



Process-controlled Expansion of Graphite Intercalation Compounds: Mechanism and Functional Performance

Ing. Divan Coetzee

The Summary of the Dissertation Thesis

Title of the thesis: Process-controlled Expansion of Graphite Intercalation Compounds: Mechanism and Functional Performance

Author: Ing. Divan Coetzee, BSc.

Field of study: Industrial Engineering

Mode of study: Full Time

Department: Department of Material Engineering

Supervisor: prof. Ing. Jakub Wiener, Ph.D.

Chairman:

prof. Ing. Michal Vik, Ph.D.

FT TUL, Department of Material Engineering

Vice-chairman:

prof. Ing. Jiří Militký, CSc.

FT TUL, Department of Material Engineering

prof. Dr. Ing. Miroslav Černík, CSc.

CxI TUL, Institute of Novel Technologies and Applied Informatics

prof. Ing. Gražyna Simha Martynková, Ph.D. (opponent)

VSB - Technical University of Ostrava
Centre for Energy and Environmental Technologies

doc. Ing. Eva Kuželová Košťáková, Ph.D. (opponent)

FP TUL, Department of Chemistry

Ing. Josef Večerník, CSc.

Večerník s.r.o.

Ing. Karel Kupka, Ph.D.

TriloByte Statistical Software, s.r.o.

The dissertation is available at the Dean's Office FT TUL.

Liberec 2026

Abstract

Commercial expanded graphite (EG) is typically produced by thermal or microwave shock of graphite intercalation compounds (GICs), a diffuse heating approach that is energy-intensive and yields broad distributions in expansion and microstructure. This dissertation demonstrates that laser-induced expansion offers an energy-efficient, tunable route to application-specific EG by jointly controlling intercalant chemistry and laser fluence. Using H_2SO_4 - and HNO_3 -GICs as model systems, this work explores a process window from 254 to 1020 $\text{J}\cdot\text{cm}^{-2}$ fluence. It reveals, through ANOVA and multiscale characterisation techniques (SEM, XRD, TGA/DSC), that HNO_3 -GICs achieve maximum volume and lowest bulk density at an intermediate fluence range of approximately 600–750 $\text{J}\cdot\text{cm}^{-2}$. Conversely, under the same conditions, H_2SO_4 -GICs tend to develop denser morphologies due to lesser expansion. The thermo-analytical results highlight this contrast: HNO_3 -GIC expands rapidly at lower temperatures, releasing concentrated gases well suited to the localised heating from the laser. In contrast, H_2SO_4 -GIC exhibits a broader, redox-driven decomposition thermal profile that requires longer, more intense heating, leading to underexfoliation under rapid laser conditions. In thermal-shock conditions, however, the higher energy enables complete exfoliation of H_2SO_4 -GIC, whereas HNO_3 -GIC experiences lower expansion due to nitric acid's instability, leading to deintercalation and varying intercalation stages. XRD analysis supports this, showing peak broadening and smaller c-axis crystallite sizes for laser-expanded HNO_3 samples, indicating greater nanocrystalline fragmentation compared to H_2SO_4 or furnace-expanded materials.

Based on this scientific comparison of conventional and novel laser methods coupled to the intercalant chemistries, this work then connects the process–structure map to three functional domains. In environmental sorption, three commercial, thermal-shock-EGs (EG1–EG3) with different intercalation histories are benchmarked for heavy-oil uptake and heavy-metal removal. EG1, the most exfoliated and sulfur-rich material, absorbs up to approximately 55 $\text{g}_{\text{oil}}/\text{g}_{\text{EG}}$ (24 hours) thanks to more uniform interlayer exfoliation. In contrast, EG3, which is more crystalline and HNO_3 -dominant, shows the widest metal selectivity and nearly complete lead removal. This demonstrates that porosity determines oil capacity, and narrow galleries or residual functionality facilitate metal trapping. Relating density, Raman and XRD to capacity/selectivity turns these trends into predictive tools.

Utilising the laser-expansion behaviour of the H_2SO_4 -GIC, it was investigated for its application in protective textiles. An acrylic coating filled with H_2SO_4 -GIC (selected for its energy-intensive decomposition profile) was developed on Kevlar, forming a thick intumescent char that provides high protection grades under laser irradiation of ~ 239 – $290 \text{ J}\cdot\text{cm}^{-2}$ at a particle loading of $25 \text{ g}\cdot\text{m}^{-2}$. Martindale testing indicated 10,000-cycle abrasion durability.

In conductive applications, EG is primarily used as an intermediate material for producing graphene, owing to the readily accessible graphene layers in its

exfoliated structure. This makes EG a promising candidate for conductive composites; however, its particle porosity can reduce mechanical integrity. The balance between conductivity and mechanical performance was examined in this work. Vacuum processing of EG-filled polyester (PES) composites and adding carbon fibres (CF) achieved surface resistivities in the tens-of-ohms range at 3–5 wt% EG, but still at the cost of tensile strength. In nanofibrous yarns, ultrasonicated EG (uEG) combined with PEDOT:PSS produced marginally conductive, cytocompatible textiles suitable for antistatic and sensing applications.

Together, these results validate that laser-tuned exfoliation and intercalant choice provide a controllable, energy-efficient platform to engineer EG microstructures that meet the divergent requirements of sorption, protection and conductive/biocompatible systems, establishing a coherent process–structure–property framework for application-specific design.

Keywords:

Graphite intercalation compounds (GICs), sulfuric acid GIC, nitric acid GIC, laser expansion, thermal shock, heavy metal sorption, oil sorption, thermal laser protection, conductive composite, biocompatible composites

Anotace

Komerční expandovaný grafit (EG) se obvykle vyrábí tepelným nebo mikrovlnným šokem interkalačních sloučenin grafitu (GIC), což je metoda difúzního ohřevu, která je energeticky náročná a vede k širokému rozptylu v rozměrech a mikrostruktuře. Tato disertační práce dokazuje, že laserem indukovaná expanze nabízí energeticky účinný a nastavitelný způsob výroby EG pro konkrétní aplikace prostřednictvím společné regulace chemického složení interkalačního činidla a laserového toku energie. S využitím H_2SO_4 - a HNO_3 -GIC jako modelových systémů tato práce zkoumá procesní okno s laserovým tokem energie od 254 do 1020 $\text{J}\cdot\text{cm}^{-2}$. Pomocí ANOVA a vícerozměrných charakterizačních technik (SEM, XRD, TGA/DSC) odhaluje, že HNO_3 -GIC dosahují maximálního objemu a nejnižší objemové hmotnosti v mezilehlém rozsahu středního toku přibližně 600–750 $\text{J}\cdot\text{cm}^{-2}$. Naopak za stejných podmínek mají H_2SO_4 -GIC tendenci vyvíjet hustší morfologie kvůli menší expanzi. Výsledky termoanalýzy tento kontrast zdůrazňují: HNO_3 -GIC se rychle rozšiřuje při nižších teplotách a uvolňuje koncentrované plyny, které se dobře hodí pro lokalizované zahřívání laserem. Naproti tomu H_2SO_4 -GIC vykazuje širší, redoxem řízený teplotní profil rozkladu, který vyžaduje delší a intenzivnější zahřívání, což vede k nedostatečné exfoliaci za podmínek rychlého laserového záření. V podmínkách tepelného šoku však vyšší energie umožňuje úplnou exfoliaci H_2SO_4 -GIC, zatímco HNO_3 -GIC vykazuje nižší expanzi v důsledku nestability kyseliny dusičné, což vede k odstranění interkalace a různým fázím interkalace. Tuto skutečnost potvrzuje analýza XRD, která u vzorků HNO_3 expandovaných laserem ukazuje rozšiřování vrcholů a menší velikost krystalitů na ose c, což naznačuje větší nanokrystalickou fragmentaci ve srovnání s materiály expandovanými H_2SO_4 nebo v peci.

Na základě tohoto vědeckého srovnání konvenčních a nových laserových metod v kombinaci s chemickým složením interkalantů tato práce následně propojuje mapu proces–struktura se třemi funkčními oblastmi. V oblasti environmentální sorpce jsou tři komerční EG s tepelným šokem (EG1–EG3) s odlišnou historií interkalace porovnány z hlediska absorpce těžkých olejů a odstraňování více kovů. EG1, materiál s nejvyšší exfoliační schopností a nejvyšším obsahem síry, absorbuje až přibližně 55 g oleje na gram EG (24 hodin) díky rovnoměrnější mezivrstvé exfoliaci. Naproti tomu EG3, který je krystaličtější a v němž převládá HNO_3 , vykazuje nejširší selektivitu vůči kovům a téměř úplné odstranění olova. To dokazuje, že pórovitost určuje kapacitu pro olej a úzké kanálky nebo zbytková funkčnost usnadňují zachycování kovů. Vztah mezi hustotou, Ramanovou spektroskopií a XRD a kapacitou/selektivitou proměňuje tyto trendy v prediktivní nástroje.

S využitím vlastností H_2SO_4 -GIC při laserovém působení bylo zkoumáno jeho použití v ochranných textiliích. Na kevlaru byl vyvinut akrylový povlak plněný H_2SO_4 -GIC (vybraný pro svůj profil energeticky náročného rozkladu), který vytváří silnou intumescentní uhlíkovou vrstvu, která poskytuje vysoký stupeň ochrany při laserovém ozáření ~ 239 – $290 \text{ J}\cdot\text{cm}^{-2}$ při obsahu částic 25 $\text{g}\cdot\text{m}^{-2}$. Martindale testy ukázaly odolnost proti oděru 10 000 cyklů.

V aplikacích vyžadujících vodivost se EG používá především jako meziprodukt při výrobě grafenu, a to díky snadno dostupným vrstvám grafenu v jeho exfoliované struktuře. Díky tomu je EG slibným kandidátem pro vodivé kompozity; jeho poréznost však může snižovat mechanickou pevnost. V této práci byla zkoumána rovnováha mezi vodivostí a mechanickými vlastnostmi. Vakuovým zpracováním kompozitů z polyesteru (PES) plněných EG a přidáním uhlíkových vláken (CF) bylo dosaženo povrchové rezistivity v řádu desítek ohmů při 3–5 % hmotnostních EG, avšak stále na úkor pevnosti v tahu. V nanovlákněných přízích vytvořil ultrazvukem ošetřený EG (uEG) v kombinaci s PEDOT:PSS mírně vodivé, cytokompatibilní textilie vhodné pro antistatické a senzorické aplikace.

Tyto výsledky společně potvrzují, že laserem řízená exfoliace a volba interkalantu představují kontrolovatelnou a energeticky úspornou platformu pro vytváření mikrostruktur z EG, které splňují rozmanité požadavky sorpčních, ochranných a vodivých/biokompatibilních systémů, čímž vytvářejí ucelený rámec pro vztah mezi procesem, strukturou a vlastnostmi, který umožňuje návrh řešení přizpůsobených konkrétním aplikacím.

Klíčová slova:

Grafitové interkalační sloučeniny (GIC), GIC s kyselinou sírovou, GIC s kyselinou dusičnou, laserová expanze, teplotní šok, sorpce těžkých kovů, sorpce oleje, tepelná laserová ochrana, vodivé kompozity, biokompatibilní kompozity

Summary

1	<i>Introduction</i>	9
1.1	Motivation and problem statement	9
1.2	EG and intercalation chemistry	9
1.3	Research concept and overarching hypothesis	10
2	<i>Subject and objectives of the dissertation</i>	10
2.1	Main subject of the dissertation	10
2.2	Research objectives, questions and working hypotheses	11
3	<i>Overview of the current state of the art</i>	12
3.1	Conventional preparation of EG	12
3.2	Laser-assisted graphite exfoliation and expansion	12
3.3	EG for environmental sorption and filtration	13
3.4	EG in protective textile coatings	13
3.5	EG in conductive applications	13
3.6	Identified gaps addressed by this dissertation	14
4	<i>Experiment</i>	14
4.1	Materials and sample preparation	14
4.1.1	Laser-induced controlled expansion of GICs	14
4.1.2	Sorption applications	15
4.1.3	Protective coating applications	15
4.1.4	Conductive applications	15
4.2	Sample testing and characterisation methods	16
4.2.1	Laser-induced controlled expansion of GICs	16
4.2.2	Sorption applications	16
4.2.3	Protective coating applications	16
4.2.4	Conductive applications	17
4.2.5	Data availability	17
4.3	Results and discussion – controllable exfoliation	17
4.3.1	Expansion behaviour and process window mapping	17
4.3.2	Thermo-analytical mechanisms of intercalant decomposition	20
4.3.3	XRD evidence of structural disruption and defect generation	22
4.3.4	The mechanistic difference observed between traditional thermal shock and laser exfoliation.	25
4.3.5	Structure–process–property relationships for EG	25
4.4	Results and discussion – environmental sorption and filtration	25
4.4.1	Structural and compositional differences in commercial EGs	26
4.4.2	Oil sorption capacity and kinetics	29
4.4.3	Heavy metal sorption profiles from oil	29
4.4.4	Implications for oil filtration and waste-oil purification	31

4.5	Results and discussion – laser-protective composites	31
4.5.1	Coating design and microstructure.....	31
4.5.2	Laser irradiation response and protection grading.....	32
4.5.3	Thickness of expansion	33
4.5.4	Thermogravimetric behaviour of coatings.....	34
4.5.5	Abrasion durability.....	35
4.5.6	Implications for laser protective wear	36
4.6	Results and discussion - Conductive composites	36
4.6.1	Application overview and rationale	37
4.6.2	Microstructure and filler architecture	37
4.6.3	Effect of EG on electrical percolation and resistivity	41
4.6.4	Effect of EG on composite mechanical performance	44
4.6.5	Biocompatibility of EG composite nanofibrous yarns.....	48
4.6.6	Integration back to the core exfoliation framework.....	49
5	<i>Proposal for further activities within the dissertation topic</i>	50
5.1	Process-level optimisation and scale-up	50
5.2	Advanced structural/chemical characterisation	50
5.3	Next-generation functional systems	50
6	<i>References</i>	50
7	<i>List of the author's works related to the problem under study.....</i>	52
7.1	Articles in impacted journals.....	52
7.2	Book Chapters	53
7.3	Conference contributions and proceedings.....	53
7.4	Manuscripts under review	53
8	<i>Brief characteristics of previous professional, research and scientific activities.....</i>	54
9	<i>Curriculum Vitae</i>	55

1 Introduction

1.1 Motivation and problem statement

Commercial expanded graphite (EG) production mainly uses high-temperature furnace or microwave methods, even though only a small part of this energy is needed for exfoliation. This process heats the entire batch and equipment, making it energy-inefficient and limiting local control, which is problematic for applications requiring precise properties and sustainable methods. Thermal fields are diffuse, so exfoliation depends more on packing and history than on targeted energy input, causing variability in expansion, density, and defects even under similar conditions. Conversely, laser-assisted methods focus energy within graphite, allowing rapid, localised, and tunable exfoliation at lower power, with better process control [1], [2], [3].

Graphite intercalation compounds (GICs) offer an underused lever, as different intercalants have unique decomposition pathways, temperatures, and gas-evolution kinetics that affect expansion and microstructure. For example, sulfuric (H_2SO_4) and nitric (HNO_3)-GICs display distinct thermal behaviours and expansion volumes under the same conditions, influencing porosity, crystallinity, and residual functionalisation, which impact oil and heavy-metal sorption, char structure in coatings, and their applications. In polymer composites, expanded graphite (EG) is a common conductive filler that reaches percolation at low loadings, thereby boosting conductivity. However, the combined effects of GIC chemistry, expansion conditions, and morphology on mechanical reinforcement remain underexplored, despite their importance [4], [5], [6].

As EG advances into environmental, protective, and biomedical fields, there's an increasing need for materials combining tailored porosity and conductivity with biocompatibility. High porosity, exfoliated structures maximize surface area and void volume for oil and heavy metal sorbents, while controlled architectures and robust char layers are vital in thermal and laser protection. Carbon fillers like EG and graphene enable conductive networks without harmful ion release, supporting biocompatible nanofibrous yarns and textile electrodes. EG composites show high electrical conductivity at low filler content ($\sim 10^1\text{--}10^2 \Omega$ at 3–5 wt.%), though this often reduces mechanical strength due to porosity. These factors drive the development of tunable, chemistry-aware expansion strategies to produce EG with tailored morphologies for specific applications [5], [7], [8], [9].

1.2 EG and intercalation chemistry

GICs form when guest species, such as strong acids, oxidants, or metal salts, are inserted between graphite layers, increasing the interlayer spacing and creating a host–guest structure of alternating carbon and intercalant galleries. The intercalation stage (stage-1: every gallery filled, stage-2: every second) and the intercalant type alter graphite's electronic structure, density, crystallography, and reactivity. Common intercalants, also called expandable graphite, include H_2SO_4 and HNO_3 acids, often with oxidisers like persulfates or permanganates, producing graphite bisulfate or nitrate species with strong intumescent potential when heated [3], [10], [11].

GICs expand into EG mainly due to intercalated species converting to gases under rapid heating, creating high pressure that separates graphene layers along the c-axis. In furnace or microwave processes, quick heating decomposes intercalants and oxygen groups, releasing gases like SO_2 , CO_2 , H_2O , or NO_x , causing expansion over 100-fold if heating is fast enough to prevent gas escape before

delamination. Laser-induced expansion is similar but with localised energy absorption, leading to rapid heating, intercalant decomposition, and gas release. Its focused energy allows for sharp thresholds, quick heating, and precise exfoliation [3], [10], [11], [12], [13], [14], [15].

H₂SO₄-GICs decompose in multiple steps over broad ranges, with redox activity affecting the carbon lattice, while HNO₃-GICs deintercalate and decompose at lower temperatures, causing more explosive expansion and different oxidation levels. These variations impact expansion volume, density, crystallite size, and heteroatom content, which in turn affect oil sorption, heavy-metal uptake, char morphology, and electrical properties in composites [3], [5], [16], [17], [18].

GIC chemistry and expansion route define a versatile design space for application-specific EG morphologies, suitable for selecting the functional properties as described in this thesis [5], [9], [11], [19], [20].

1.3 Research concept and overarching hypothesis

This dissertation explores laser-induced expansion of GICs as an energy-efficient, controllable method for producing EG and compares it with traditional thermal-shock methods. By focusing on laser fluence and intercalant chemistry, the work aims to develop a tunable “process window” where parameters like expansion volume, porosity, crystallinity, and defect density can be programmed rather than just observed. H₂SO₄- and HNO₃-GICs serve as models to show how differences in decomposition pathways, onset temperatures, and gas-evolution affect exfoliation and EG architecture under the same conditions. These microstructures influence EG’s performance in environmental sorbents, protective coatings, and conductive systems. For oil and heavy-metal sorption, the study assesses how expansion severity, residual heteroatoms, and pore structure affect capacity and selectivity, building on evidence that different intercalation histories lead to varied sorption behaviours. In textiles, EG coatings on Kevlar transform into char layers under laser loading, linking chemistry and expansion to protection and durability. In composites, EG and carbon fillers create conductive networks that avoid metal ion release and biocidal effects, emphasising conductivity, mechanics, and biocompatibility.

By systematically linking GIC chemistry, conventional thermal shock, and laser process parameters to the EG microstructure and, in turn, to application-level performance across these three domains, the thesis seeks to establish a coherent, experimentally grounded process–structure–property framework for energy-efficient, application-specific EG. This is explained by the working hypothesis, research objectives and questions in the following section.

2 Subject and objectives of the dissertation

2.1 Main subject of the dissertation

The subject of this dissertation is energy-efficient, controllable exfoliation of GICs and the resulting structure–property–application relationships in functional EG systems. Specifically, it investigates laser-induced expansion of H₂SO₄- and HNO₃ GICs as a tunable alternative to conventional thermal shock methods, establishing how process parameters (intercalant chemistry, laser fluence) control EG microstructure (porosity, crystallinity, defect density, residual functionalisation) and how these structural features determine performance across environmental sorption, thermal/laser protection, conductive composites and biocompatible nanofibrous systems.

2.2 Research objectives, questions and working hypotheses

The dissertation pursues the following specific objectives:

- **O1:** Quantify the effects of intercalant chemistry (H_2SO_4 vs HNO_3 GICs) and laser fluence on expansion volume, bulk density, porosity development and structural disruption during laser-induced exfoliation, identifying optimal process windows that maximise exfoliation efficiency while minimising over-expansion or collapse and compare it to traditional thermal shock methods.
- **O2:** Correlate thermo-analytical signatures (TGA/DSC decomposition profiles) and microstructural descriptors (XRD crystallite size/FWHM, Raman D/G ratios, SEM morphology) with expansion behaviour, elucidating how GIC chemistry governs gas evolution kinetics, defect formation and residual heteroatom content.
- **O3:** Establish quantitative relationships between EG microstructure and environmental performance, specifically oil sorption capacity, heavy-metal removal efficiency and selectivity from model oils, as functions of expansion severity, pore architecture and intercalation history.
- **O4:** Develop and characterise expandable graphite-based acrylic coatings on Kevlar textiles for laser protection, linking EG loading, intumescent expansion behaviour and char morphology to protection grades, backside temperature rise and abrasion durability under controlled 100 W laser irradiation.
- **O5:** Demonstrate the feasibility of expanded-graphite-filled composites for conductive and biocompatible applications, quantifying the trade-offs between electrical percolation, mechanical properties and cytocompatibility as influenced by filler morphology and processing.

