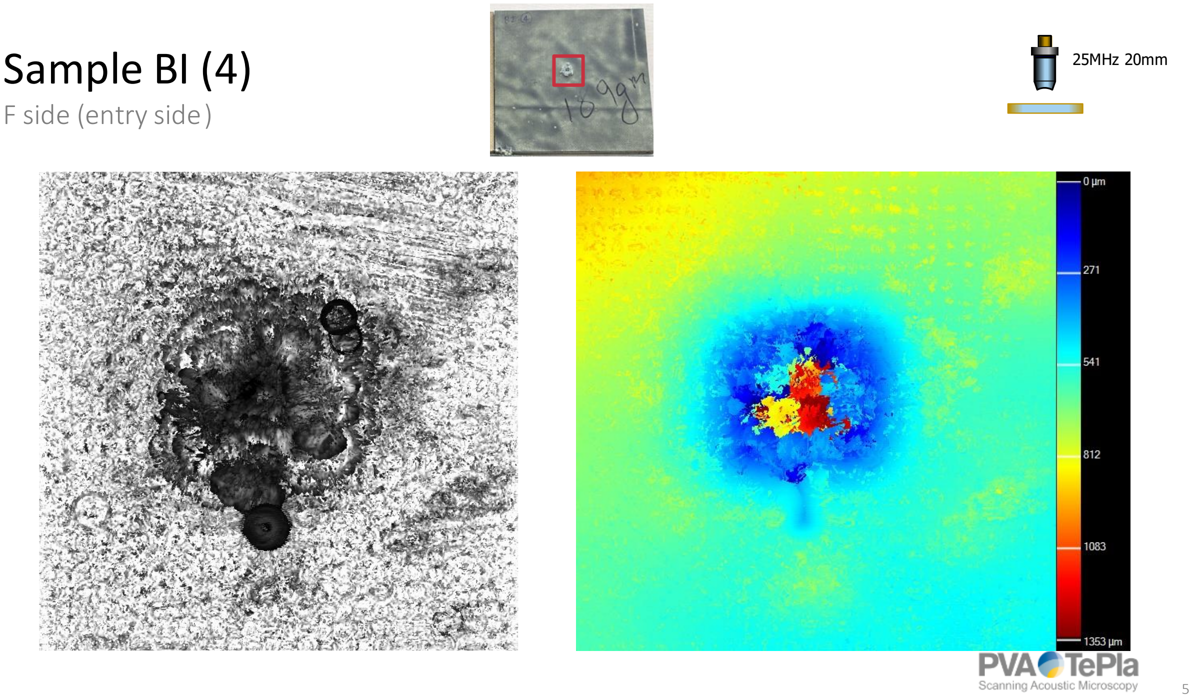
Some of the ultrasonic C scan images and thermographic analysis are shown in figure 27 (a-d).



Sample I (12)

F side (entry side)

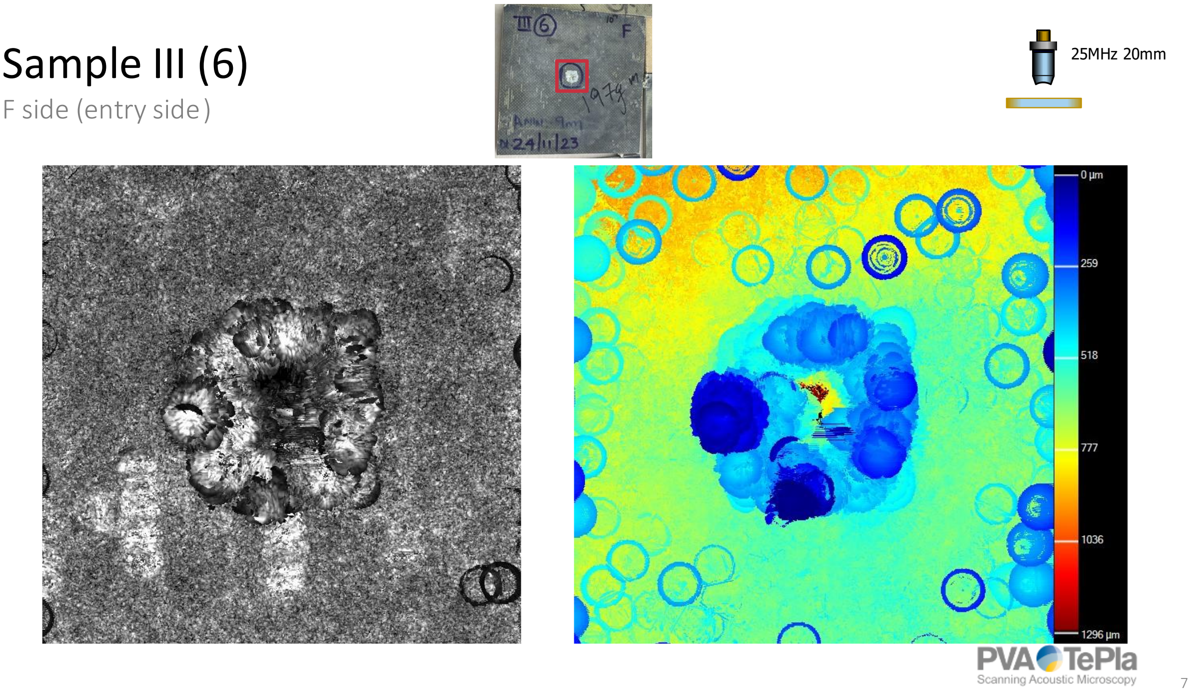
(a)