The research is guided by the following questions and working hypotheses:

Research questions:

- **RQ1:** How does intercalant chemistry shift the laser-fluence window for optimal expansion compared to thermal shock methods, and what microstructural signatures distinguish under-, optimally and over-expanded regimes?
- **RQ2:** To what extent do expansion-controlled variations in porosity, crystallinity and surface chemistry predict oil uptake and heavy-metal sorption profiles across commercial EGs?
- **RQ3:** Can EG coatings be engineered to provide effective laser protection on high-performance textiles while maintaining flexibility and durability?
- **RQ4:** How do EG fillers balance electrical conductivity, mechanical reinforcement and biocompatibility in nanofibrous yarns and viscous resin composites?

Working hypotheses:

- **H1:** Each GIC exhibits a distinct intermediate laser-fluence window, maximising expansion volume/porosity with minimal structural collapse, positioned differently for H_2SO_4 vs HNO_3

systems due to decomposition kinetics, which also influences their difference in thermal shock expansion methods.

- **H2:** Microstructural metrics (density, crystallite size, D/G ratio) from controlled expansion correlate strongly with oil sorption capacity and metal selectivity, with higher exfoliation favouring oil uptake but functionalisation driving metal affinity.
- **H3:** EG-based coatings at optimised loadings ($\approx 25 \text{ g m}^{-2}$) form stable intumescent char under laser loading, achieving no detectable backside damage up to 290 J cm^{-2} while retaining abrasion resistance after 10,000 cycles.
- **H4:** Expanded-graphite-containing composites can achieve useful conductive behaviour (e.g., $10^1\text{--}10^2 \text{ } \Omega$ surface resistivity at low loadings) while exhibiting biocompatible behaviour, provided that filler morphology (uEG/vacEG) and dispersion are tuned to balance electrical percolation, mechanical integrity (despite viscous-matrix strength trade-offs) and cytotoxicity.

3 Overview of the current state of the art

3.1 Conventional preparation of EG

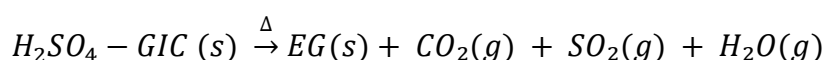
EG production is dominated by rapid thermal shock of GICs in furnaces or by microwave heating, where intercalated acids decompose to gaseous products that force the graphene layers apart along the c-axis. In classical thermal shock (also programmable), GICs are heated to $800\text{--}1000 \text{ }^\circ\text{C}$ at high rates, forming worm-like structures with low density, depending on the intercalant and process. Microwave heating can achieve similar expansion using dielectric coupling, with comparable expansion and oil sorption when properly tuned [1], [17], [18].

3.2 Laser-assisted graphite exfoliation and expansion

Laser-induced expansion of GICs has recently emerged as an energy-efficient alternative to furnace and microwave methods. Studies have shown that activation temperatures of $140 \text{ }^\circ\text{C}$ are reached, with energy below 100 kJ mol^{-1} and densities of 800 mL g^{-1} using only a 2 W blue laser [2], [21].

Laser-induced expansion of GICs occurs via a photothermal process where incident photons target the delocalised π -electron system of graphite, quickly converting to lattice vibrations through electron–phonon coupling, raising local temperature within the interlayer galleries. When this temperature surpasses the decomposition threshold of the confined acid, gases form and cannot escape swiftly. Their buildup pressure separates graphene layers along the c-axis, creating a worm-like, porous morphology. Due to energy being deposited in a small, optically confined volume, heating rates are high and spatially restricted, resulting in sharp activation thresholds and varied thermal histories within the same sample. [2], [3].

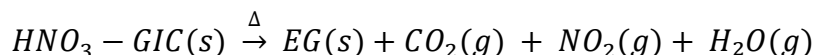
Equation 1: Thermal expansion reaction of graphite bisulfate [22].



Thermogravimetric (TGA) and differential scanning calorimetry (DSC) studies reveal a three-stage mass-loss profile: initial desorption of weakly bound species; broad primary decomposition from about 105 to 500 °C, peaking near 200 °C; and secondary high-temperature oxidation [3], [4], [21].

In contrast, HNO_3 -GICs (graphite nitrate) undergo a sharper, more violent expansion, reflecting the lower thermal stability and higher volatility of intercalated HNO_3 . Thermoanalytical data reveal an earlier onset of mass loss, around 140 °C, and a narrow primary decomposition range (approximately 140–300 °C) with a dominant DTG peak near 180 °C [3], [4], [18].

Equation 2: Thermal expansion of graphite nitrate [12].



Existing laser studies mainly focus on individual intercalant systems and demonstrate feasibility or high expansion ratios, rather than systematically comparing different GIC chemistries under unified laser conditions.

3.3 EG for environmental sorption and filtration

EG has gained attention as an oil sorbent due to its low density, high porosity, and oleophilic carbon surface. Graphite-based sorbents for oil spills have capacities of 50–80 g(oil)/g(sorbent), due to hierarchical porosity, hydrophobicity, and capillary forces. Investigations show that milder expansion conditions and suitably sized particles enhance oil uptake, emphasising control over textural properties and particle shape [5], [7], [18].

Beyond oil, EG has been explored for removing heavy metals and organic contaminants from water and oils. Studies linked performance differences to variations in degree of exfoliation, crystallinity and residual heteroatom content [5], [23].

3.4 EG in protective textile coatings

In flame-retardant and thermal-protective uses, expandable graphite acts as an intumescent additive forming a stable, voluminous char when heated, insulating the polymer and reducing heat and mass transfer [24], [25], [26].

Protective textiles use coating architectures with expandable graphite in polymer binders on high-performance fabrics with non-intumescent coatings, showing promising results [27], [28], [29]. Despite advances, most studies view EG as a commercial filler with fixed properties and optimize coating formulations empirically, without linking GIC chemistry and microstructure to coating performance under laser or high-heat flux, a gap this dissertation addresses.

3.5 EG in conductive applications

EG is widely studied as a conductive filler in polymers due to its worm-like, exfoliated structure offering accessible graphene layers and high aspect ratio pathways for electron transport at low loadings. In EG–pitch composites, percolation theory shows a conductive network can form at about 1.5 wt%, well below the levels needed for micrometre-scale graphite, reflecting its effective cluster formation and contact probability [30], [31].

Several studies have quantified percolation thresholds and conductivity plateaus for EG in different thermoset and thermoplastic systems, highlighting the strong influence of matrix chemistry, filler dispersion and co-fillers [31]. The type of graphite filler and its pre-treatment significantly affect both electrical and thermal conduction pathways in epoxy matrices [30], [32]. Although high EG loadings can provide strong conductivity enhancements, they often introduce trade-offs in mechanical performance due to the intrinsic porosity and weak inter-particle cohesion [33], [34].

These developments relate to conductive yarns and textile electronics, where carbon nanomaterials and graphitic fillers create flexible, sturdy conductors for sensing and actuation. Reviews highlight that stable conductivity during bending, stretching, and washing depends on low percolation thresholds and strong filler–matrix interfaces that preserve pathways under deformation. Strategies for EG-derived stacked graphene in epoxy, like promoting localisation at fibre surfaces and balancing filler dispersion with matrix integrity, are relevant for designing EG-based yarns and coatings that combine electrical functionality with mechanical performance and biocompatibility. [34], [35]. EG serves as a versatile precursor bridging graphite fillers and few-layer graphene, providing a tunable platform to engineer conductive architectures in bulk composites, laminates, and fibrous systems.

3.6 Identified gaps addressed by this dissertation

Existing studies lack a comprehensive process–structure map integrating GIC chemistry and laser fluence to systematically correlate expansion behaviour and structural metrics across validated experimental conditions [3].

There is no unified framework establishing how controllable exfoliation parameters and expansion history govern the microstructural features that determine environmental sorption capacity and selectivity [3], [5].

Flame-retardant and protective textile formulations overlook how GIC chemistry and expansion route can be tuned to optimise char morphology and multifunctionality, a gap addressed by the developed laser-protective Kevlar coating architecture [9].

Research rarely connects EG morphology with combined electrical, mechanical, and biocompatible performance, which this dissertation elucidates across composite and nanofibrous yarn formats [19], [20].

4 Experiment

4.1 Materials and sample preparation

4.1.1 Laser-induced controlled expansion of GICs

Two types of GICs, H₂SO₄- and HNO₃-intercalated expandable graphite (Sorbetin s.r.o., Czech Republic), with different decomposition kinetics, were used as precursors. For laser expansion, 0.1 g portions of each GIC were spread on 18×18 mm ceramic plates as thin beds (1–2 mm thick) for consistent energy delivery and minimal shadowing. Expansion used a 100 W CO₂ laser (150 Flexi Marcatex, 10.6 μm wavelength), with pixel dwell times varied to achieve laser fluences from 254–1020 J/cm² across eight levels, mapping under-expansion, optimal exfoliation, and over-expansion. Fluence was total energy per scanned area. Post-expansion, the EG samples were characterized by volume change and mass

retention to determine bulk density. Controls underwent rapid thermal shock at 800 °C for comparison and mechanistic study [3].

4.1.2 Sorption applications

Three commercial EG grades (EG1, EG2, EG3; Sorbetin s.r.o., Czech Republic) were selected to cover variations in intercalation chemistry: EG1 (high sulfur from H₂SO₄), EG2 (balanced H₂SO₄/HNO₃), and EG3 (H₂SO₄/HNO₃, high crystallinity, lower exfoliation). They were characterised as received for baseline structure (worm morphology, porosity) before sorption testing. Recovered marine heavy oil (RMUTT, Thailand; viscosity 88.6 cSt at 40 °C, per ASTM D445) served as the contaminated matrix, containing metals (Ag, Cd, Cr, Cu, Fe, Ni, Pb, V, Zn). For sorption, ~0.5 g EG samples were placed in polypropylene mesh bags to prevent loss while allowing oil access, then fully immersed in excess oil by pouring over the particles for kinetic (30 min) and equilibrium (24 h) uptake per ASTM F726-17, then 2 min mechanically drained before measuring sorbed oil capacity (g oil/g EG, n=3) and excess oil [5].

4.1.3 Protective coating applications

Kevlar 49T fabric (style 968, 335 g/m², ¼ satin weave; DuPont) formed the substrate due to its high tensile strength and thermal stability (non-melting to 450 °C). Coatings used water-based acrylic varnish (Balakryl Venkovní Lak, PPG Deco CZ; 39 vol.% solids, density 1.03–1.04 g/cm³, with UV stabilisers and biocides). A three-layer process included: (1) a base coat (160 g/m²) for wetting and fiber penetration; (2) manual application of H₂SO₄ expandable graphite at densities 4.2–37.5 g/m² for intumescence testing; (3) a 280 g/m² sealing topcoat for encapsulation, adhesion, and abrasion resistance. Dried coatings were conditioned (60 °C for 10 min, then 24 h at room temp) before laser exposure (100 W CO₂, 1×1 cm spot, 50% duty cycle, 109–1338 J/cm²) and durability tests [9].

4.1.4 Conductive applications

4.1.4.1 PES/EG composites

PES resin (UN1866, Havel Composites CZ s.r.o.; kinematic viscosity 400–600 mPa·s at 20 °C) was used as the viscous thermoset matrix, catalysed with 2 wt% methyl ethyl ketone peroxide (MEKP) hardener. Fillers included: (1) as-received EG (Sorbetin s.r.o., sulfuric acid GIC-derived; 1, 3, 5 wt%); (2) ultrasonicated EG (uEG: 50:50 EG: distilled water slurry, 45 W/40 kHz probe sonication for 1 h at controlled 78 °C, ice-bath cooled, vacuum filtered, oven-dried at 80 °C/30 min; 0.1–5 wt%); (3) vacuum-processed EG (vacEG: post-mixing degassing at 400 mbar absolute/24 h prior to cure; 1–5 wt%); (4) milled carbon fibre (CF, Easy Composites, UK; 100±50 µm length, 7–10 µm diameter; 0.5–5 wt%) for hybrid reinforcement. Formulations (total 60 g resin) were mechanically premixed (overhead stirrer, 500 rpm/5 min), hardener added (2 min/500 rpm), degassed (10 min rest), poured into silicone moulds (ISO 527-2 Type 1A: 50×10×4 mm gauge), and thermally cured (60 °C oven, 6 h) to yield dense composites free of macroscopic voids [20].

4.1.4.2 Nanofibrous yarns

Nanofibrous yarns were electrospun via AC high-voltage system (TUL PV 2022-370 grant-funded setup) from degradable/semidegradable polymer dopes: polyamide 4,6 (Stanyl, DSM), polyvinyl butyral (PVB, 55 kDa), polyvinyl alcohol (PVA, 125 kDa, 89% hydrolysis). Conductive fillers comprised ultrasonicated EG (uEG) or micronised graphite (mGraph; 5–30 wt% total carbon loading) combined with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, 10–15 wt%) for dual percolation and processability. Polymer solutions (10–15 wt% in formic/acetic acid or water/DMSO) were loaded into 5 mL syringes and electrospun at 35 kV peak-to-peak (50 Hz AC), collected on a 200 mm diameter

rotating disc (9000 rpm twirler) to form continuous twisted yarns (linear density 10–50 tex). Yarns were post-conditioned (24 °C, 42% RH, 24 h) before bundling for electrical/mechanical testing under the same conditions according to ASTM D4496 [19].

4.2 Sample testing and characterisation methods

4.2.1 Laser-induced controlled expansion of GICs

Laser-expanded GICs were systematically characterised across multiple length scales to quantify exfoliation efficiency, thermal decomposition pathways, and induced structural disruption. Expansion performance was evaluated by transferring irradiated particles (0.1 g initial mass, spread over 18×18 mm ceramic plates) into graduated test tubes for direct volumetric displacement measurement (V_{exp} in mL; $n=3$ replicates per acid/fluence condition), yielding bulk density via $\rho = m_{\text{exp}} / V_{\text{exp}}$ (g/mL). Statistical analysis employed two-way ANOVA (factors: acid [H_2SO_4 vs HNO_3] × fluence [8 levels: 254–1020 J/cm²]; Type II sums of squares: acid $F=148.56$ $p<0.0001$, fluence $F=10.72$ $p<0.0001$, interaction $F=4.31$ $p=0.0018$), supplemented by independent t-tests ($p<0.05$) and nonlinear regressions in OriginPro 2025. Thermal profiles were obtained via coupled TGA-DSC (25–900 °C, 10 °C/min under N_2 /air purge). Structural metrics derived from powder XRD (Cu K α $\lambda=0.15418$ nm; Bragg–Brentano geometry; 5–70° 2 θ at 0.02626° step/59.925 s integration; Pixcel1D detector): interlayer spacing d_{002} via Bragg equation, crystallite size L_c via Scherrer ($K=0.89$ at 002 ~26.5° 2 θ), FWHM broadening (laser-EG vs furnace-EG controls). Morphological evolution (under-expansion → worm formation → collapse) and defect density were imaged via SEM (Vega3 TESCAN). All processing used SciPy v1.13.1/Statsmodels v0.14.4 [3].

4.2.2 Sorption applications

Sorption efficacy of commercial EGs (EG1–EG3, differing intercalant ratios) was quantified per ASTM F726-17 using polypropylene mesh-contained samples (~0.5 g) immersed in recovered marine heavy oil ($\eta=88.6$ cSt@40 °C), equilibrated 30 min (kinetic) or 24 h (equilibrium), followed by 2 min drip; capacities computed as g oil/g EG ($n=3$). Excess oil underwent multi-elemental ICP-OES (calibration 0.1–10 ppm; LOD 0.01–0.1 ppm; analytes Ag/Cd/Cr/Cu/Fe/Ni/Pb/V/Zn) to derive % entrapment. Baseline structural heterogeneity established via SEM (Vega3 TESCAN), powder XRD (Bragg d-spacing $n\lambda=2d \sin\theta$; Scherrer L_c /FWHM at 002/100/004), Raman spectroscopy was used to determine the degree of exfoliation with the ID/IG peak areas at 1350/1580 cm⁻¹, and CHNS elemental analysis (Elementar Vario EL cube) was used to determine residual heteroatom content of the EG samples [5].

4.2.3 Protective coating applications

Kevlar® fabric (49T 968; 335 g/m²; ¼ satin weave) coated with acrylic varnish (Balakryl Venkovní Lak) and EG (0/4.2/12.5/25/37.5 g/m²; dual varnish layers 160+280 g/m²) underwent controlled laser irradiation: 100 W CO₂ (150 Flexi Marcatec; 1×1 cm spot, 50% duty cycle) at fluences 109/160/239/290/410/683/945/1338 J/cm² ($n=4$ –5/coating); wearer's-side damage graded 0–10 (0=complete degradation; 10=no change). Per-fluence one-way ANOVA (EG loading: $R^2=0.79$ –0.98, $F=18$ –310 $p<0.001$), Tukey HSD, two-way ANOVA (loading × fluence), linear/quadratic regressions (protection $\propto$ loading). Expansion height was quantified pre/post expansion via digital calliper. Statistical evaluation was performed via SciPy v1.13.1/Statsmodels v0.14.4. Thermal stability was measured via TGA (25–900 °C, 10 °C/min air, Mettler Toledo. Abrasion resistance per ASTM D4966 (Martindale; 12 kPa, 10k cycles) was measured to determine coating durability. Post-exposure SEM (Vega3 TESCAN) cross-sections revealed intumescent char depth/adhesion [9].

4.2.4 Conductive applications

4.2.4.1 PES/EG composites

Tensile properties followed ISO 527-2 Type 1A (Tiratest 2300; 23 °C/50% RH; 2 mm/min to rupture, $n=5$). Sample densities were calculated ($\sim 0.8\text{--}1.16\text{ g/cm}^3$), which enabled specific σ/E ($\text{MPa/cm}^3\cdot\text{g}$) determination. Surface resistivity (ρ_s , Ω/sq) per ASTM D257 ($\log_{10}$ -transformed; 2-probe collinear 1 cm gap; HP 4339B high- $p > 10^8\ \Omega\ \text{uEG/CF}$; Agilent 53131A low- $p < 10^8\ \Omega\ \text{vacEG/hybrids}$; 10 reads/specimen). Fracture morphology was analysed via SEM (Vega3 TESCAN). Powder XRD (Philips PANalytical PRO MPD Cu $K\alpha$; $5\text{--}50^\circ\ 2\theta$) was used to determine FWHM and d-spacing. Statistics: Q-test outliers ($\alpha=0.05$); one-way ANOVA (5 families)/Tukey HSD ($p<0.05$); regressions ($\rho_s \propto \text{EG wt}^{-1.20}$). FEA validation: ANSYS 2024 R2 Explicit Dynamics (homogenised orthotropic, quasi-static tensile matching experimental failure). Statistical evaluation was performed via SciPy v1.13.1/Statsmodels v0.14.4 [20].

4.2.4.2 Nanofibrous yarns

AC electrospun nanofibrous yarns (TUL PV 2022-370; PA/PVB/PVA matrices + uEG / mGraph / PEDOT:PSS; disc 200 mm, 35 kV/50 Hz, twirler 9000 rpm, winding $1\text{--}1.8\text{ m/min}$) were characterised for multifunctionality. Linear density was determined gravimetrically. Bulk resistance was measured and used to determine single yarn resistance (HP 4339B LCR; 1 cm gauge, 100 V, 10A, 24°C , 42 %RH). Tensile properties were measured to determine the effect of filler addition (Instron 3343; ASTM D2256-adapted: 50 mm gauge, $20\text{--}50\text{ mm/min}$, 1 N; $n=10$; tex-normalised $\sigma_{\text{max}}\text{ cN/tex}$, $\epsilon_{\text{break}}\%$). Cytocompatibility per ISO 10993-5 (DMEM extracts $37^\circ\text{C}/24\text{--}72\text{ h}$; L929 fibroblasts $10^4/\text{well}$; MTT 570 nm/LDH kinetic; one-way ANOVA/Kruskal-Wallis vs negative control $p<0.05$, $n=8$). Filler retention was measured by TGA (residue at $760\text{--}780^\circ\text{C}$ under air). Yarn structure was analysed using SEM (Vega3 TESCAN). Statistical evaluation was performed via SciPy v1.13.1/Statsmodels v0.14.4 [19].

4.2.5 Data availability

This dissertation and the work comprising it were prepared in accordance with open data-sharing principles. The raw data and the processing thereof, including simulations, are available in the following repositories for select manuscripts. All other data are presented as generated.

COETZEE, D. (2026). Measurement data for laser-exfoliation of sulfuric and nitric acid GICs (1.0 Initial upload) [Data set]. Zenodo. <https://doi.org/10.5281/zenodo.18877246>

COETZEE, D. (2026). Raw and processed data for Laser Protective Kevlar Manuscript (1.0 Initial upload) [Data set]. Zenodo. <https://doi.org/10.5281/zenodo.19153611>

COETZEE, D. (2026). Tensile and Electrical Measurement Data for Improving the Mechanical and Electrical Properties of PES Resin EG Composites [Data set]. Zenodo. <https://doi.org/10.5281/zenodo.18625999>

4.3 Results and discussion – controllable exfoliation

4.3.1 Expansion behaviour and process window mapping

The expansion volume and bulk density of the H_2SO_4 - and HNO_3 -GICs, illustrated in Figure 1, which were expanded by laser, are presented in the graph in Figure 2.