Sample BI (4)

F side (entry side)

(b)

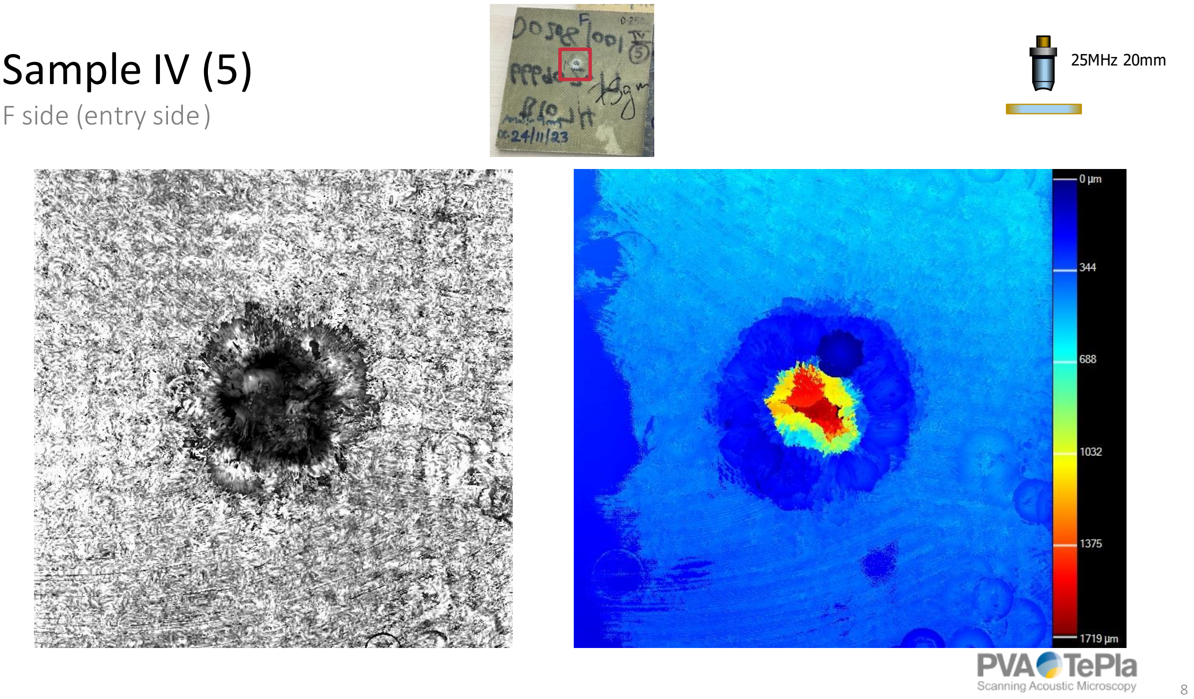


## Sample III (6)

F side (entry side)

25MHz 20mm

(c)