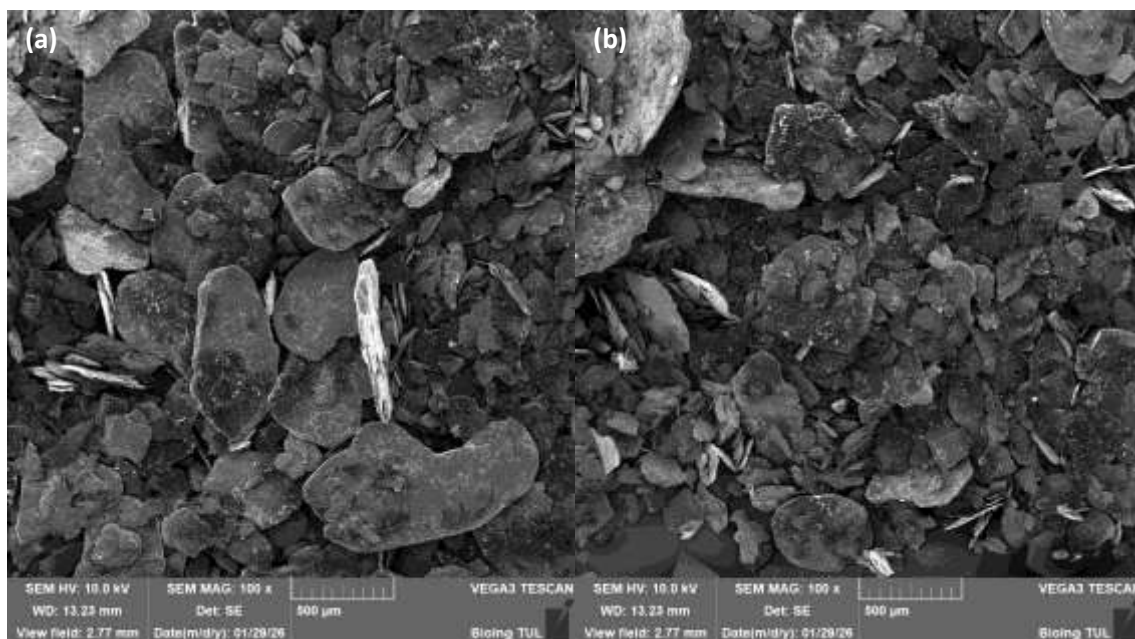


Figure 1: SEM of (a) unexpanded H_2SO_4 -GIC; (b) unexpanded HNO_3 -GIC [3].

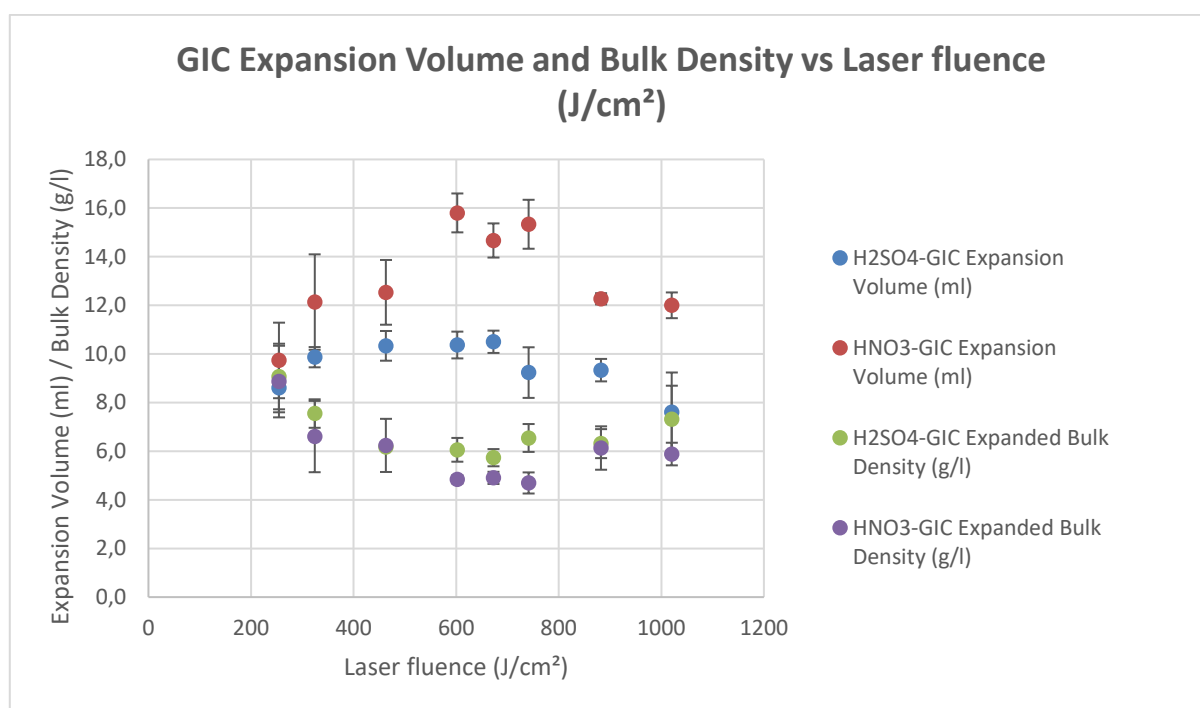


Figure 2: Expansion volume and bulk density of H_2SO_4 - and HNO_3 -GICs expanded by laser at varying fluence [3].

- Low fluence ($254\text{--}324\text{ J}\cdot\text{cm}^{-2}$) produced modest expansion for both H_2SO_4 - and HNO_3 -GIC, with partial “worms” and unreacted particles visible in SEM, indicating only partial decomposition due to insufficient local energy [3].

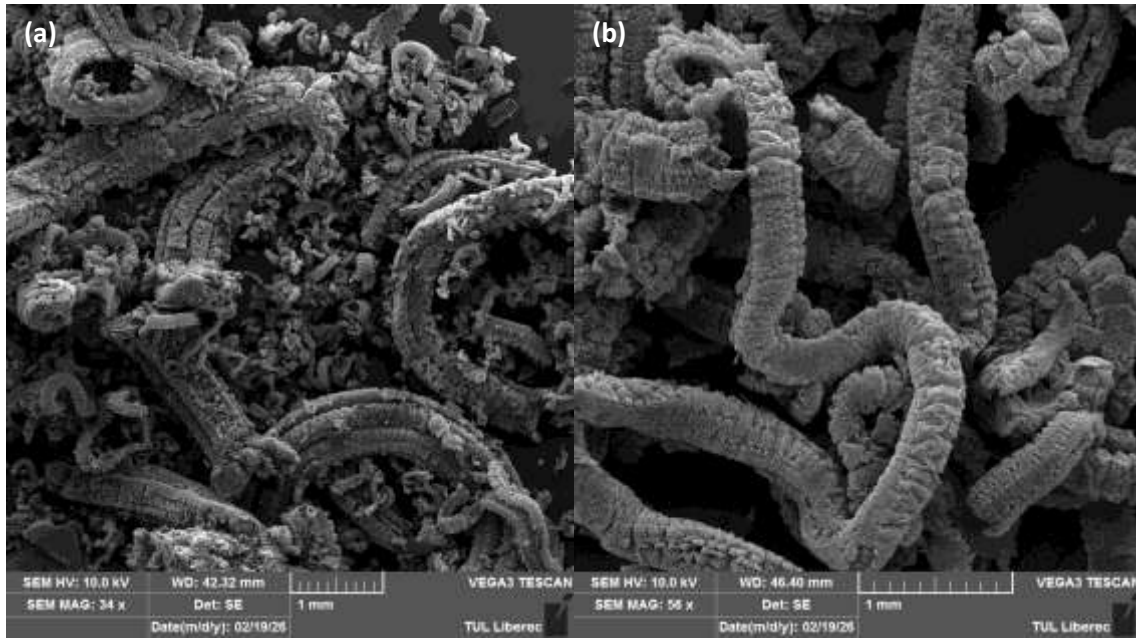


Figure 3: SEM of (a) H_2SO_4 - and (b) HNO_3 -GICs expanded under 254 J/cm^2 [3].

- Intermediate fluence ($463\text{--}741 \text{ J}\cdot\text{cm}^{-2}$) revealed a clear divergence: HNO_3 -GIC expanded significantly more than H_2SO_4 -GIC, peaking at $15.80 \pm 0.80 \text{ mL}$ at $602 \text{ J}\cdot\text{cm}^{-2}$, with well-developed, open worm morphologies evident in SEM [3].

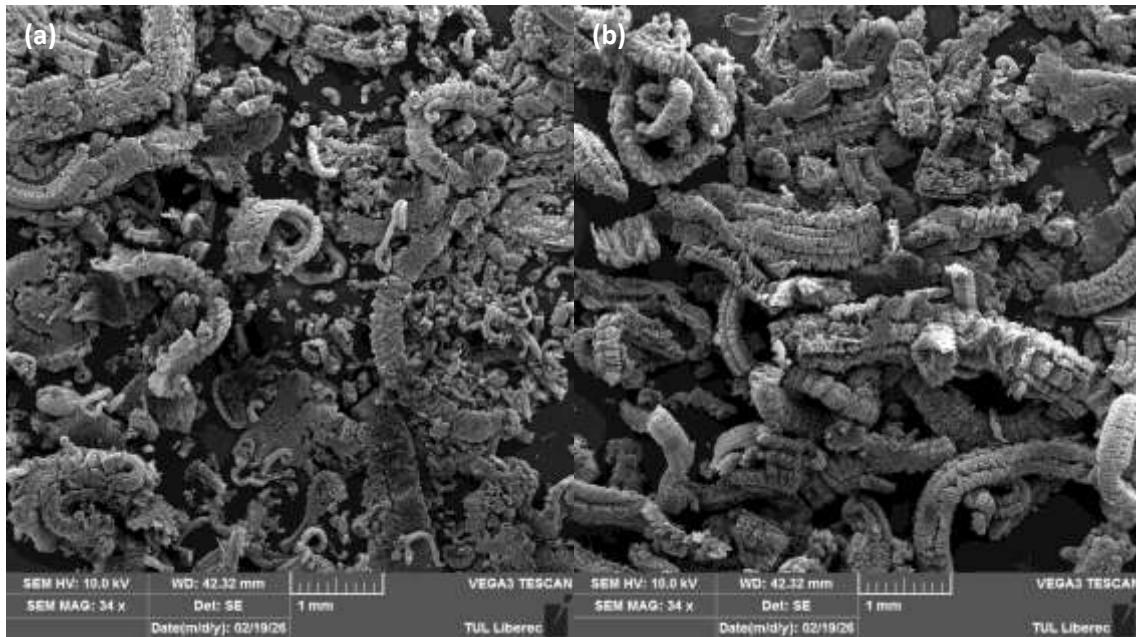


Figure 4: SEM of (a) H_2SO_4 - and (b) HNO_3 -GICs expanded under 673 and 602 J/cm^2 respectively [3].

- High fluence ($882\text{--}1020 \text{ J}\cdot\text{cm}^{-2}$) showed that both systems plateaued or declined in effective expansion, with compacted and fractured worms indicating over-expansion and structural collapse, while two-way ANOVA confirmed that acid type, fluence and their interaction significantly shape the expansion response, with HNO_3 -GIC outperforming H_2SO_4 -GIC most strongly in the $600\text{--}750 \text{ J}\cdot\text{cm}^{-2}$ window [3].

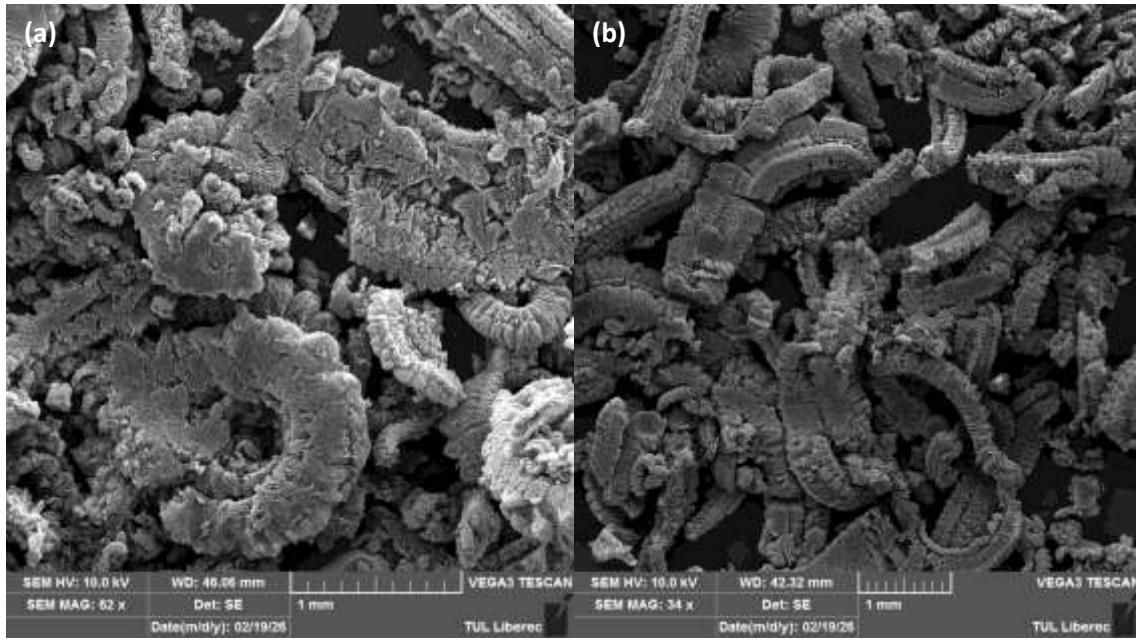


Figure 5: SEM of (a) H_2SO_4 - and (b) HNO_3 -GICs expanded under 1020 J/cm^2 [3].

- Bulk density trends confirm porosity evolution across fluence levels, with both acids forming dense EG (6–9 g/L) at low fluences and no significant inter-acid difference.
- At intermediate fluences ($\approx 600\text{--}750 \text{ J}\cdot\text{cm}^{-2}$), HNO_3 -EG shows significantly lower density than H_2SO_4 -EG ($p = 0.0152$), indicating higher porosity and more efficient intercalant conversion.
- At high fluences, density differences diminish ($p \geq 0.16$), suggesting both acids converge toward similarly compacted microstructures.
- Two-way ANOVA confirms acid type and fluence significantly affect density ($p < 0.01$), but without interaction— HNO_3 -EG remains overall less dense while following a comparable density–fluence profile.
- An optimal fluence window ($\approx 600\text{--}750 \text{ J}\cdot\text{cm}^{-2}$) is identified for HNO_3 -GIC, maximising volume and porosity while avoiding collapse, validating hypothesis H1.
- Furnace expansion reverses the laser trend: H_2SO_4 -EG attains lower density (4.21 g/L) and larger worm-like pores than HNO_3 -EG (6.18 g/L), due to higher intercalant loading and vigorous redox gas evolution.
- Thermal-shock behaviour aligns with industrial norms favouring H_2SO_4 for greater volumetric yield, while laser processing uniquely benefits HNO_3 due to its faster reaction kinetics.
- Overall, laser-induced local heating enhances HNO_3 -GIC exfoliation efficiency, whereas H_2SO_4 -GIC expansion remains more effective under uniform high-temperature shock.

4.3.2 Thermo-analytical mechanisms of intercalant decomposition

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine how the decomposition pathways of H_2SO_4 - and HNO_3 -GICs underpin the distinct expansion regimes observed under laser irradiation, as illustrated in Figures 6 and 7.

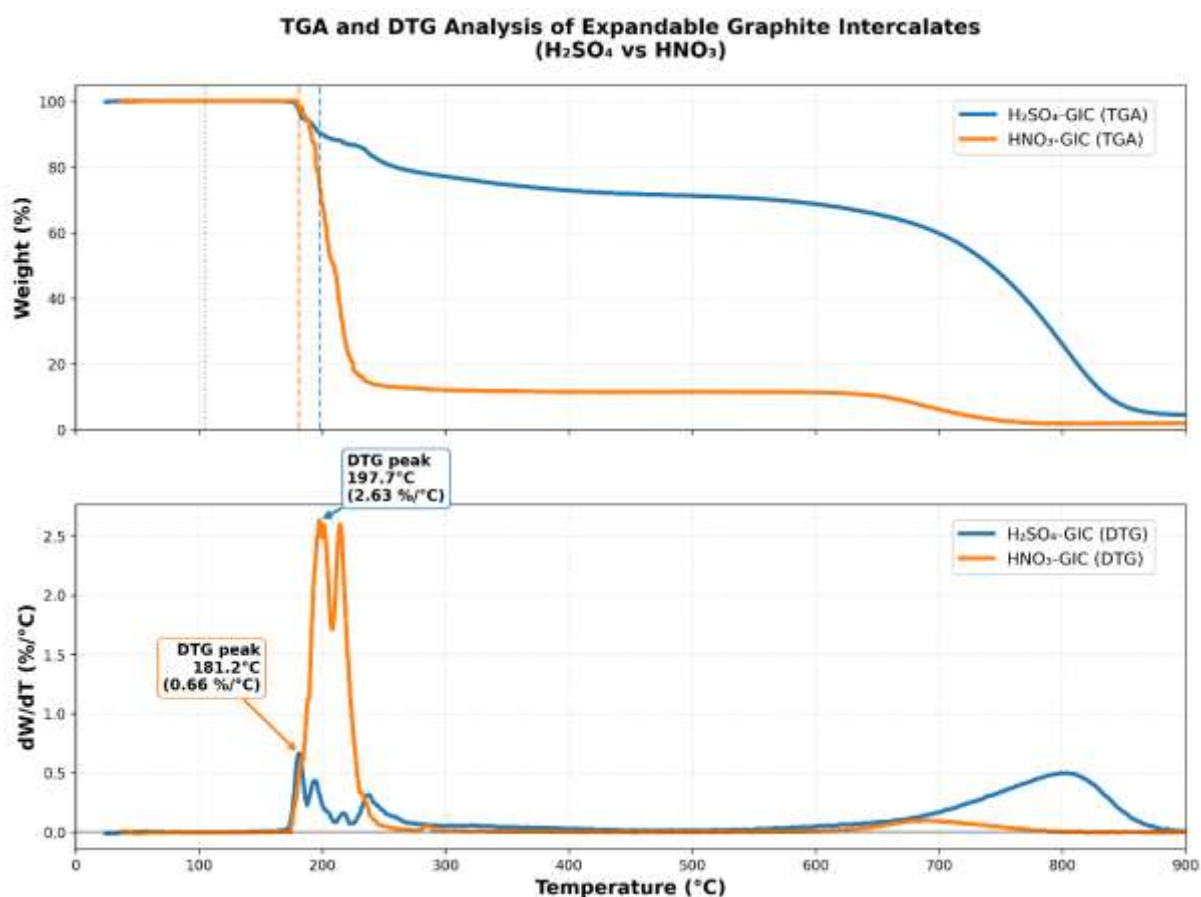


Figure 6: TGA (top) and DTG (bottom) of H₂SO₄- and HNO₃-GICs [3].

- H₂SO₄-GIC exhibited broad, multi-stage decomposition, with the main mass-loss event occurring between ~105 and 500 °C and a DTG peak at 197.7 °C (2.632%·°C⁻¹) [3], [14], [22].
- HNO₃-GIC showed a narrower decomposition window, with major mass loss between 140 and 300 °C and a lower DTG peak at 181.2 °C (0.663%·°C⁻¹), indicating more rapid deintercalation and gas evolution [3], [12], [30], [36].

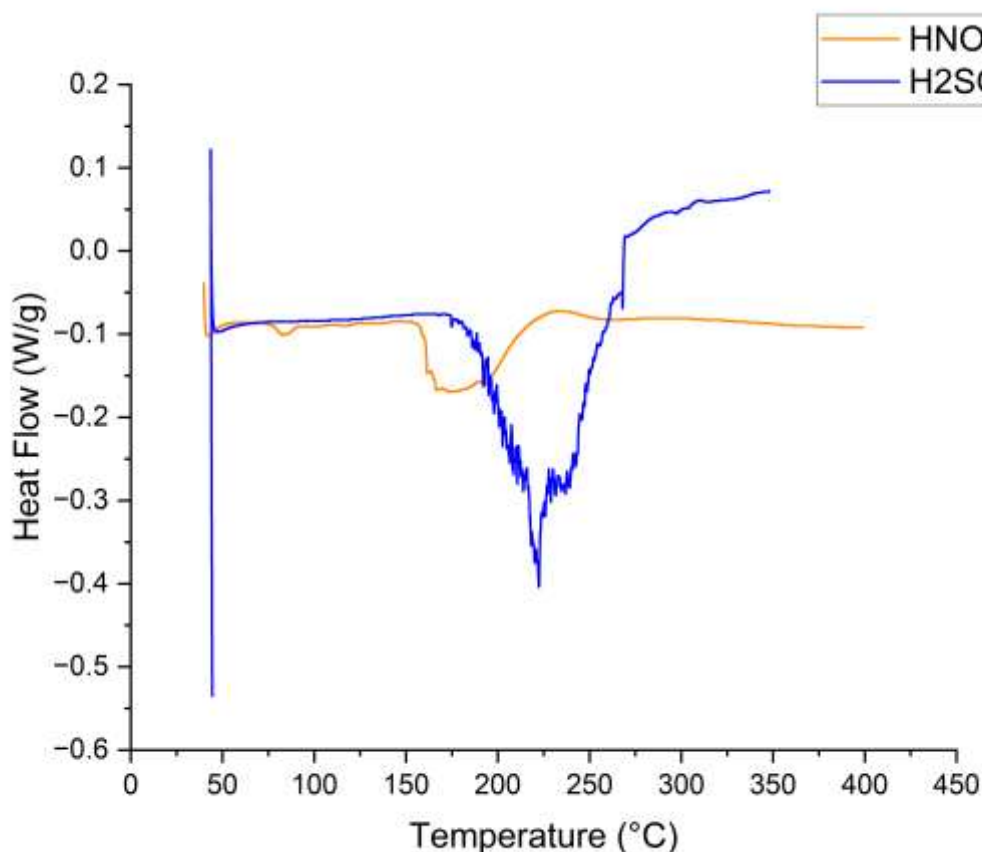


Figure 7: DSC of H_2SO_4 - and HNO_3 -GICs [3].

- DSC confirmed distinct thermal signatures for the two GICs: HNO_3 -GIC showed a minor endotherm at ~ 80 – 120 $^{\circ}\text{C}$ and a main event starting at ~ 153 $^{\circ}\text{C}$ with a peak at 173 $^{\circ}\text{C}$ (≈ -0.170 $\text{W}\cdot\text{g}^{-1}$), whereas H_2SO_4 -GIC exhibited a delayed, broader response beginning near 167 $^{\circ}\text{C}$ and peaking at ~ 222 $^{\circ}\text{C}$ with a larger magnitude (≈ -0.404 $\text{W}\cdot\text{g}^{-1}$) [3].
- These differences show that HNO_3 -GIC deintercalates at lower temperature within a narrower window, while H_2SO_4 -GIC undergoes broader redox-driven gas evolution and structural oxidation [3].
- Together with the expansion data, these thermal signatures explain the intercalant-dependent process window in Section 4.3.1 and support Objective O2 and Hypothesis H2, by showing that decomposition kinetics and microstructural descriptors predict functional performance in sorption and coating applications [3].

4.3.3 XRD evidence of structural disruption and defect generation

X-ray diffraction measured laser-induced disruption in H_2SO_4 - and HNO_3 -GICs and benchmarked EG against controls. Peak positions and FWHM from corrected spectra, with crystallite size and interlayer spacing calculated via specified equations. Raw FWHM from the (002) peak used in Scherrer equation without correction. Instrumental broadening (~ 0.05 – $0.10^{\circ} 2\theta$) is less than 15% of measured FWHM, leading to conservative estimates of cap L_c (~ 0.20 – 0.24 nm). This maintains relative differences, supporting greater nanocrystalline fragmentation in HNO_3 systems.

Equation 3: Scherrer's equation for crystallite size [3].

$$D = \frac{K\lambda}{\beta \cos(\theta)}$$

Equation 4: Bragg's equation for interlayer spacing [3].

$$d = \frac{\lambda}{2\sin(\theta)}$$

Where, β = FWHM in radians, $\theta = (2\theta) / 2$ and $\lambda = 0.15418 \text{ nm} / 1.5418 \text{ \AA}$.

Table 1: XRD data of GICs and laser-expanded samples with their determined peak angle and FWHM used to calculate the crystallite size and interlayer spacing [3].

Sample	GIC Type	Laser fluence (J/cm ²)	Peak Position (2 θ °)	FWHM (°)	Crystallite Size, D, (nm)	Interlayer Spacing, d, (Å)
H ₂ SO ₄ -GIC	H ₂ SO ₄		26.21	0.7175	0.23	3.49
255 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	255	26.24	0.8017	0.20	3.48
324 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	324	26.26	0.7309	0.22	3.48
463 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	463	26.24	0.7273	0.22	3.48
602 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	602	26.24	0.7206	0.23	3.48
673 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	673	26.24	0.7085	0.23	3.48
741 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	741	26.26	0.6858	0.24	3.48
883 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	883	26.24	0.7292	0.22	3.48
1020 Joule/cm ² H ₂ SO ₄ -GIC	H ₂ SO ₄	1020	26.32	0.7180	0.23	3.48
Furnace Expanded H ₂ SO ₄ -GIC	H ₂ SO ₄		26.29	0.7281	0.23	3.48
HNO ₃ -GIC	HNO ₃		25.90	0.5141	0.29	3.53

(Second Peak)	HNO ₃		26.55	0.2243	0.82	3.45
(Third Peak)	HNO ₃		27.92	0.8536	0.92	3.29
255 Joule/cm² HNO₃-GIC	HNO ₃	255	26.21	0.7587	0.21	3.49
324 Joule/cm² HNO₃-GIC	HNO ₃	324	26.26	0.7389	0.22	3.48
463 Joule/cm² HNO₃-GIC	HNO ₃	463	26.26	0.7143	0.23	3.48
602 Joule/cm² HNO₃-GIC	HNO ₃	602	26.29	0.7297	0.23	3.48
673 Joule/cm² HNO₃-GIC	HNO ₃	673	26.24	0.7137	0.23	3.48
741 Joule/cm² HNO₃-GIC	HNO ₃	741	26.26	0.7580	0.22	3.48
883 Joule/cm² HNO₃-GIC	HNO ₃	883	26.24	0.6957	0.23	3.48
1020 Joule/cm² HNO₃-GIC	HNO ₃	1020	26.26	0.7334	0.22	3.48
Furnace Expanded HNO₃-GIC	HNO ₃		26.29	0.7210	0.23	3.48

- The (002) peak position remained close to graphite for all samples, showing that laser and furnace expansion mainly altered stacking coherence and defect density, not the average interlayer spacing [3].
- Laser-expanded H₂SO₄-GIC showed broader peaks and slightly smaller crystallite sizes than the furnace control, indicating increased microstrain, stacking faults and progressive vertical fragmentation with fluence [3].
- Laser-expanded HNO₃-GIC displayed the strongest disorder, with broader peaks, smaller crystallites and additional sub-peaks linked to mixed staging and domain heterogeneity during rapid deintercalation [3].
- Overall, laser processing produced a more defect-rich and heterogeneous EG structure than furnace expansion, and these XRD descriptors support Hypothesis H2 by linking crystallographic disorder to later differences in sorption and coating performance.

4.3.4 The mechanistic difference observed between traditional thermal shock and laser exfoliation.

- Furnace expansion favours H_2SO_4 -GIC, because high, uniform heating allows stage-1 bisulfate to decompose throughout the galleries, generating greater gas volume and lower bulk density [22], [23].
- HNO_3 -GIC gives higher density under furnace shock, likely because its stage-2 structure and pre-deintercalation reduce the effective gas pressure available for full exfoliation [18], [37].
- Laser expansion reverses this trend, since the short, localised heat pulse matches the rapid deintercalation kinetics of HNO_3 -GIC, producing more intense gas evolution and greater porosity at intermediate fluences.
- Overall, the opposite density hierarchy reflects the interaction between intercalant chemistry and heating profile: furnace shock benefits H_2SO_4 -GIC, while laser heating benefits HNO_3 -GIC.

4.3.5 Structure–process–property relationships for EG

- The combined expansion, thermal, and XRD data establish a structure–process–property framework showing that laser fluence and intercalant chemistry define distinct, intercalant-dependent process windows, with an intermediate fluence range for HNO_3 -GIC that maximises expansion and porosity and supports Hypothesis H1.
- Structural descriptors from TGA/DSC, XRD, Raman and SEM show that H_2SO_4 -GIC produces more moderate expansion and more coherent crystallites, making it suitable for protective coatings and conductive applications, whereas HNO_3 -GIC yields highly porous, defect-rich EG that is better suited to oil sorption [3], [5].
- This framework also explains the downstream property trends: high-expansion, low-density EG favours oil uptake, while more crystalline or narrowly structured EG supports heavy-metal entrapment, coating integrity and conductivity–strength trade-offs in composites and yarns [19], [20].
- Overall, the thesis demonstrates that laser exfoliation is a tunable process rather than a simple alternative to furnace expansion, directly addressing Objectives O1–O5 and Hypotheses H1–H4.

4.4 Results and discussion – environmental sorption and filtration

This section discusses O2 (relating microstructure to expansion behaviour) and O3 (quantifying EG microstructure–sorption relationships) by analysing three commercial thermally expanded graphenes (EG1–EG3) for oil sorption and heavy metal removal from used oil. It tests RQ2, which asks how variations in porosity, crystallinity, and surface chemistry predict oil uptake and metal sorption, and H2, suggesting that microstructural metrics from controlled expansion correlate with these properties. Unlike the model GICs studied under laser expansion in Section 4.3, these materials result from industrial thermal-shock expansion of mixed H_2SO_4 - HNO_3 GICs, providing a real-world benchmark. The goal is to show how variations in exfoliation, crystallinity, and heteroatom content, shaped during thermal shock, influence oil uptake, metal affinity, and the potential for waste-oil purification.

4.4.1 Structural and compositional differences in commercial EGs

4.4.1.1 Elemental analysis of EGs

Elemental analysis showed that the three commercial EGs differ in their overall heteroatom contents, as illustrated in Table 2. This provided a basic indication of residual impurities and oxidative history rather than a quantitative fingerprint of the exact intercalant composition.

Table 2: Elemental analysis of EGs [5].

Sample	N %	C %	H %	S %	Rest %
EG1	0.96	91.57	0.10	1.41	5.97
EG2	0.80	98.80	0.04	0.30	0.06
EG3	0.11	96.65	0.03	0.60	2.62

- EG1 had the highest sulphur and slightly elevated nitrogen, consistent with a more heavily oxidised, predominantly sulfuric-acid-derived material [5].
- EG2 showed the highest carbon purity and the lowest sulphur, indicating a cleaner mixed-acid EG produced under milder conditions [5].
- EG3 had intermediate sulphur but the lowest nitrogen, suggesting a more nitrate-influenced and comparatively crystalline grade based on the following XRD section. The Nitrogen presence was the most difficult to quantify by this method due to its lower degree of physical interaction with the graphene layers [5].
- Overall, the elemental data support a qualitative distinction between sulphur-rich, mixed-acid, and nitrate-influenced EG grades, although any inference on specific functionalisation remains tentative without targeted spectroscopy [5].

4.4.1.2 Raman spectroscopic analysis of EGs

- Raman spectroscopy showed a clear exfoliation/defect trend of EG1 > EG2 > EG3, with ID/IG values of 0.0669, 0.0213 and 0.0085, respectively [5].
- This is consistent with EG1 originating from a strongly oxidised, stage-1 bisulfate precursor under aggressive thermal shock, whereas EG3 likely contained more gently expanding graphite nitrate domains [5].
- Overall, the Raman results suggest that oil sorption should favour EG1, while metal entrapment in narrower, more ordered galleries may favour EG3 [5].

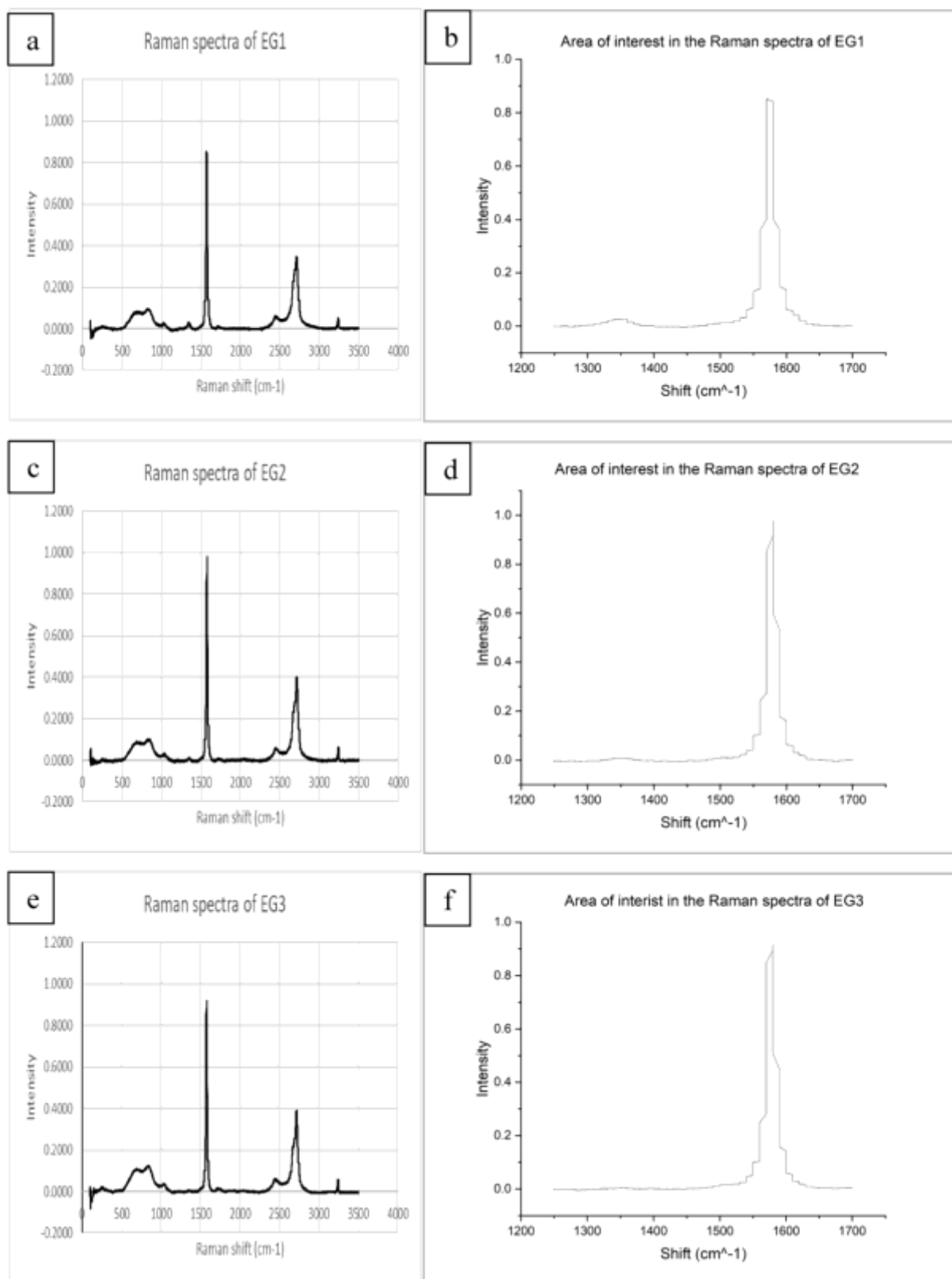


Figure 8: (a) Raman diffraction of EG1; (c) EG2 and (e) EG3 with their respective areas of interest for analysis (b, d, f) [5].

4.4.1.3 XRD of EGs

- XRD confirmed that EG3 retained the most graphitic order, with the sharpest (002) peak and the largest crystallite size [5].

- EG1 and EG2 showed broader peaks and smaller crystallites, indicating greater microstrain, disorder and fragmentation from more severe expansion [5].
- These differences are consistent with the furnace-expansion mechanism, where stage-1 bisulfate GICs undergo more violent expansion, while stage-2 nitrate GICs preserve more crystalline order with varying degrees of layer exfoliation and fragmentation [5], [18].

Table 3: XRD of EG1-EG3 [5].

	Peak angle (2θ)	Peak Area	FWHM	Peak area percentage of total (%)	Interlayer distance, d (Å)	Crystallite size, D (nm)
EG1	15.44	3653.18	3.06	10.58	5.74	0.05
	19.95	16247.74	4.60	47.05	4.45	0.03
	26.67	12269.53	1.28	35.53	3.34	0.11
	36.14	57.59	1.32	0.17	2.48	0.11
	42.78	168.07	0.87	0.49	2.11	0.17
	44.54	1749.07	2.50	5.06	2.03	0.06
	54.88	390.47	1.23	1.13	1.67	0.13
Avg					3.12	0.09
EG2	15.46	7171.64	3.56	13.14	5.73	0.04
	20.19	28804.45	4.54	52.78	4.39	0.03
	26.69	15491.65	0.71	28.39	3.34	0.20
	36.17	284.75	2.00	0.52	2.48	0.07
	42.75	554.96	1.13	1.02	2.11	0.13
	44.65	1773.92	1.42	3.25	2.03	0.10
	54.85	493.76	0.70	0.90	1.67	0.22
Avg					3.11	0.11
EG3	14.66	2790.93	1.73	2.70	6.04	0.08
	19.91	38691.69	6.10	37.36	4.46	0.02
	26.61	56500.47	0.38	54.56	3.35	0.37
	42.48	479.36	0.42	0.46	2.13	0.35
	43.40	674.09	0.73	0.65	2.08	0.20
	44.58	2338.60	1.15	2.26	2.03	0.13
	54.73	2082.29	0.42	2.01	1.68	0.36
Avg					3.11	0.22

4.4.1.4 SEM of EGs

- EG1 represents a highly exfoliated, sulphur-rich, worm-like EG with large meso-/macropores and high defect density, analogous to strongly expanded H_2SO_4 -GIC [5].
- EG2 is a more moderate, cleaner porous scaffold, combining significant exfoliation with lower heteroatom content [5].
- EG3 is a more crystalline, partially expanded grade influenced by nitrate-rich staging, featuring lower overall porosity but a heterogeneous hierarchy of narrow gallery-type cavities that enhance heavy-metal selectivity, differences that are subtle in SEM and mainly resolved by spectroscopic and diffraction analysis [5].

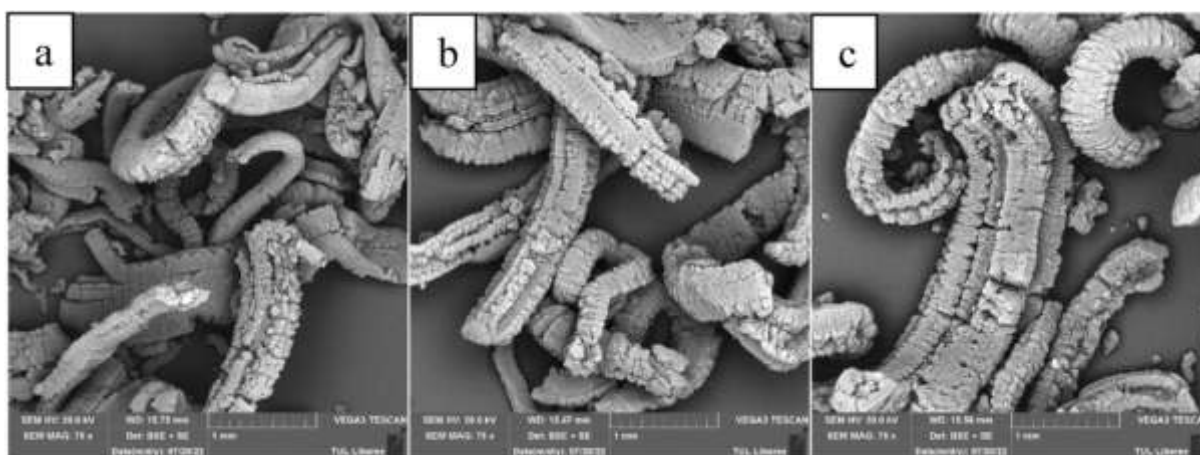


Figure 9: (a) SEM images of samples EG1, (b) EG2 and (c) EG3 [5].

4.4.2 Oil sorption capacity and kinetics

- EG1 outperformed EG2 and EG3 in oil sorption, reaching 55.16 g/g after 24 h, followed by EG2 (48.82 g/g) and EG3 (37.29 g/g), consistent with its higher exfoliation and defect-assisted porosity [5].
- Kinetics were dominated by rapid capillary uptake into macropores in the first 30 min (≈ 80 –85% of capacity), with a slower 18–20% rise to 24 h as viscous oil diffused into narrower mesopores and interlayer galleries [5].
- The ranking $\text{EG1} > \text{EG2} > \text{EG3}$ in both capacity and uptake rate reflects the structural hierarchy: EG1 has the most open, defect-rich worms (Due to predominant Stage 1 H_2SO_4 -GIC expansion), EG2 is a cleaner but still highly porous scaffold, and EG3 is more compact and crystalline with smaller pore volumes (Characteristic of HNO_3 -GIC expansion) [5].
- Overall, these results confirm that heavier expansion and lower density correlate with higher oil uptake and faster kinetics, directly fulfilling Objective O3 and answering Research Question RQ2 [5], [7], [23], [37].

4.4.3 Heavy metal sorption profiles from oil

Oil sorption is governed by pore volume and accessibility, but removing heavy metals from used oil adds complexity, relying on physical entrapment and chemical interactions with the carbon surface. In this study, ICP-OES measured the metal content of excess heavy oil after contact with each EG grade

for 30 min and 24 h, determining removal percentages for elements like Pb, Ni, V, Fe, Cd, As, Li, and others. The results of this analysis are illustrated in Figure 10. [5].