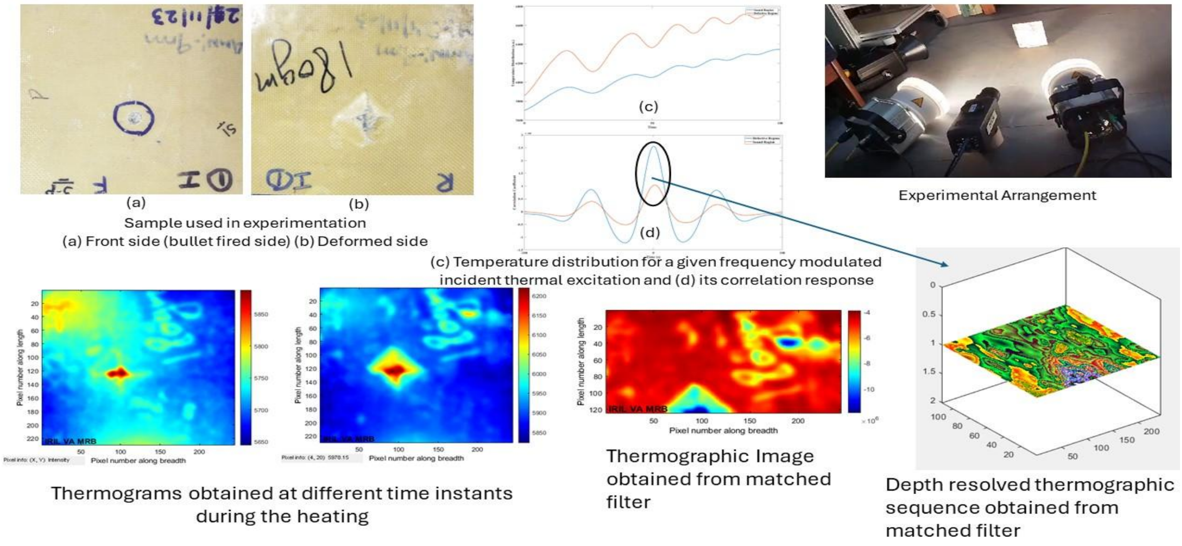


## Sample IV (5)

F side (entry side)

25MHz 20mm

(d)



(e)

**Figure 27: Few ultrasonic C-Scan Images (a-d) and (e) thermographic analysis of failed laminates in ballistic plates.**

# Chapter 6

# Results and Future Perspectives

## 6.1 Conclusions drawn from the study

Following conclusions were derived from these studies:

i. Addition of graphene nanoparticle to hybrid Kevlar/GFRP composites led to substantial improvements in mechanical properties as well as thermal behaviour and ballistic resistance. The compositions containing 0.25 wt.% to 0.75 wt.% graphene achieved the best performance results in every test conducted.

ii. Tensile strength and modulus were observed to improve with graphene addition, with a peak improvement of ~22% in tensile strength at 0.25 wt.% graphene. At this point the mechanical properties showed minor reductions because of suspected agglomeration phenomena.

iii. The combination of 0.5 wt.% and 0.25 wt.% graphene content produced the best results for bending stiffness and interfacial bonding strength in flexural and interlaminar shear strength (ILSS) tests because it enhanced stress transfer between matrix and fibre reinforcements.

iv. The Charpy impact strength of the composites showed continuous improvement with graphene addition reaching 13.8 J at 1.0 wt.% graphene while the control achieved 8.5 J indicating better sudden impact energy dissipation.

v. The addition of graphene in the composites enhanced their thermal stability according to results from thermogravimetric analysis (TGA). The thermal degradation onset point moved up by almost 30 degrees Celsius at 1.0 wt.% graphene because of the improved flame retardancy and thermal barrier properties of graphene.

vi. The ballistic performance tests demonstrated that graphene addition created a non-linear improvement pattern. The 0.75 wt.% graphene-reinforced composite exhibited maximum energy absorption of ~165 J, confirming it as the most effective configuration for high-velocity impact resistance.

vii. The damage zones from ultrasonic C-scan analysis became more localised and delamination decreased in graphene-reinforced samples particularly when using 0.75 wt.%, which validated the proposed crack-bridging mechanisms.

Overall, the above research study establishes the enhancement in different properties of composites by reinforcing graphene in epoxy matrix systems and identifies an optimal range for graphene wt.% that balance performance and limiting the dispersion.