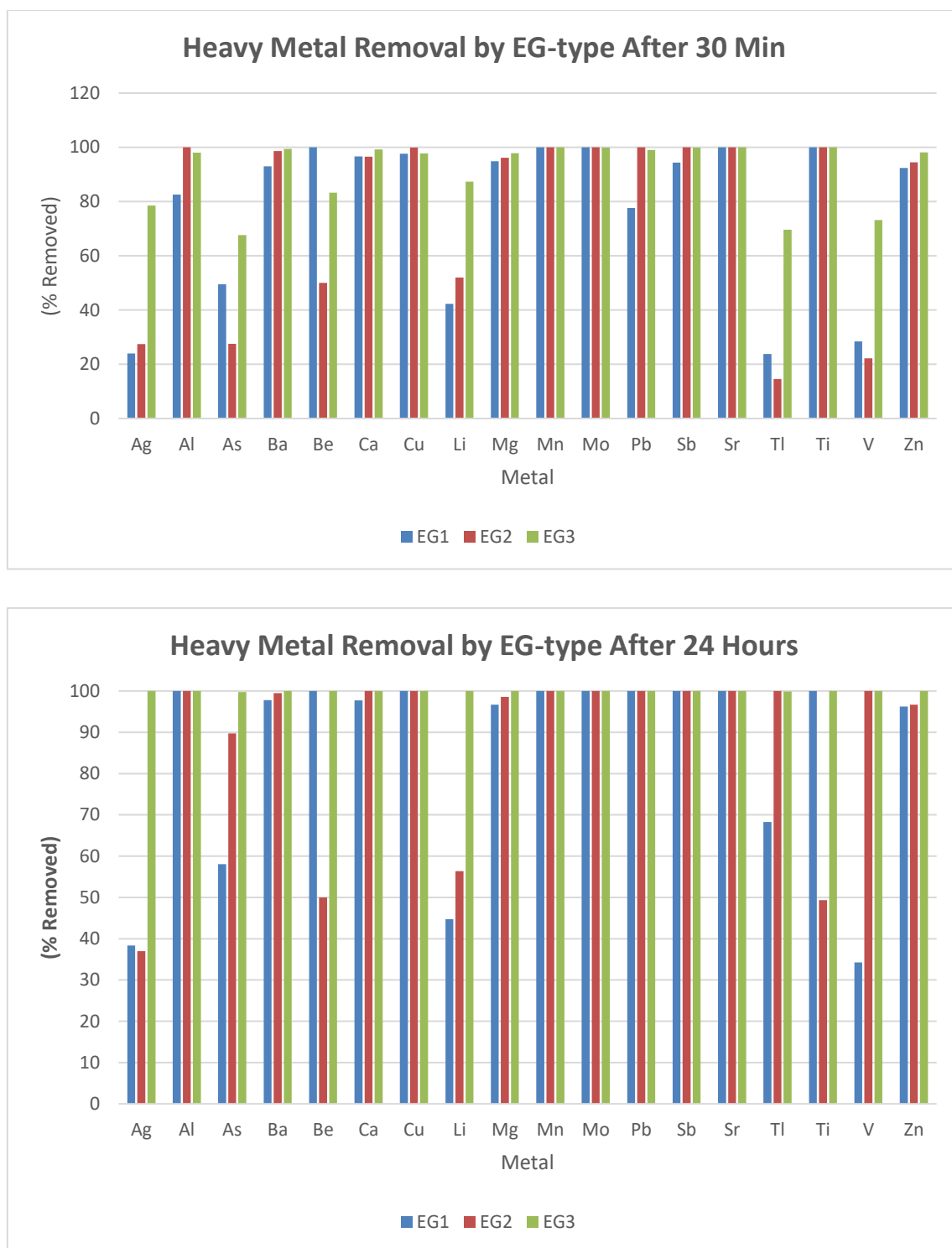


Figure 10: Results of heavy metal removal from used marine oil by EG after 30 min of filtration (top) and 24 hours (bottom) [5]

- All three EGs removed essentially 100 % of Pb from heavy oil after 24 h without any added metal-oxide phases, highlighting the strong affinity of Pb for graphitic/defect sites in this hydrophobic environment [5], [38], [39].

- EG2 showed slightly better performance for arsenic and lithium, while EG3 gave the broadest and most consistent high removal across multiple metals, especially transition and post-transition metals, already at 30 min [5].
- The selectivity differences are explained by two mechanisms: (i) structural entrapment in pore and interlayer architecture (more open EG1 vs confined EG3) and (ii) chemical interactions with residual heteroatoms and functional groups introduced by intercalation and thermal shock [5], [7], [37].
- EG1's elevated sulphur content supports strong cation coordination, EG2 behaves as a cleaner carbon sorbent driven by dispersion and defect-based interactions, and EG3 combines nitrate-rich staging with narrow interlayer galleries that enhance size-selective entrapment and coordination, particularly for soft Lewis acids like Pb^{2+} [5], [7], [12], [22], [37].
- EG3's staged graphite nitrate history thus produces a heterogeneous but relatively narrow distribution of interlayer gaps, enabling high multi-metal selectivity despite lower oil capacity, consistent with the hypothesis that nitrate-rich expansion history tunes selectivity beyond bulk porosity.

4.4.4 Implications for oil filtration and waste-oil purification

- EG1–EG3 are all effective oil sorbents, with capacities up to 55.16 g/g, confirming that commercial thermally expanded graphite is competitive with leading sorption materials [5], [7], [23].
- The grades differ in application focus: highly expanded, sulphur-rich EG1 is best for rapid oil removal and volume reduction, while more crystalline, nitrate-influenced EG3 is better suited to recovering oils that also contain metals [5], [7], [38], [39].
- Near-quantitative Pb removal without added oxides shows that unmodified EG can simultaneously capture oil and certain metals, reducing the need for more complex chemical treatment [5].
- Overall, the results support EG as a sustainable platform for oil recovery and waste-oil purification, with grade selection determined by whether the priority is maximum oil uptake or broader multi-metal removal [5].

4.5 Results and discussion – laser-protective composites

This section assesses how acrylic-expandable graphite coatings turn Kevlar into an active intumescent barrier under 100 W laser, relating coating design, irradiation response, expansion, thermal stability, and abrasion resistance to Hypothesis H3 and research goal O4.

4.5.1 Coating design and microstructure

The coating system includes H_2SO_4 -GIC in a water-borne acrylic varnish applied to Kevlar 49T (335 g/m² ¼ satin weave) in three steps: 160 g/m² base varnish, spreading of EG at 4.2 to 37.5 g/m², and a 280 g/m² topcoat. This setup concentrates EG near the surface for easy expansion, while the acrylic matrix wets and binds the coating to the textile, enhancing adhesion and abrasion resistance. As noted in section 4.3, H_2SO_4 -GIC absorbs energy through multistage exfoliation, ensuring good coverage. Providing adequate coverage [9], [22].

- Cross-sectional SEM (Figure 11) reveals that the coating penetrates only the uppermost Kevlar layers and that EG expansion is strongly anisotropic, with worm-like char growing outward at the air interface and densifying into a compact barrier near the fibre bed [9].

- This morphology is typical of intumescent EG coatings, where a low-density, insulating char cap forms over a more consolidated, mechanically cohesive layer that maintains adhesion and integrity [24], [25].

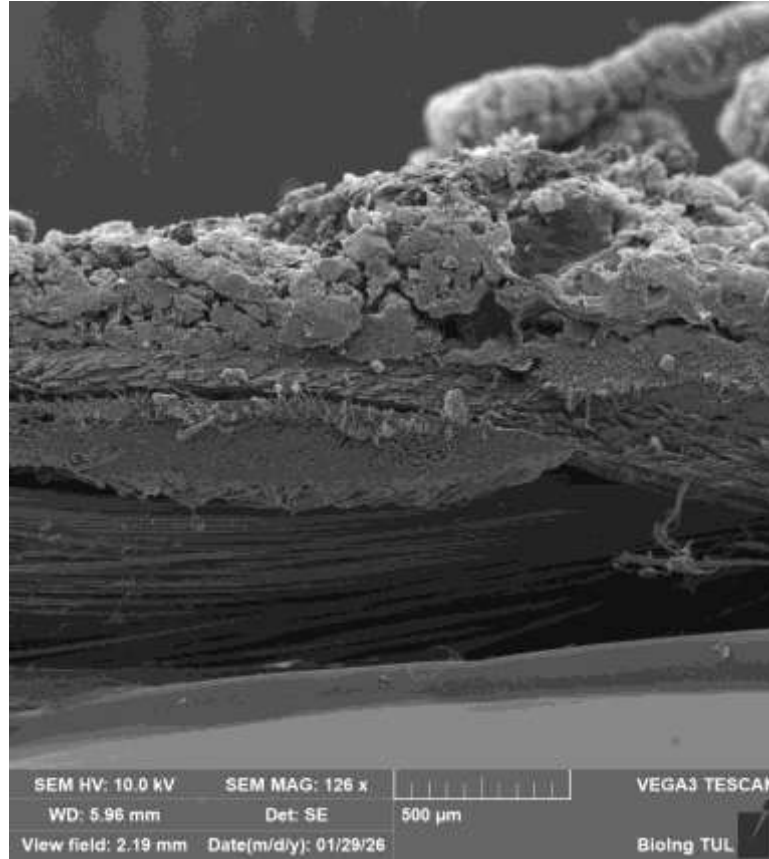


Figure 11: Cross-section of the sample irradiated at 410 J/cm² with loading 25 g/m² EG [9].

4.5.2 Laser irradiation response and protection grading

- Protection grading (Table 4) showed a clear dose–response: unfilled coatings degraded rapidly with fluence, while H₂SO₄-GIC-filled samples maintained high grades, with 25 g/m² sustaining near-perfect ratings (9–10) up to 239–290 J/cm² [9].
- ANOVA and regression confirmed that EG areal density explains most of the variance in grade, with protection improving approximately monotonically as H₂SO₄-GIC loading increases [9].
- At 25 g/m², the coating prevented detectable back-side thermal damage up to 290 J/cm² and retained a significant protective advantage even at the highest fluence (1338 J/cm²), demonstrating that the intumescent EG char effectively shields Kevlar from direct laser heating [9].

Table 4: Protection grading of laser irradiated samples containing H₂SO₄-GIC vs fluence [9].

	Irradiation intensity (Joule/cm ²)							
H ₂ SO ₄ -GIC content (g/m ²)	109	160	239	290	410	683	945	1338
0	8.4	6.4	4.0	3.0	3.0	2.0	0.6	0.0
4.2	9.8	8.0	7.6	7.0	4.0	4.0	2.8	0.0
12.5	10.0	9.8	8.2	8.0	4.2	4.0	3.0	2.3
25	10.0	10.0	10.0	9.0	6.8	4.0	3.8	3.0
37.5	10.0	10.0	9.0	9.0	7.2	4.2	4.0	3.2
Grading Scale								
0	Complete degradation of the irradiated area							
1	Almost complete degradation of the irradiated area							
2	Significant degradation of the irradiated area with hole formation							
3	Graphitisation with Kevlar degradation							
4	Graphitisation of the full irradiated area							
5	Onset of graphitisation							
6	Thermal damage of the full irradiated area							
7	More significant thermal damage							
8	Minimal signs of thermal damage							
9	Slight visual difference or particle penetration							
10	No visible change							

4.5.3 Thickness of expansion

- Expansion thickness increased with H₂SO₄-GIC loading but in a non-monotonic way, peaking around 4.2 g/m² (≈792 %) before dropping at 12.5 g/m² and recovering at 25–37.5 g/m², with a quadratic fit confirming that crowding and dispersion control effective expansion [9].
- Despite maximising expansion at 4.2 g/m², the best protection grades were achieved at 25 g/m², showing that high performance requires not only large expansion but also a sufficiently thick, continuous and mechanically robust char layer [9].

- These results indicate that optimum protection balances expansive EG filling with coating continuity, so that the intumescent char shields Kevlar without becoming overly porous or fragile [9].

Table 5: Increase in EG layer thickness after irradiation in terms of % height increase at given fluence [9].

	Irradiation intensity (Joule/cm ²)							
H ₂ SO ₄ -GIC content (g/m ²)	109	160	239	290	410	683	945	1338
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4.2	605.9	723.5	868.6	868.6	866.7	915.7	745.0	745.0
12.5	362.2	462.2	486.6	525.6	629.3	745.1	632.5	767.5
25	428.0	566.7	656.0	697.3	837.3	876.6	968.8	868.8
37.5	473.8	593.8	700.0	876.3	900.0	912.5	1189.6	1185.7

4.5.4 Thermogravimetric behaviour of coatings

- Pure Kevlar is highly thermally stable, whereas coating with acrylic alone lowers onset temperatures and leaves much less char, reflecting the binder's lower stability and poor charring ability, as indicated in the TGA results in Figure 12 [9].
- Adding 25 g/m² H₂SO₄-GIC shifts the system to an intermediate regime: mass loss starts earlier due to acrylic and intercalant decomposition, but the main Kevlar scission peak occurs at nearly the same temperature and T₅₀% rises, indicating that EG-driven charring helps stabilise the structure and redistribute heat [9].
- The lower final residue with H₂SO₄-GIC reflects volatile release from both acrylic and intercalant, showing that the EG char is more porous and transient under slow heating, whereas under fast laser exposure it forms a dynamic, low-conductivity buffer that is critical for real-time protection but not fully evident in TGA residue alone [9].

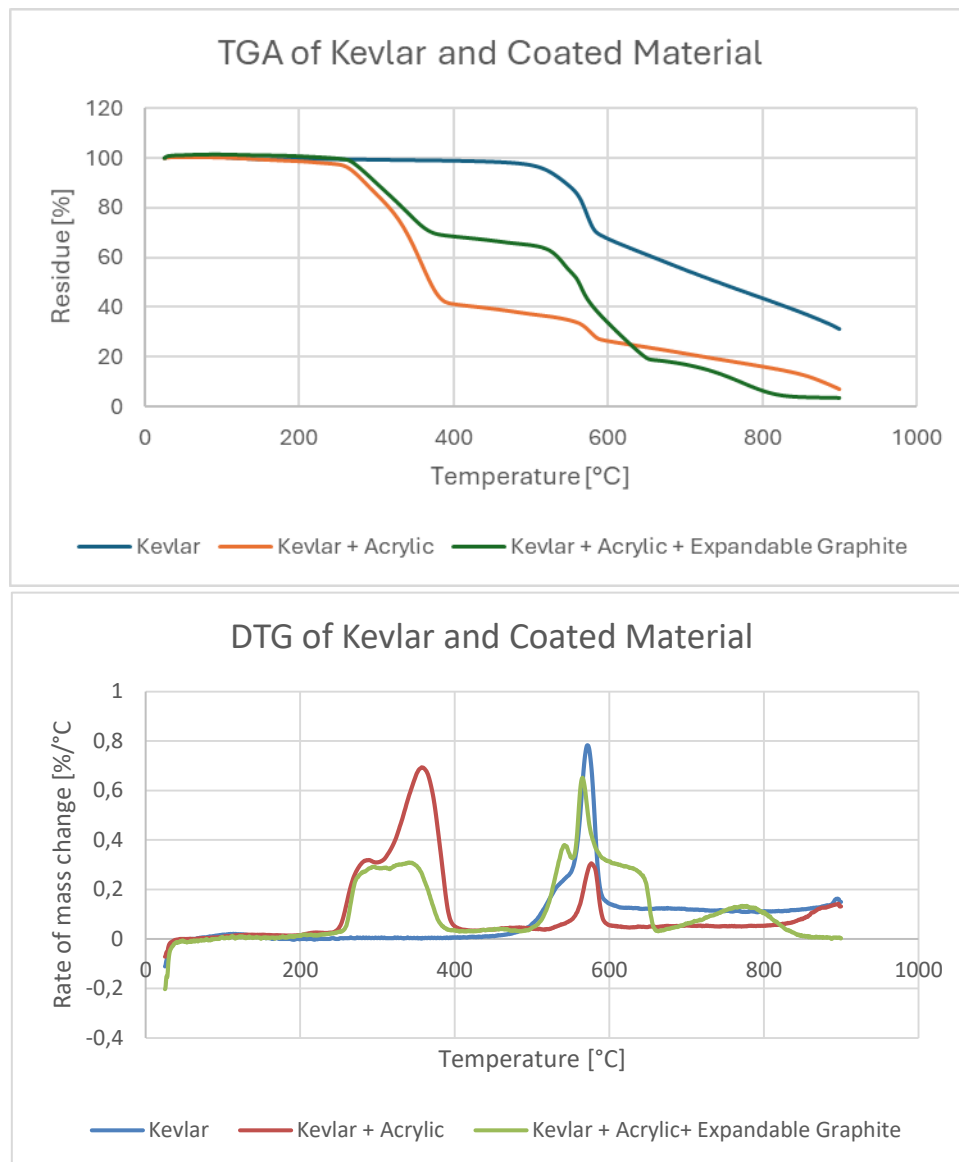


Figure 12: TGA and DTG curves of Kevlar material and the coated material containing 0 and 25 g/m^2 H_2SO_4 -GIC [9].

4.5.5 Abrasion durability

- Martindale testing (10,000 cycles, 12 kPa) showed that the acrylic + H_2SO_4 -GIC coating (25 g/m^2) reduced mass loss dramatically compared with uncoated Kevlar, demonstrating that the coating acts as a durable, wear-resistant layer [9].
- Visual and SEM inspection confirmed that coated samples retain a smooth, intact surface with no underlying fibre damage, indicating that the EG-reinforced char remains mechanically supported by the acrylic varnish and Kevlar network [9].
- With abrasion resistance comparable to light-to-moderate use standards, the coating architecture proves suitable for practical protective-textile applications [9], [40].

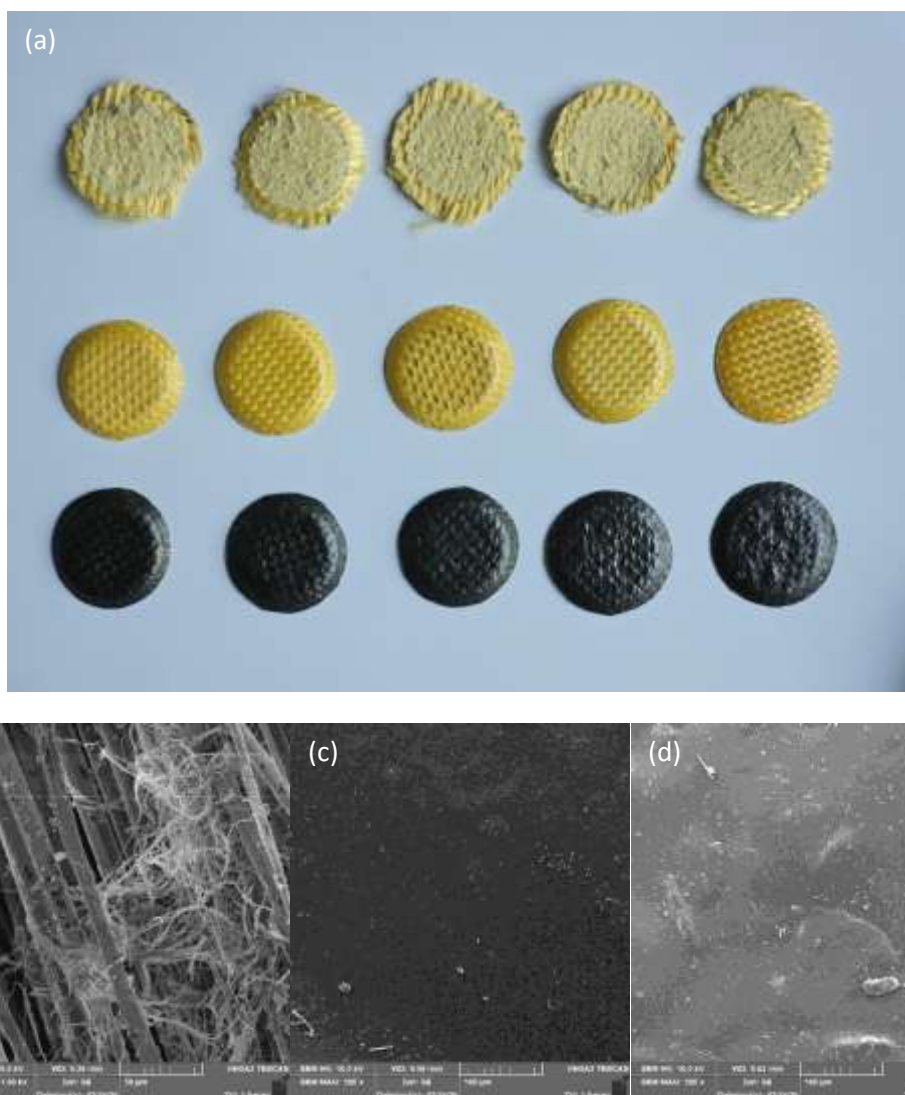


Figure 13: Image of samples after subject to abrasion testing (a) (top) Kevlar untreated, (middle) Kevlar with acrylic, (bottom) Kevlar with expandable graphite acrylic coating. SEM images of (b) Kevlar untreated, (c) Kevlar with acrylic, d) Kevlar with expandable graphite acrylic coating [9].