## 6.2 Future Directions

i. Future investigation in the development of graphene reinforced composites should focus on the study of carboxyl and amine functionalized graphene to improve the epoxy matrix interfacial adhesion while dispersing such materials over 1.0 weight percent therein.
ii. The production process should optimize fabrication techniques particularly resin transfer moulding (RTM) and vacuum-assisted resin infusion (VARI) to achieve large-scale manufacturing with uniform graphene dispersion suitable for industrial applications.
iii. More Mult hitting ballistics tests should be conducted to evaluate long-term durability against repeated impacts.
iv. A detailed finite element modelling (FEM) analysis of ballistics using verified experimental data should be researched to predict ballistic performance and simulate damage progression under different velocity, thereby enabling designers enabling designers to build predictive personal protection equipment for military applications.

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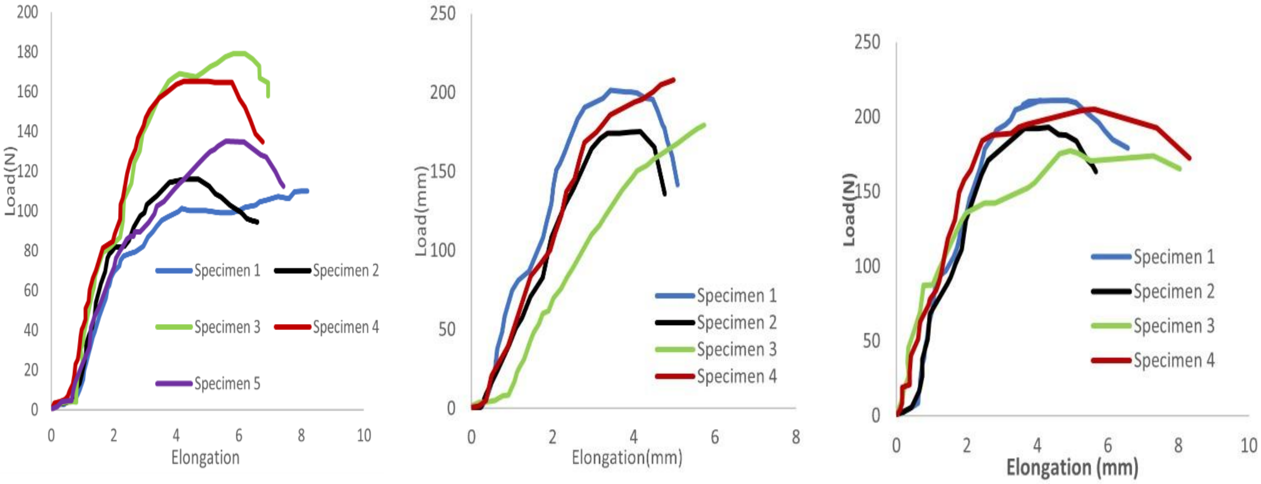
# APPENDIX 1

## Load- Displacement Curves of Composite Laminates in Flexural and Interlaminar Shear Stress Tests and SEM Images obtained in Tensile Tests

### 1. Flexural Tests

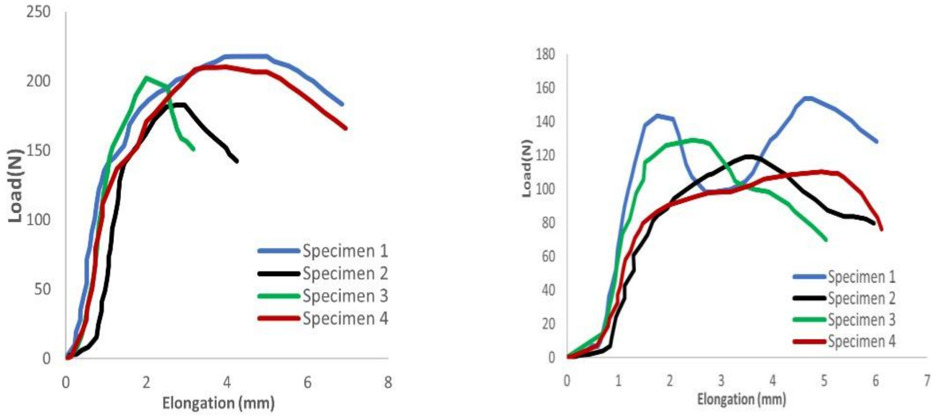
LOAD-ELONGATIONS CURVES



(a) Plane Samples

(b) 0.1% Wt. Graphene

(c) 0.25% Wt. Graphene

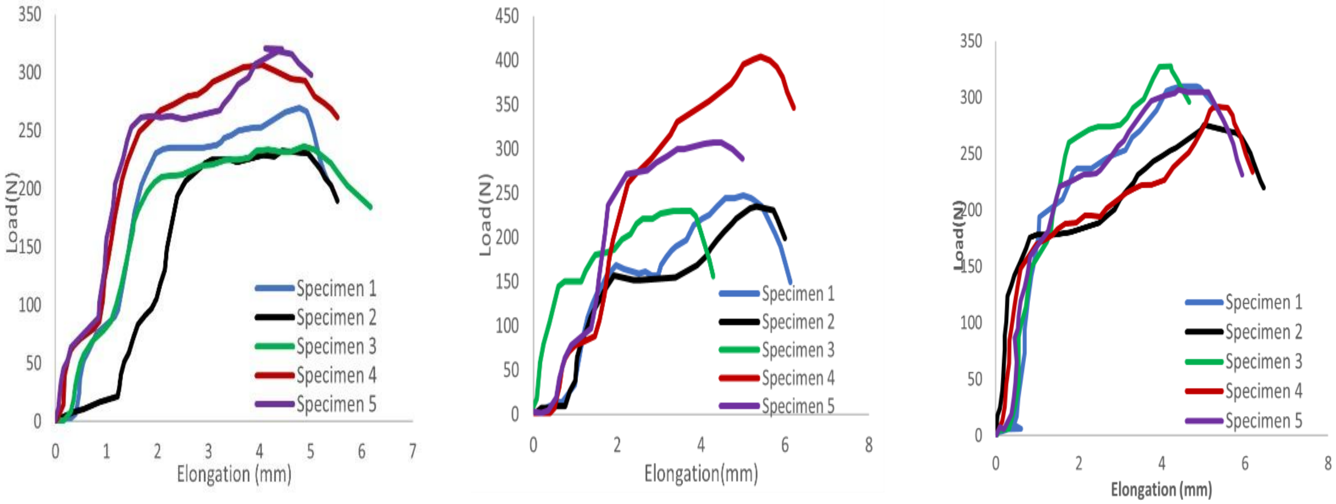


(d) 0.5 % Wt. Graphene

(e) 1 % Wt. Graphene

## 2. ILSS Tests

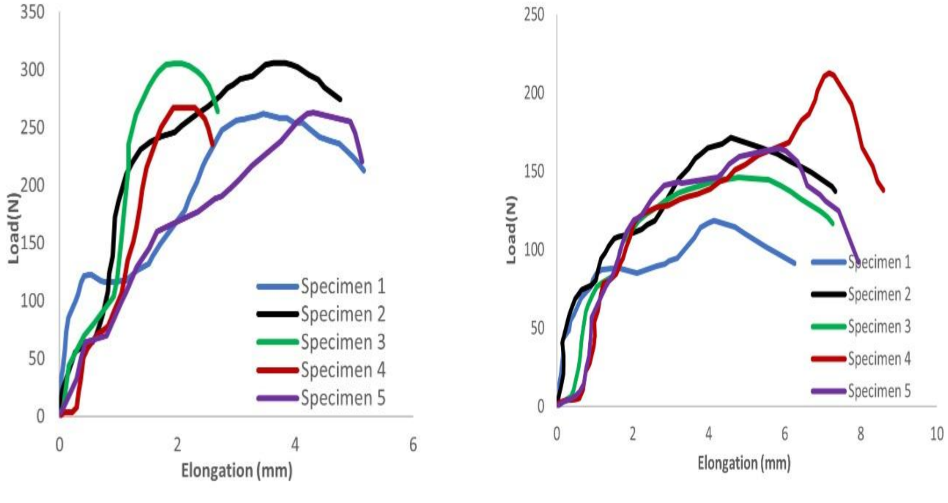