4.5.6 Implications for laser protective wear

Martindale testing showed that the acrylic + H_2SO_4 -GIC coating (25 g/m^2) reduced mass loss dramatically compared with uncoated Kevlar, demonstrating that the coating acts as a durable, wear-resistant layer [9].

Visual and SEM inspection confirmed that coated samples retain a smooth, intact surface with no underlying fibre damage, indicating that the EG-reinforced char remains mechanically supported by the varnish and Kevlar network [9], [41].

With abrasion resistance comparable to light-to-moderate use standards, the coating architecture proves suitable for practical protective-textile applications [9], [42], [43].

4.6 Results and discussion - Conductive composites

This section showed that EG morphology enabled conductivity in both bulk PES resin composites and nanofibrous yarns, despite trade-offs. The PES composites used vacuum-processed EG and EG/CF hybrids to achieve low resistivities at moderate filler loadings, but with lower tensile strength.

Nanofibrous yarns favoured biocompatibility and scalability, accepting lower conductivity and yarn strength for cytocompatible, carbon-based networks.

4.6.1 Application overview and rationale

Conductive EG composites in viscous PES resin were primarily targeted at structural or semi-structural components where electrical percolation and mechanical integrity had to be balanced. For example, in conductive housings, EMI shielding panels, or current-carrying secondary elements are bonded to stiffer substrates. In this context, the key questions were whether EG-based fillers could deliver surface resistivities in the tens-of-ohms range at practical loadings and how strongly this conflicted with tensile strength and stiffness in a relatively high-viscosity thermoset [20].

By contrast, the nanofibrous yarns are a novel field of research, and their scalability has advanced more recently with the invention of the patented AC electrospinning process developed at the Technical University of Liberec [44]. The aim was to deliver highly porous, flexible, and biocompatible conductors suitable for flexible sensors or biomedical interfaces, with scalable processing. uEG and PEDOT:PSS were therefore combined with degradable or semi-degradable polymers (PA, PVB, PVA) so that the same EG-based chemistry used in the PES composites also underpinned a yarn-like architecture intended to operate at different positions in the strength–conductivity–biocompatibility design space [19], [45], [46].

4.6.2 Microstructure and filler architecture

- Figure 14 SEM shows that vacEG forms highly porous, worm-like networks in PES (d), while uEG creates finer, more resin-wetted graphene-like sheets (c), and CF appears as short rods with debonding (a, b); in hybrids (b), EG builds a near-continuous conductive skeleton with CF acting mainly as a mechanical reinforcement [20].
- Figure 15 SEM reveals that uEG in nanofibrous yarns reaches nanometre-thick, micrometre-wide flakes only partially embedded in PA/PVB/PVA fibres, often protruding or bridging between them, which limits both conductivity and strength [19].
- TGA and retention data show that PVB and PA matrices best retain carbon fillers during AC electrospinning, with PVB mGraph achieving ~30 wt% incorporation and PVB uEG/pedot-based PVA systems showing synergistic recovery, whereas uEG losses of 10–40% highlight the role of filler morphology, electrostatics, and processing speed in governing final loading and performance [19].

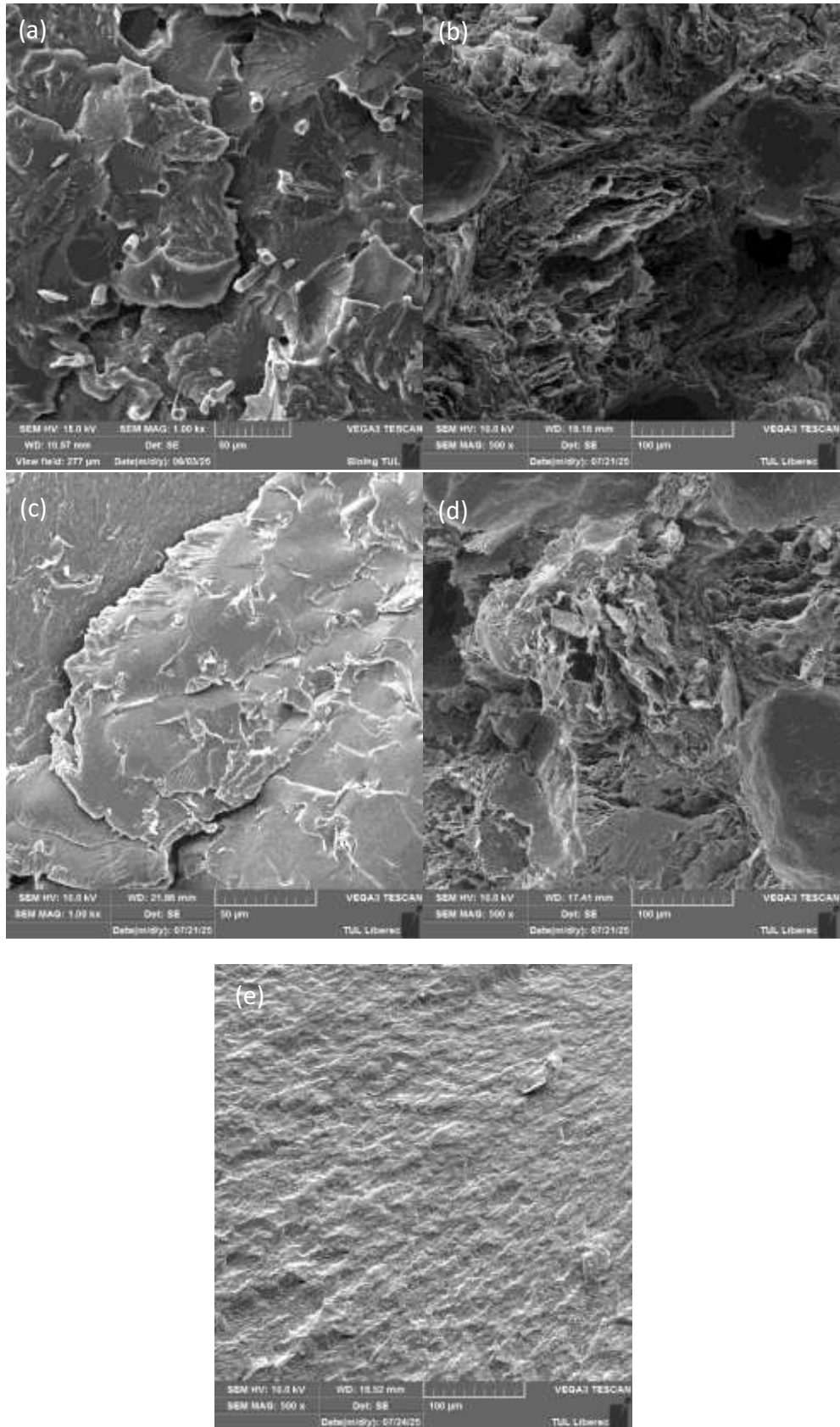
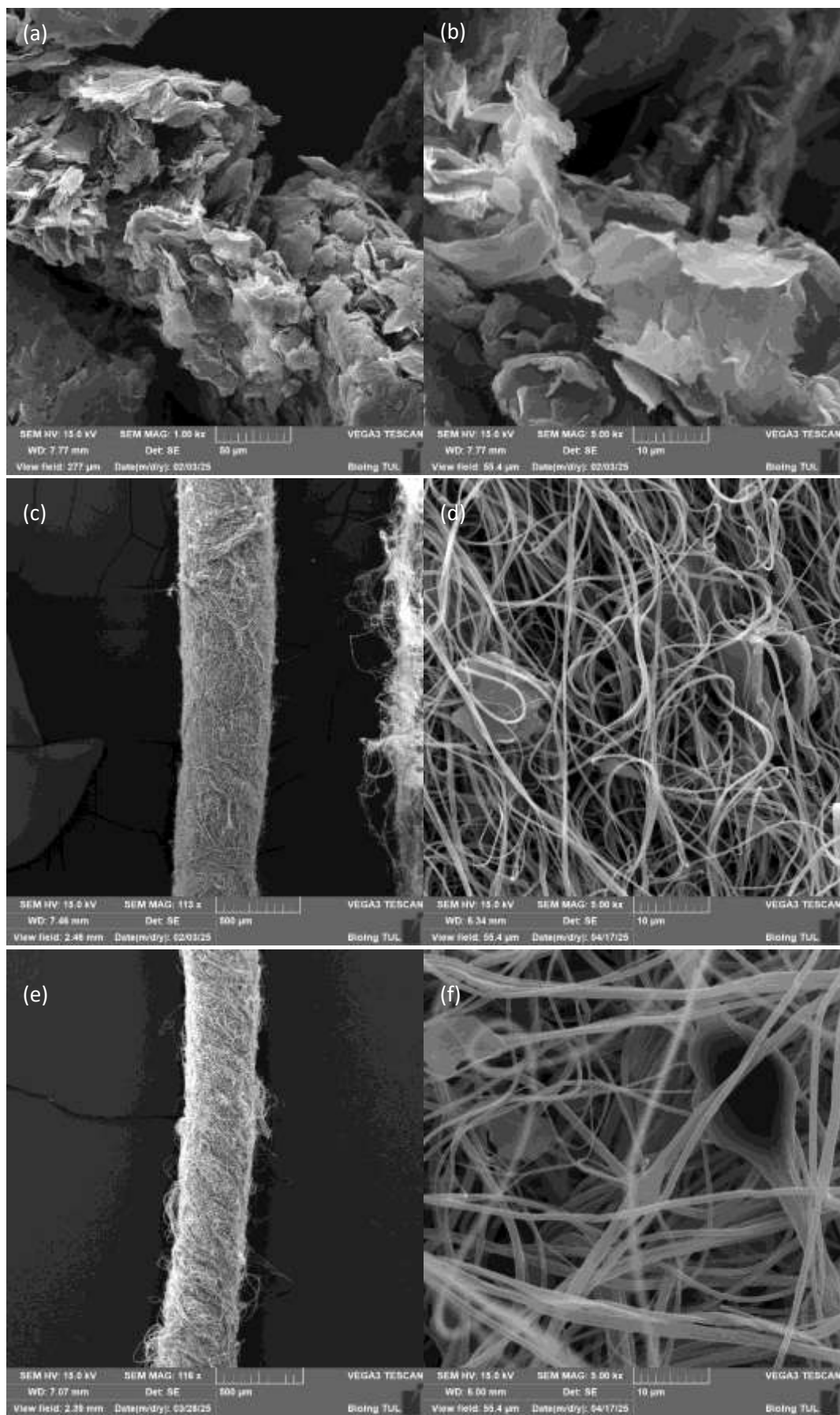


Figure 14: SEM images of samples (a) 5%CF, (b) 5%CF5%EG, (c) 5%uEG, (d) 5%vacEG, (e) polyester resin with no filler [20].



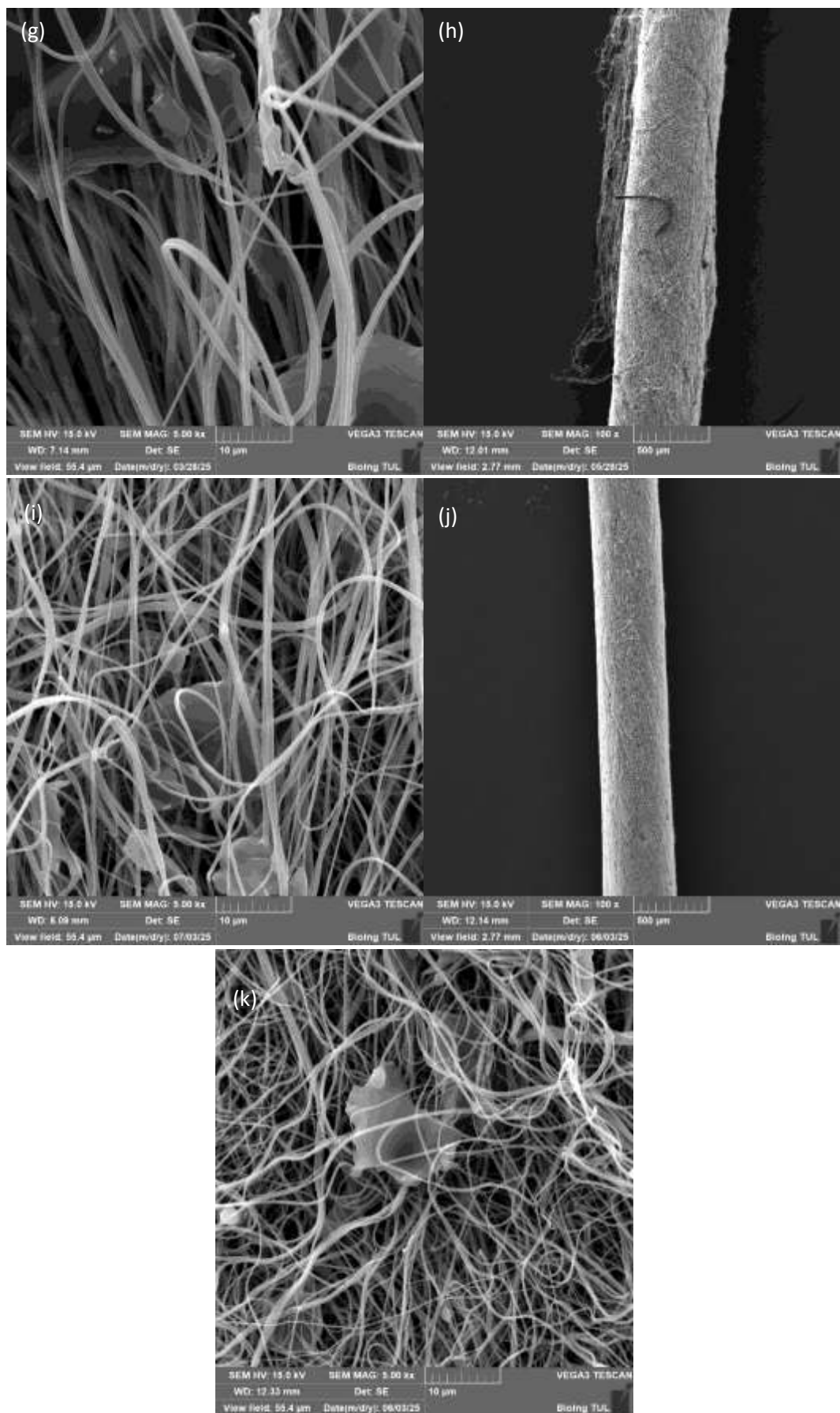


Figure 15: SEM of uEG at 1000x magnification (a); uEG at 5000x magnification (b); nanofibrous yarns- (c) pure PVA; (d) magnified image of PA yarn containing 10 % uEG; (e) pure PVB; (f) magnified image of PVB containing 30 % mGraph; (g) magnified image of PVB containing 20 % uEG; (h) pure PVA (i) PVA containing 10% uEG (j) PVA with PEDOT:PSS (k) PVA:PEDOT:PSS with 10 % uEG [19]

4.6.3 Effect of EG on electrical percolation and resistivity

- Figure 15(a,b) and section-4.3 show that H₂SO₄-EG's homogeneous layer exfoliation and larger crystallite domains preserve more intact, accessible graphene planes, explaining its higher conductivity compared with HNO₃-EG and facilitating platelet separation during ultrasonication [3], [11]. The selection of the H₂SO₄ system was based on previous studies indicating higher electrical conductivity, as explained in the section based on the identified mechanisms [46], [47].
- Electrical data (Table 6) reveal that vacEG and EG-rich CF-EG hybrids drive the PES system into the highly conductive regime (resistivity dropping ~6 orders of magnitude relative to the neat resin), with ANOVA and Tukey's test confirming that vacEG and the EG-rich hybrids are significantly more conductive than uEG-only and CF-only composites ($p < 0.05$) [20].
- Within the uEG series, resistivity falls in the 10^9 – 10^{10} Ω range and ANOVA shows no statistically significant difference from the neat resin or CF-only systems; linear regression of log resistivity versus uEG content yields only a modest negative slope (~0.12 decades per 1 wt %, with non-significant p due to small $n=3$) [20].
- CF-only composites reduce resistivity by ~1–2 orders of magnitude (also 10^9 – 10^{10} Ω), with regression giving a moderate slope of ~0.36 decades per 1 wt % CF ($R^2=0.82$, p just above 0.05), indicating only a weak trend [20].
- In the CF-EG hybrids, multiple linear regression ($R^2=0.94$) shows a strongly negative coefficient for EG content (~0.63 decades per 1 wt % EG, $p \ll 0.05$) and a near-zero, non-significant coefficient for CF; Tukey's HSD confirms that high-EG hybrids (e.g., 3–5 wt % EG) and vacEG composites are statistically indistinguishable in mean resistivity but far more conductive than uEG or CF-only systems, demonstrating that the EG skeleton controls percolation while CF contributes mainly to mechanical, not electrical, performance [20].

Table 6: Electrical resistivity data of PES composite samples [20].

Sample Name	Filler Content %	Resistivity (Ω)	Standard Deviation (Ω)
Neat	0	5.36×10^{11}	7.73×10^{11}
uEG			
1uEG	1	1.08×10^{10}	6.18×10^9
3uEG	3	9.90×10^9	4.40×10^9
5uEG	5	3.75×10^9	9.06×10^8
CF			
Neat	0	5.36×10^{11}	7.73×10^{11}
0.5CF	0.5	1.73×10^{11}	1.52×10^{11}

1CF	1	4.24×10^{10}	3.63×10^9
3CF	3	3.90×10^9	8.10×10^8
5CF	5	3.58×10^9	1.91×10^9
CF/EG Hybrids			
0.5CF-1EG	CF=0.5 / EG=1	1.06×10^4	1.00×10^4
1CF-1EG	CF=1 / EG=1	1.19×10^4	9.71×10^3
3CF-1EG	CF=3 / EG=1	5.64×10^3	8.85×10^3
5CF-1EG	CF=5 / EG=1	1.11×10^4	1.20×10^4
0.5CF-3EG	CF=0.5 / EG=3	274	420
1CF-3EG	CF=1 / EG=3	115	55
3CF-3EG	CF=3 / EG=3	121	53
5CF-3EG	CF=5 / EG=3	152	87
0.5CF-5EG	CF=0.5 / EG=5	28.2	9.65
1CF-5EG	CF=1 / EG=5	24.0	9.61
3CF-5EG	CF=3 / EG=5	24.2	8.72
5CF-5EG	CF=5 / EG=5	34.4	7.15
vacEG			
Neat	0	5.36×10^{11}	7.73×10^{11}
1vacEG	1	1.82×10^6	1.66×10^5
3vacEG	3	1.45×10^3	1.11×10^3
5vacEG	5	29.1	6.07

- Single-yarn measurements (Table 7) show that adding uEG, mGraph or PEDOT:PSS to nanofibrous PA/PVB/PVA yarns reduces resistivity by up to ~2 orders of magnitude versus the neat polymer, but the porous structure and partial particle encapsulation prevent formation of efficient percolating networks, as seen in SEM [19].
- The most conductive yarns, such as PVB 30 wt % mGraph ($\sim 1.8 \times 10^{11} \Omega \cdot \text{cm}$) and PVA 15 wt % PEDOT:PSS + 15 wt % uEG ($\sim 2.2 \times 10^{11} \Omega \cdot \text{cm}$), reach the antistatic regime yet remain far above the tens-of-ohms level in dense PES composites, highlighting the limiting effect of particle separation and low filler connectivity [19].

- Normalisation by tex improved apparent performance (e.g., PVA 15 PEDOT:PSS 15 uEG reaching $\sim 1.37 \times 10^5 \Omega$), but the actual volume-based resistivities emphasise that the yarns are poor conductors, which is acceptable for antistatic and sensing textiles rather than power-carrying wires [19].
- Parallel bundles reduced effective resistivity further (e.g., down to $\sim 4.6 \times 10^9 \Omega \cdot \text{cm}$ for PVA 15 PEDOT:PSS 15 uEG), demonstrating that macroscopic parallelisation can compensate for weak intra-yarn percolation, while preserving the intended functionality in wearable and biocompatible sensor systems [19].

Table 7: Measured electrical resistance, cross-sectional area and calculated single yarn resistance, volume resistivity, linear weight and normalised resistivity of nanofibrous composite yarns [19].

Sample	R of 48 parallel yarns (Ω)	CSA of a single yarn (μm^2)	R of single yarn (Ω)	ρ ($\Omega \cdot \text{m}$)	Tex (g/1000m)	ρ / Tex ($\Omega \cdot \text{m}/\text{tex}$)
PA	1.78×10^{12}	639.6	8.54×10^{13}	5.46×10^6	39.58	2.16×10^8
PA 5 uEG	2.84×10^{11}	293	1.36×10^{13}	3.99×10^5	26.04	1.04×10^7
PA 10 uEG	4.01×10^{10}	515.4	1.92×10^{12}	9.92×10^4	11.84	1.17×10^6
PVB	1.71×10^{12}	439.5	8.21×10^{13}	3.61×10^6	63.68	2.30×10^8
PVB 10 mGraph	8.56×10^{11}	448.1	4.11×10^{13}	1.84×10^6	59.34	1.09×10^8
PVB 20 mGraph	1.31×10^{10}	707.8	6.29×10^{11}	4.45×10^4	78.76	3.51×10^6
PVB 30 mGraph	3.80×10^9	1140.5	1.82×10^{11}	2.08×10^4	66.02	1.37×10^6
PVB 10 uEG	6.61×10^{10}	356.1	3.17×10^{12}	1.13×10^5	42.40	4.79×10^6
PVB 20 uEG fast	7.30×10^9	357.5	3.50×10^{11}	1.25×10^4	41.84	5.24×10^5
PVB 20 uEG slow	1.94×10^{10}	357.5	9.31×10^{11}	3.33×10^4	19.52	6.50×10^5
PVA	3.61×10^{11}	452.4	1.73×10^{13}	7.84×10^5	46.62	3.65×10^7
PVA 10 uEG	3.38×10^{10}	351.5	1.62×10^{12}	5.70×10^4	24.54	1.40×10^6
PVA 10 PEDOTPSS	5.84×10^9	600.5	2.80×10^{11}	1.68×10^4	36.30	6.11×10^5

PVA 10 PEDOTPSS 10 uEG	2.88x10 ¹⁰	372.7	1.38x10 ¹²	5.15x10 ⁴	17.84	9.19x10 ⁵
PVA 15 PEDOTPSS 15 uEG	4.58x10 ⁹	429.3	2.20x10 ¹¹	9.44x10 ⁴	14.50	1.37x10 ⁵

4.6.4 Effect of EG on composite mechanical performance

- Tensile tests (Tables 8–9) show that all graphite-containing PES composites (uEG, vacEG, hybrids) suffered significant reductions in tensile strength and specific strength versus neat PES, with ANOVA and Tukey HSD confirming that these losses are statistically significant ($p < 0.05$), while CF-only composites retained most load-bearing capacity without significant differences from the neat resin [20].
- Modulus and specific modulus reveal a more nuanced picture: neat PES is the stiffest and specific-strength-optimal system, while vacEG and CF are significantly stiffer than uEG and hybrids, and vacEG exhibits by far the highest specific modulus (large positive slope of $\sim 40 \text{ MPa}\cdot\text{cm}^3/\text{g}$ per 1 wt % EG, $R^2 \approx 1$), driven by low density despite porosity-induced strength loss [20].
- Regression within families shows clear negative trends in strength with uEG and vacEG loading, whereas CF has only modestly detrimental effects on strength but strongly reduces both absolute and specific modulus at 5 wt %; in CF–EG hybrids, multiple regression reveals that CF has a small positive effect on load whereas EG reduces ultimate strength but significantly increases specific modulus (significant EG coefficient) [20].
- ANSYS FEA on the 23 PES formulations reproduces experimental ultimate strengths with high fidelity ($R^2 = 0.962$, mean 8.3 % error), capturing neat, low-CF, and moderate-hybrid systems well (< 3 % error), but under-predicting highly porous or heterogeneous systems (e.g., 1 uEG and 5 vacEG with 24–40 % errors), highlighting the limits of homogenised models for defect- and porosity-dominated EG microstructures [20].
- Overall, the data confirm that EG enhances specific modulus and conductivity at the expense of strength in PES, with processing and CF addition only partially compensating for defect-driven losses, directly supporting Hypothesis H2, answering RQ4, and fulfilling Objective O5 by mapping the mechanical-electrical design space for EG-PES composites [20].

Table 8: Tensile test results of PES composites with ANSYS model validation [20].

Sample	Density (g/cm ³)	Measured Breaking Force (N)	Tensile Modulus (MPa)	Spec. Stress (MPa/cm ³ ·g)	Spec. Modulus (MPa·cm ³ /g)	Measured Breaking Stress (MPa)	ANSYS Predicted Stress (MPa)	Rel. Error (%)
Neat PES								
0 Filler	1.16	1354	2210	29.27	1911	33.85	31.44	7.11
uEG								
1 uEG	1.13	961	191	21.85	168	24.03	14.46	39.82
3 uEG	1.15	660	232	14.40	203	16.50	13.54	17.92
5 uEG	1.09	599	206	13.78	190	14.98	12.73	15.02
CF								
0.5 CF	1.13	918	819	20.30	725	22.95	23.45	2.16
1 CF	1.09	980	907	22.53	834	24.50	25.21	2.80
3 CF	1.12	921	860	20.53	766	23.03	23.50	2.03
5 CF	1.11	882	337	19.85	303	22.05	22.07	0.09
vacEG								
1 vacEG	0.96	405	1026	10.55	1068	10.13	10.97	8.29
3 vacEG	0.80	165	934	5.15	1168	4.13	4.51	9.20
5 vacEG	0.80	188	981	5.88	1227	4.70	3.58	23.80
CF/EG Hybrids								
0.5 CF1EG	0.84	498	174	14.83	207	12.45	12.18	2.17
1 CF 1 EG	0.89	386	195	10.83	219	9.65	9.48	1.70
3 CF 1 EG	0.97	563	236	14.55	244	14.08	13.57	3.63

5 CF 1 EG	0.93	644	218	17.28	234	16.10	12.70	21.11
0.5 CF 3 EG	0.73	228	203	7.75	276	5.70	5.58	2.10
1 CF 3 EG	0.68	172	143	6.30	209	4.30	4.27	0.60
3 CF 3 EG	0.74	194	142	6.58	192	4.85	4.98	2.68
5 CF 3 EG	0.73	269	126	9.15	171	6.73	5.81	13.67
0.5 CF 5 EG	0.76	301	184	9.88	241	7.53	7.52	0.13
1 CF 5 EG	0.96	339	356	8.58	371	8.48	8.80	3.70
3 CF 5 EG	0.85	397	249	11.68	293	9.93	9.26	6.70
5 CF 5 EG	0.94	426	345	11.35	368	10.65	10.97	3.40

- Tensile tests on nanofibrous yarns (Table 9) show that all graphite-containing yarns (PVB and PVA) suffer reductions in normalised breaking strength and modulus versus their neat polymer counterparts, with PVB 30 wt % mGraph dropping from 44 MPa/tex to 8 MPa/tex and similarly filled uEG yarns showing comparable losses [19].
- In PVA-based systems, uEG and PEDOT:PSS further reduce normalised strength versus already weak neat PVA (e.g., PVA 15 PEDOT:PSS 15 uEG: 67 MPa/tex vs. 35 MPa/tex for neat PVA), yet some filled compositions retain sufficient integrity for textile handling despite limited aqueous stability [19].
- The microscale filler size, partial encapsulation, and high porosity mean that graphite particles act primarily as defect sites and stiffness inhomogeneities rather than reinforcements, consistent with SEM observations and underscoring the need for finer or better-distributed fillers to improve mechanical performance [19].

Table 9: Tensile measurements of nanofibrous composite yarns [19].

Sample	Measured Breaking Force (N)	Breaking stress, σ (MPa)	σ / Tex (MPa/tex)	Modulus, E (MPa)	E / Tex (MPa/tex)	Elong. (%)
PA	1.08 (0.16)	1689 (250)	43 (6)	13714 (2002)	346 (51)	29.6 (3.1)
PA 5 μ EG	0.68 (0.07)	2321 (239)	89 (9)	8616 (939)	331 (36)	26.4 (2.6)
PA 10 μ EG	0.18 (0.03)	349 (58)	29 (5)	2296 (358)	194 (30)	16.5 (4.2)
PVA	0.73 (0.07)	1614 (155)	35 (3)	9248 (858)	198 (18)	14.6 (2.3)
PVA 10 μ EG	0.43 (0.08)	1223 (228)	50 (9)	5518 (1051)	225 (43)	64.2 (6.4)
PVA 10 PEDOTPSS	1.22 (0.13)	2031 (216)	56 (6)	15508 (1594)	427 (44)	30.8 (5.2)
PVA 10 PEDOTPSS 10 μ EG	0.62 (0.04)	1664 (107)	93 (6)	7951 (546)	446 (31)	13.0 (6.0)
PVA 15 PEDOTPSS 15 μ EG	0.42 (0.05)	978 (116)	67 (8)	5363 (659)	370 (45)	21.4 (2.6)
PVB	1.23 (0.16)	2798 (364)	44 (6)	15613 (2070)	245 (33)	53.5 (11.6)
PVB 10 μ EG	0.29 (0.05)	814 (140)	19 (3)	3678 (700)	87 (17)	28.7 (6.1)
PVB 20 μ EG slow	0.30 (0.03)	839 (84)	43 (4)	3780 (393)	194 (20)	25.3 (6.0)
PVB 20 μ EG fast	0.31 (0.06)	867 (168)	21 (4)	3965 (738)	95 (18)	31.3 (8.3)
PVB 10 mGraph	0.80 (0.17)	1786 (379)	30 (6)	10186 (2216)	172 (37)	33.7 (9.0)
PVB 20 mGraph	1.02 (0.17)	1441 (240)	18 (3)	13007 (2167)	165 (28)	25.1 (6.1)

PVB 30 mGraph	0.63 (0.12)	552 (105)	8 (2)	8059 (1479)	122 (22)	27.4 (9.5)
---------------	-------------	-----------	-------	----------------	----------	---------------

4.6.5 Biocompatibility of EG composite nanofibrous yarns

- Figure 16 cytotoxicity data show that graphite-loaded nanofibrous yarns, despite modest mechanical and electrical performance, significantly improve biocompatibility versus control polymers: uEG and mGraph reduce cytotoxicity, with the highest uEG and mGraph loadings giving the lowest toxicity and several PVB-graphite composites (e.g., 20–30 wt % mGraph) achieving viability statistically comparable to DMEM and significantly higher than Triton ($p < 0.01$) [19].
- One-way ANOVA ($F = 235.54$, $p < 0.0001$) confirms strong group-wise differences, with most graphite-containing yarns and PEDOT:PSS-filled samples significantly outperforming Triton and, for the best-performing systems, not significantly differing from the DMEM control (viability $>70\%$) [19].
- Un-crosslinked PVA was initially cytotoxic but graphite and PEDOT:PSS partially reverse this effect, with high-uEG PVA formulations (e.g., vz 5 and 6) showing non-toxic viability indistinguishable from DMEM yet still significantly better than Triton ($p < 0.01$) [19].
- Overall, the yarns trade conductivity and strength for high biocompatibility, flexibility, and scalability, establishing EG-based nanofibrous yarns as a viable platform for textile-integrated conductors and soft biomedical applications where metals or rigid composites are unsuitable [19].

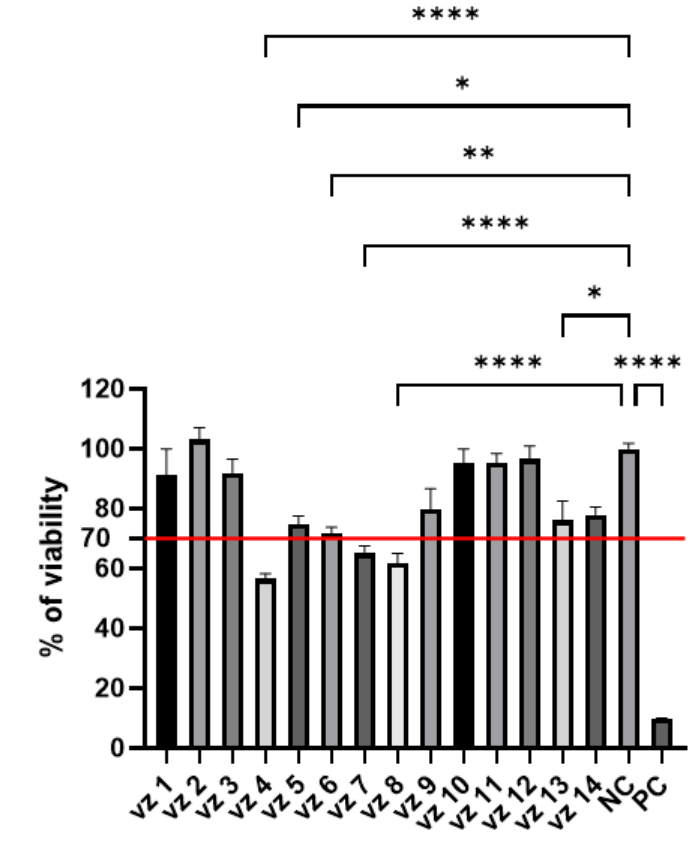


Figure 16: Cytotoxicity analysis with samples : vz 1: PA; vz 2: PA 10% uEG; vz 3: PA 5% uEG; vz 4: PVA; vz 5: PVA 10% uEG; vz 6: PVA 15% PEDOT:PSS 15% uEG; vz 7: PVA 10% PEDOT:PSS; vz 8: PVA 10% PEDOT:PSS 10% uEG; vz 9: PVB; vz 10: PVB 10% mGraph; vz 11: PVB 20% mGraph; vz 12: PVB 30% mGraph; vz 13: PVB 10% uEG; vz 14: PVB 20% uEG slow [19].

4.6.6 Integration back to the core exfoliation framework

- PES composites show that vacuum-processed EG and CF-EG hybrids achieve highly conductive, tens-of-ohms surface resistivity at 3–5 wt % EG (regression slope ≈ 1.2 decades per 1 wt %, $R^2 = 0.97$), but ANOVA confirms that this comes with large, statistically significant strength losses due to the porous, brittle EG skeleton, making them suitable for non-load-bearing, conductive-stiff components [20].
- Nanofibrous yarns constrain uEG-loaded structures to 10^9 – 10^{11} $\Omega \cdot \text{cm}$ due to micrometre-scale filler dimensions, partial encapsulation, and high porosity, limiting intra-yarn percolation, but simultaneously deliver good biocompatibility and flexibility for textile-integrated antistatic or sensing applications [19].
- From a design standpoint, PES-based EG systems fit compact, high-conductivity components where strength is secondary, while EG-nanofibrous yarns fit flexible, biocompatible conductors where modest conductivity and cytocompatibility are prioritised, reinforcing the dissertation's core theme that process-controlled EG morphology governs the coupling of conductivity, mechanics, and biological response, validating Hypothesis H4 and the rationale for selecting H_2SO_4 -derived EG due to its more homogeneous staging and exfoliation, which supports both thermal-shock expansion and ultrasonication to produce uEG.

5 Proposal for further activities within the dissertation topic

5.1 Process-level optimisation and scale-up

Future work should refine laser-exfoliation conditions via in-situ thermal imaging and controlled fluence mapping, then translate the validated process window for different intercalants and staging levels from single-flake geometries to continuous or roll-to-roll platforms, building on existing low-power, high-expansion and high-conductivity demonstrations for industrial-scale EG and graphene-derived architectures [2], [21], [22], [48].

5.2 Advanced structural/chemical characterisation

The thesis shows that subtle differences in crystallite size, interlayer spacing and residual heteroatom content strongly affect sorption and metal selectivity, highlighting the need for advanced techniques such as solid-state NMR, XPS, and in-situ XRD/Raman to build a quantitative, multi-scale process–structure map that decouples the roles of defects, functional groups and staging in functional performance [5], [49].

5.3 Next-generation functional systems

Laser-tuned EG offers direct routes to environmental sorbents, thermal/EMI-management composites, and conductive-yet-biocompatible textiles; by leveraging the laser-defined process window, future work can deliberately engineer EG microstructures to close the loop from controllable exfoliation to application-specific devices such as oil-and-metal-removal sorbents, compact PCM-based thermal modules, and lightweight, multifunctional structural-electrical components [5], [50], [51], [52], [53], [54].

6 References

- [1] J. M. Mendoza-Duarte *et al.*, 'Preparation and Study of an Expanded Graphite Obtained Through Torch and Microwave-assisted Heating', *Microscopy and Microanalysis*, vol. 29, no. Supplement_1, pp. 176–177, Jul. 2023, doi: 10.1093/micmic/ozad067.079.
- [2] R. Elkaffas *et al.*, 'Unprecedented expansion of graphite with low power laser for high-quality liquid phase exfoliated graphene', *Scientific Reports* 2025 15:1, vol. 15, no. 1, pp. 32733–, Sep. 2025, doi: 10.1038/s41598-025-17947-6.
- [3] D. Coetzee and J. Wiener, 'Laser-Induced Controlled Expansion of Sulfuric Acid and Nitric Acid Intercalated Expandable Graphite', *Carbon Trends (Under Review)*, 2026.
- [4] C. S. Chou, S. H. Lin, and C. I. Wang, 'Preparation and characterization of the intumescent fire retardant coating with a new flame retardant', *Advanced Powder Technology*, vol. 20, no. 2, pp. 169–176, Mar. 2009, doi: 10.1016/j.apt.2008.07.002.
- [5] D. Coetzee *et al.*, 'Effects of expanded graphite's structural and elemental characteristics on its oil and heavy metal sorption properties', *Scientific Reports*, vol. 14, no. 1, pp. 1–10, May 2024, doi: 10.1038/s41598-024-64695-0.
- [6] T. Y. Kim, J. H. Park, O. Y. Kim, and S. H. Hwang, 'The effect of chemically modified expandable graphite on flame-retardant properties of waterborne intumescent flame-retardant coating', *Journal of Industrial and Engineering Chemistry*, vol. 149, pp. 366–373, Sep. 2025, doi: 10.1016/j.jiec.2025.01.050.
- [7] M. Vocciant, A. D. F. D'auris, and A. P. Reverberi, 'A Novel Graphite-Based Sorbent for Oil Spill Cleanup', *Materials*, vol. 15, no. 2, p. 609, Jan. 2022, doi: 10.3390/ma15020609.
- [8] X. Tang, B. Liu, and X. Su, 'Low-Temperature Synthesis of Sulfur-Free Expandable Graphite with Minimized Acid Consumption: Preparation, Intercalation Behavior, and Structural Properties', *Diamond & Related Materials*, vol. 158, no. 158, pp. 1–9, Oct. 2025, doi: 10.2139/ssrn.5217916.
- [9] D. Coetzee and J. Wiener, 'Laser-Protective Kevlar with Acrylic-Based Expandable Graphite Coating', *Textiles (Under Review)*, 2026.
- [10] P. Karlsson, 'Intercalation and exfoliation of graphite - For a route to scalable production of conductive inks for printed electronics', PhD Thesis, Chalmers University of Technology, 2016.