INTERLAMINAR SHEAR TESTS LOAD VS. ELONGATION CURVES



(a) Plane Samples

(b) 0.1% Wt. Graphene

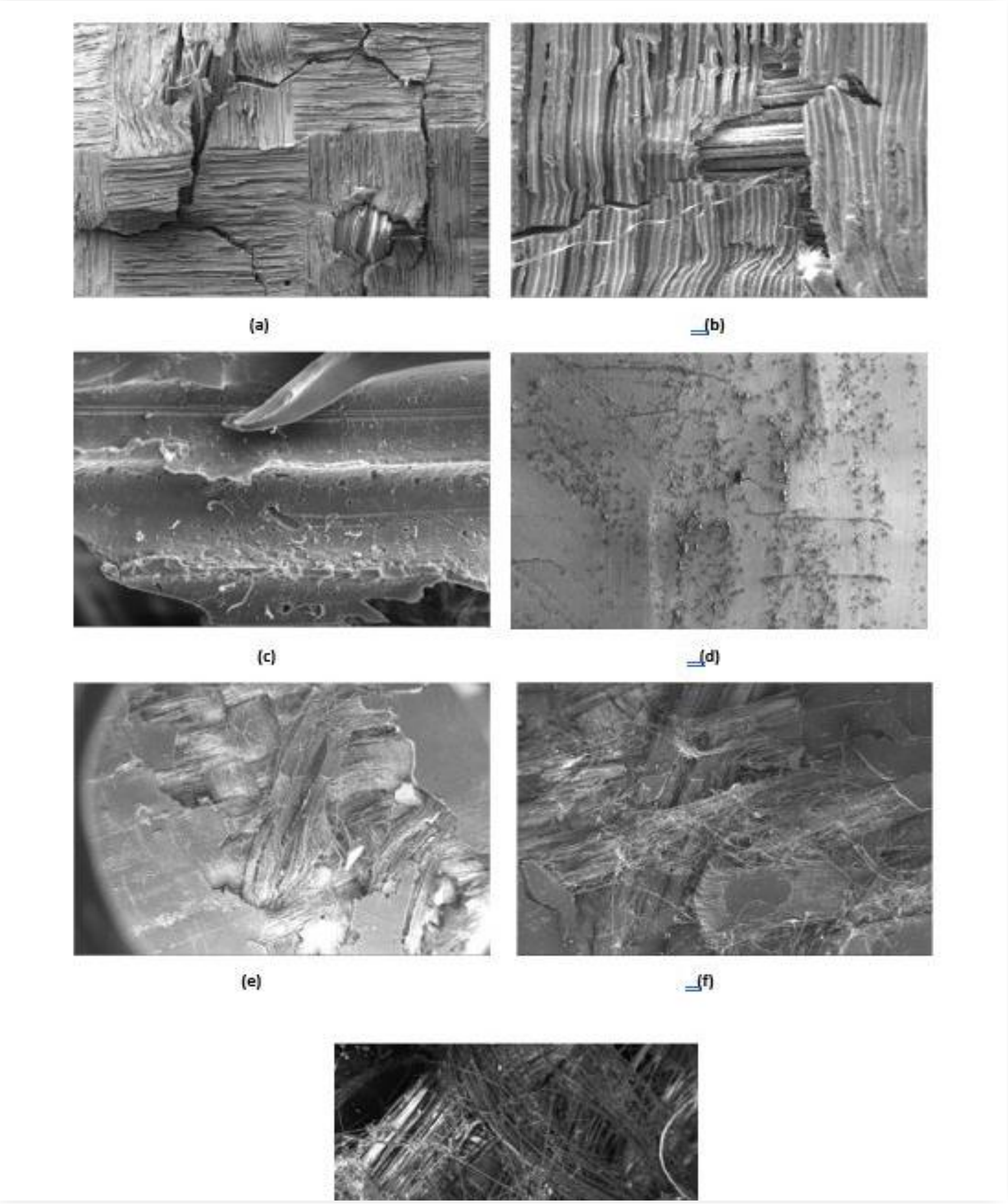
(c) 0.25% Wt. Graphene



(d) 0.5% Wt. Graphene

(e) 0.5% Wt. Graphene

## 3. SEM Images of Failed Laminates in Tensile Tests



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