- [11] D. Coetzee, J. Militký, J. Wiener, and M. Venkataraman, 'Comparison of the Synthesis, Properties, and Applications of Graphite, Graphene, and Expanded Graphite', in *Advanced Structured Materials*, vol. 201, J. Militký and M. Venkataraman, Eds, Springer, Singapore, 2023, pp. 71–87. doi: 10.1007/978-981-99-6002-6_4.
- [12] P. Scharff, Z. Y. Xu, E. Stumpp, and K. Barteczko, 'Reversibility of the intercalation of nitric acid into graphite', *Carbon*, vol. 29, no. 1, pp. 31–37, Jan. 1991, doi: 10.1016/0008-6223(91)90091-V.
- [13] V. V. Avdeev, N. E. Sorokina, N. V. Maksimova, I. Y. Martynov, and A. V. Sezemin, 'Synthesis of ternary intercalation compounds in the graphite-HNO₃-R (R = H₂SO₄, H₃PO₄, CH₃COOH) systems', *Inorganic Materials*, vol. 37, no. 4, pp. 366–371, 2001, doi: 10.1023/A:1017527827724.
- [14] A. Longo *et al.*, 'INTERCALATION AND EXPANSION OF NOVEL GRAPHITE BISULFATE COMPOUNDS', in *IPACS, Physcon*, Oct. 2017, pp. 17–19. [Online]. Available: <https://lib.physcon.ru/doc?id=81f431262964>
- [15] G. Rimkute, M. Gudaitis, J. Barkauskas, A. Zarkov, G. Niaura, and J. Gaidukevic, 'Synthesis and Characterization of Graphite Intercalation Compounds with Sulfuric Acid', *Crystals 2022, Vol. 12, Page 421*, vol. 12, no. 3, p. 421, Mar. 2022, doi: 10.3390/cryst12030421.
- [16] Y. Geng, Q. Zheng, and J. K. Kim, 'Effects of stage, intercalant species and expansion technique on exfoliation of graphite intercalation compound into graphene sheets', *Journal of nanoscience and nanotechnology*, vol. 11, no. 2, pp. 1084–1091, Feb. 2011, doi: 10.1166/jnn.2011.3063.
- [17] A. G. Bannov *et al.*, 'Highly porous expanded graphite: Thermal shock vs. programmable heating', *Materials*, vol. 14, no. 24, p. 7687, Dec. 2021, doi: 10.3390/ma14247687.
- [18] G. Tarango-Rivero *et al.*, 'Effect of Process Parameters on the Graphite Expansion Produced by a Green Modification of the Hummers Method', *Molecules*, vol. 27, no. 21, p. 7399, Nov. 2022, doi: 10.3390/molecules27217399.
- [19] D. Coetzee, J. P. P. Aguilera, J. Wiener, and J. Militký, 'Scalable AC Electrospinning of Biocompatible Nanofibrous Yarns Based on Expanded Graphite and PEDOT:PSS', *Polymers (Under Review)*, 2026.
- [20] D. Coetzee, J. P. P. Aguilera, J. Wiener, and A. Tegginamath, 'Influence of Carbon Fibre, Ultrasonication and Vacuum Processing on the Mechanical and Conductive properties of Expanded Graphite Polyester Resin Composites.', *Polymers*, vol. 18, no. 6, p. 731, Mar. 2026, doi: <https://doi.org/10.3390/polym18060731>.
- [21] G. Carotenuto *et al.*, 'Laser-Induced Thermal Expansion of H₂SO₄-Intercalated Graphite Lattice', *Journal of Physical Chemistry C*, vol. 119, no. 28, pp. 15942–15947, Jul. 2015, doi: 10.1021/jp512800j.
- [22] M. Salvatore, G. Carotenuto, S. D. Nicola, C. Camerlingo, V. Ambrogio, and C. Carfagna, 'Synthesis and Characterization of Highly Intercalated Graphite Bisulfate', *Nanoscale Research Letters*, vol. 12, no. 1, p. 167, Dec. 2017, doi: 10.1186/s11671-017-1930-2.
- [23] M. Elbidi, M. A. M. Salleh, S. A. Rashid, and M. F. M. G. Resul, 'The potential of thermally expanded graphite in oil sorption applications', *RSC Advances*, vol. 14, no. 23, pp. 16466–16485, May 2024, doi: 10.1039/d4ra00049h.
- [24] F. Tomiak, K. Schneider, A. Schoeffel, K. Rathberger, and D. Drummer, 'Expandable Graphite as a Multifunctional Flame-Retarding Additive for Highly Filled Thermal Conductive Polymer Formulations', *Polymers*, vol. 14, no. 8, p. 1613, Apr. 2022, doi: 10.3390/polym14081613.
- [25] F. Tomiak, K. Rathberger, A. Schöffel, and D. Drummer, 'Expandable Graphite for Flame Retardant PA6 Applications', *Polymers*, vol. 13, no. 16, Aug. 2021, doi: 10.3390/polym13162733.
- [26] Y. Li, C. F. Cao, Z. Y. Chen, S. C. Liu, J. Bae, and L. C. Tang, 'Waterborne Intumescent Fire-Retardant Polymer Composite Coatings: A Review', *Polymers*, vol. 16, no. 16, p. 2353, Aug. 2024, doi: 10.3390/polym16162353.
- [27] M. Venkataraman, X. Xiong, J. Novotná, M. Kašparová, R. Mishra, and J. Militký, 'Thermal Protective Properties of Aerogel-coated Kevlar Woven Fabrics', *Journal of Fiber Bioengineering and Informatics*, vol. 12, no. 2, pp. 93–101, Jun. 2019, doi: 10.3993/JFBIM00321.
- [28] S. Talebian *et al.*, 'Electrically Conducting Hydrogel Graphene Nanocomposite Biofibers for Biomedical Applications', *Frontiers in Chemistry*, vol. 8, p. 470633, Feb. 2020, doi: 10.3389/fchem.2020.00088.
- [29] H. Wang *et al.*, 'Laser Writing of Janus Graphene/Kevlar Textile for Intelligent Protective Clothing', *ACS Nano*, vol. 14, no. 3, pp. 3219–3226, Mar. 2020, doi: 10.1021/acsnano.9b08638.
- [30] I. M. Afanasov *et al.*, 'Preparation, electrical and thermal properties of new exfoliated graphite-based composites', *Carbon*, vol. 47, no. 1, pp. 263–270, Jan. 2009, doi: 10.1016/j.carbon.2008.10.004.
- [31] N. Srivastava and R. M. Mehra, 'Study of the electrical properties of polystyrene-foliated graphite composite', *Materials Science-poland*, 2009.
- [32] A. M. Darabut *et al.*, 'Effect of graphite fillers on electrical and thermal conductivity in epoxy-based composites: Percolation behavior and analysis', *Materials Research Bulletin*, vol. 183, Mar. 2025, doi: 10.1016/j.materresbull.2024.113186.
- [33] B. Redondo-Foj *et al.*, 'Electrical conductivity properties of expanded graphite-polycarbonatediol polyurethane composites', *Polymer International*, vol. 64, no. 2, pp. 284–292, Feb. 2015, doi: 10.1002/pi.4788.
- [34] N. Naveh, O. Shepelev, and S. Kenig, 'Enhancement of mechanical and electrical properties of continuous-fiber-reinforced epoxy composites with stacked graphene', *Beilstein Journal of Nanotechnology*, vol. 8, no. 1, p. 1909, 2017, doi: 10.3762/bjnano.8.191.
- [35] L. Wei *et al.*, 'Conductive fibers for biomedical applications', *Bioactive Materials*, vol. 22, pp. 343–364, Apr. 2023, doi: 10.1016/j.bioactmat.2022.10.014.
- [36] N. V. Maksimova, N. E. Sorokina, O. N. Shornikova, and V. V. Avdeev, 'Thermal properties of graphite intercalation compounds with acids', *Journal of Physics and Chemistry of Solids*, vol. 65, no. 2–3, pp. 177–180, Mar. 2004, doi: 10.1016/j.jpcs.2003.10.013.

- [37] M. I. Saidaminov *et al.*, 'Thermal decomposition of graphite nitrate', *Carbon*, vol. 59, pp. 337–343, Aug. 2013, doi: 10.1016/j.carbon.2013.03.028.
- [38] B. Tryba, A. W. Morawski, R. J. Kaleńczuk, and M. Inagaki, 'Exfoliated graphite as a new sorbent for removal of engine oils from wastewater', *Spill Science and Technology Bulletin*, vol. 8, no. 5–6, pp. 569–571, 2003, doi: 10.1016/S1353-2561(03)00070-7.
- [39] Y. Plekhanova *et al.*, 'Modification of thermally expanded graphite and its effect on the properties of the amperometric biosensor', *3 Biotech*, vol. 12, no. 2, p. 42, Feb. 2022, doi: 10.1007/s13205-021-03107-w.
- [40] M. Irfan *et al.*, 'Development and characterization of protective gloves using waste para aramid fibers', *Journal of Industrial Textiles*, vol. 52, p. 15280837221113363, Jun. 2022, doi: 10.1177/15280837221113363.
- [41] M. Hustedt, V. Niedens, A. Brodeßer, T. Bauche, J. Hermsdorf, and S. Kaierle, 'Assessment of steel shields for protection against laser radiation', *J. Laser Appl.*, vol. 33, no. 4, p. 042053, Nov. 2021, doi: 10.2351/7.0000519.
- [42] M. Bae, H. Lee, G. Choi, and J. Kang, 'An Effective Expanded Graphite Coating on Polystyrene Bead for Improving Flame Retardancy', *Materials*, vol. 14, no. 21, p. 6729, Nov. 2021, doi: 10.3390/ma14216729.
- [43] C. Alonso *et al.*, 'Graphite flame retardant applied on polyester textiles: flammable, thermal and in vitro toxicological analysis', *Journal of Industrial Textiles*, vol. 51, no. 3_suppl, pp. 4424S–4440S, Jun. 2022, doi: 10.1177/15280837211062056.
- [44] E. Almer *et al.*, 'Apparatus and method for producing nanofiber yarn using alternating current electrospinning.', CZ 304137 B6, Aug. 22, 2018.
- [45] D. Coetzee, J. P. P. Aguilera, J. Wiener, L. Walker, T. Thekiso, and C. D. Jong, 'Advancing Electrospun Polymer-Graphite Composites: Strategies for Improved Performance', in *17th International Conference on Nanomaterials - Research & Application*, Tangerang, Oct. 2025. [Online]. Available: <https://www.confer.cz/nanocon/2025>
- [46] D. Coetzee, J. P. P. Aguilera, T. Thekiso, and J. Wiener, 'Fabrication of Nanofibrous PVA and PA4,6 Materials with Improved Electrical Conductivity by Incorporating Ultrasonicated Expanded Graphite Particles', in *STRUTEX 2024 24th International Conference*, Dec. 2024.
- [47] D. Coetzee, T. Šubrová, and J. Wiener, 'Effect of Expanded Graphite on the Thermal Conductivity of Textile-Based Composites', in *AUTEX World Conference 2024 Proceedings*, Liberec: AUTEX, Jun. 2024.
- [48] G. Carotenuto *et al.*, 'Synthesis of nanographite by laser induced thermal expansion of H₂SO₄ intercalated graphite lattice', Jul. 2014, [Online]. Available: <http://arxiv.org/abs/1407.6204>
- [49] A. D. Lucking, L. Pan, D. L. Narayanan, and C. E. B. Clifford, 'Effect of Expanded Graphite Lattice in Exfoliated Graphite Nanofibers on Hydrogen Storage', *Journal of Physical Chemistry B*, vol. 109, no. 26, pp. 12710–12717, Jul. 2005, doi: 10.1021/jp0512199.
- [50] Z. Wang *et al.*, 'Highly Enhancing Electrical, Thermal, and Mechanical Properties of Polypropylene/Graphite Intercalation Compound Composites by In Situ Expansion during Melt Mixing', *Polymers*, vol. 13, no. 18, p. 3095, Sep. 2021, doi: 10.3390/polym13183095.
- [51] S. Zecchi *et al.*, 'A Comprehensive Review of Electromagnetic Interference Shielding Composite Materials', *Micromachines*, vol. 15, no. 2, p. 187, Feb. 2024, doi: 10.3390/mi15020187.
- [52] D. Zhou, S. Xiao, and Y. Liu, 'The Effect of Expanded Graphite Content on the Thermal Properties of Fatty Acid Composite Materials for Thermal Energy Storage', *Molecules*, vol. 29, no. 13, p. 3146, Jul. 2024, doi: 10.3390/molecules29133146.
- [53] Y. Zhong, X. He, W. Wang, Y. Xu, Y. Wang, and Y. Shuai, 'Performance enhancement of graphite-based flexible composite phase change materials and heat dissipation characteristics of electronic devices', *Applied Thermal Engineering*, vol. 263, no. 22, p. 125393, Mar. 2025, doi: 10.1016/j.applthermaleng.2024.125393.
- [54] B. Wei, L. Zhang, and S. Yang, 'Polymer composites with expanded graphite network with superior thermal conductivity and electromagnetic interference shielding performance', *Chemical Engineering Journal*, vol. 404, no. 13, p. 126437, Jan. 2021, doi: 10.1016/j.cej.2020.126437.

7 List of the author's works related to the problem under study

7.1 Articles in impacted journals

- Coetzee, D.; Rojviroon, T.; Niamlang, S.; Militký, J.; Wiener, J.; Večerník, J.; Melicheríková, J.; Müllerová, J.: Effects of expanded graphite's structural and elemental characteristics on its oil and heavy metal sorption properties. *Scientific Reports*, 14, 1–10 (2024). <http://doi:10.1038/S41598-024-64695-0>.
- Coetzee, D.; Perez Aguilera, J. P.; Wiener, J.; Tegginamath, A.: Influence of Carbon Fibre, Ultrasonication and Vacuum Processing on the Mechanical and Conductive properties of

Expanded Graphite Polyester Resin Composites. *Polymers*, 18, 731 (2026).
<http://doi:https://doi.org/10.3390/polym18060731>.

7.2 Book Chapters

- Coetzee, D.; Militký, J.; Wiener, J.; Venkataraman, M.: Comparison of the Synthesis, Properties, and Applications of Graphite, Graphene, and Expanded Graphite. In *Advanced Structured Materials*; Militký, J., Venkataraman, M., Eds.; Springer, Singapore, (2023); Vol. 201, pp. 71–87 ISBN 978-981-99-6002-6.

7.3 Conference contributions and proceedings

- Coetzee, D.; Perez Aguilera, J. P.; Šubrova, T.; Wiener, J.; Militký, J.: Expanded Graphite to Enhance the Conductive and Mechanical Properties of Geopolymer, PVA and EPOXY. In *Nanocon Conference Proceedings - International Conference on Nanomaterials*; TANGER Ltd.: Brno; pp. 189–195. ISBN 978-80-88365-15-0. (2024)
- Coetzee, D.; Šubrová, T.; Wiener, J.: Effect of Expanded Graphite on the Thermal Conductivity of Textile-Based Composites. In *AUTEX World Conference*; Liberec, (2024)
- Coetzee, D., Perez Aguilera, J.P., Thekiso, T., Wiener, J.: Fabrication of Nanofibrous PVA and PA4,6 Materials with Improved Electrical Conductivity by Incorporating Ultrasonicated Expanded Graphite Particles. In *STRUTEX 2024 24th International Conference*. Liberec. (2024)
- Coetzee, D. Perez Aguilera, J.P., Wiener, J., Walker, L, Thekiso, T, De Jong, C.: Advancing electrospun polymer-graphite composites: strategies for improved performance. In *NANOCON 2025 Conference Proceedings*. Brno: NANOCON, 2025. ISBN 978-80-88365-29-7. ISSN 2694-930X. 6 s. (Accepted: Proceedings in Preparation)

7.4 Manuscripts under review

- Coetzee, D.; Wiener, J.: Laser-Induced Controlled Expansion of Sulfuric Acid and Nitric Acid Intercalated Expandable Graphite. *Carbon Trends (Under Review)*, (2026).
- Coetzee, D.; Wiener, J.: Laser-Protective Kevlar with Acrylic-Based Expandable Graphite Coating. *Textiles (Under Review)*, (2026).
- Coetzee, D.; Perez Aguilera, J. P.; Wiener, J.; Militký, J.: Scalable AC Electrospinning of Biocompatible Nanofibrous Yarns Based on Expanded Graphite and PEDOT:PSS. *Polymers (Under Review)*, (2026)

8 Brief characteristics of previous professional, research and scientific activities

Doctoral Studies

Exams	- Statistics 12/2022 - Heat and Mass Transfer in Porous Media 12/2022 - Sorption Properties 08/2024 - Quality Control and Project Planning 06/2025 - Experimental Technique of The Textile 06/2025
SDE	Comprehensive Doctoral Exam 19.11.25
Teaching Activities	Assisting and mentoring internship students from Thailand, Poland and South Africa, as well as assisting with Textile Chemistry practicals during the PhD. I have also taught Analytical Chemistry and Tissue Engineering during internships at RMUTT in Thailand and at Stellenbosch University in South Africa, respectively.
Research projects	- Special Carbon Fillers for Fibre Composites, SGS-2023-6384 (02/2023 – 12/2024). Project Leader. - Electrospun nanocomposites with improved conductivity using expanded graphite, SGS-2025-6518 (02/2025-12-2025). Project Leader - Membránové neporézní systémy pro textilní aplikace (Membrane non-porous systems for textile applications), SGS-2022-6069 (02/2022 – 12/2023). Team Member - Advanced structures for thermal insulation in extreme conditions, GAČR Reg. No. 21-32510M (08/2020-12/2024). Team Member - Project Eco-clothing collection, reg. no. TQ01000450 (08/2024- Present). Team Member - Next Generation Antiadhesive Nanofibrous Materials: Fundamental Insights Into Their Design and Function, GAČR 26-23104M (01/2026- Present). Team Member

Other Academic & Service
Activities

NANOCON 2023 (Brno, CZ)

Tissue Engineering Workshop (Lodz, PL)

AUTEX 2024 (Liberec, CZ)

STRUTEX 2024 (Liberec, CZ)

NANOCON 2025 (Brno, CZ)

RUN EU Innovation Program (Leeuwarden, NL)

9 Curriculum Vitae

Divan Coetzee | Ph.D. student and Researcher

Faculty of Textile Engineering

Technical University of Liberec

Email: divan.coetzee@tul.cz



Education

[09/2022 – Present] PhD. Industrial Engineering, Technical University of Liberec, Liberec, CZ

Research Topic: Process-controlled Expansion of Graphite Intercalation Compounds: Mechanism and Functional Properties

[09/2019-06/2022] MIng. Textile Engineering (Nonwovens and Nanofiber Materials), Technical University of Liberec, Czechia

Graduated with distinction.

Research Topic: Carbon coating to impart electrical conductivity to textile material.

[02/2011 – 12/2013 & 02/2017 – 12/2018] BSc. Chemistry Textile and Polymer Science, Stellenbosch University, South Africa

Awarded the Dean's medal for outstanding performance in Inorganic Chemistry.

Internship Experience

**RMUTT, Faculty of Engineering, Department of Environmental Engineering, Kingdom of Thailand
01/2023-03/2023**

Oil and Heavy Metal Sorption Analysis of Expanded Graphite. Teaching Analytical Chemistry.

Stellenbosch University, Science Faculty, Department of Chemistry and Polymer Science, Republic of South Africa 08/2023-10/2023

Scientific analysis (XRD, NMR) of functionalised carbon particles.

Universidad de La Laguna, Physics Faculty, Tenerife, Kingdom of Spain [various times 2024-2026]

XRD, and DSC analysis of Expanded-, Expandable Graphite particles and composite materials and their novel characterisation methods.

Professional experience

08/2020- Present: Researcher, Faculty of Textile Engineering, TUL, CZ

Researcher on GAČR Projects, as well as participation in faculty projects.

01/2019-10/2029: Graduate Research Assistant, Department of Chemistry and Polymer Science, Stellenbosch University, RSA

Performed research on Permethrin leaching from textiles under the supervision of Dr Adine Gericke.

08/2015-10/2019: Interim Manager, Thule Partner Stellenbosch, RSA

I started as a shop assistant and worked my way up to manager whilst completing my studies full-time at Stellenbosch University. I took a 3-month leave to take up an internship at TUL, which led me to continue my studies there.

01/2014-12/2014: Candidate Property Sales Advisor, Engel & Voelkers Stellenbosch, RSA

Gained experience in the property market and the sales environment.

Language Skills

English (Native), Afrikaans (Native), German (Elementary, A2), Dutch (Elementary, A2)

Recommendation of the supervisor

Opinion of the supervisor on PhD. thesis of Divan Coetzee

I evaluate the doctoral thesis of Ing. Divan Coetzee, B.Sc. entitled “Process-controlled Expansion of Graphite Intercalation Compounds: Mechanism and Functional Performance” very positively.

The topic of the thesis is highly relevant and innovative. It focused on the process-controlled expansion of graphite intercalation compounds using laser-induced methods as an energy-efficient and precise alternative to conventional thermal shock methods.

The work successfully connects fundamental research on expansion mechanisms with practical applications in environmental sorption, protective textiles, and conductive/biocompatible composites.

Throughout his PhD studies, Ing. Divan Coetzee demonstrated a high level of independence, creativity, and experimental competence. He independently designed and carried out a comprehensive experimental plan, advanced characterization techniques (SEM, XRD, Raman spectroscopy, TGA/DSC, ICP-OES). I appreciate his ability to link theoretical insights with the application potential of the obtained results.

The thesis contains several novel findings. During his studies, the author published multiple papers in impacted journals and actively presented his results at international conferences. The submitted dissertation is comprehensive, logically structured, methodologically precise, and supported by high-quality experimental data and detailed discussion.

The thesis passed the plagiarism check without any problems, with a similarity rate of practically 0 %.

Ing. Divan Coetzee proved to be a reliable and independent PhD student with optimal organizational skills and a consistently positive approach to problem-solving. His work significantly contributes to the development of materials engineering and functional materials at our faculty.

I recommend the doctoral thesis of Ing. Divan Coetzee for defense.

Liberec, 24.5.2026

prof. Ing. Jakub Wiener, PhD.,

supervisor

Reviews of the opponents



Technical University of Liberec

Faculty of Textile Engineering

Department of Material engineering

Study programme: P0723D270004 Industrial Engineering

Student: Ing. Divan Coetzee, B.Sc.

Supervisor: prof. Ing. Jakub Wiener, Ph.D., TUL

Oponent: prof. Ing. Gražyna Simha Martynková, Ph.D., CNT, CEET VSB-Technical University of Ostrava

Opinion on Doctoral Thesis

"
Process-controlled Expansion of Graphite
Intercalation Compounds: Mechanism and
Functional Performance

Thesis by Ing. Divan Coetzee, B.Sc. is demonstrating a laser-induced expansion of graphite as an energy-efficient, tuneable route to application-specific expanded graphite.

Thesis has state motivation for research by the need to make expanded graphite production more energy-efficient, controllable, and application-specific. Conventional furnace and microwave expansion consume high energy and offer limited local control, often producing variable morphology and properties. Laser-assisted and chemistry-aware strategies can tune exfoliation, porosity, conductivity, defect content, and biocompatibility, enabling expanded graphite materials tailored for environmental sorption, protective coatings, conductive composites, and biomedical textiles.

This dissertation shows that laser-induced expansion is an energy-efficient and tunable method for producing application-specific expanded graphite. By controlling intercalant chemistry and laser fluence, H_2SO_4 - and HNO_3 -GICs develop distinct morphologies. HNO_3 -GICs expand most effectively at $600\text{--}750\text{ J}\cdot\text{cm}^{-2}$, forming low-density, highly exfoliated structures, while H_2SO_4 -GICs require stronger thermal input and tend to produce denser morphologies under rapid laser heating.

The topic chosen for the dissertation is therefore current and scientifically valuable.

The dissertation is composed of five main parts. The Introduction includes the motivation for the work, while the second chapter presents the research subject and objectives. The third chapter, the State of the Art, provides a general description of the materials and techniques used in the study and identifies existing research gaps. Chapter 4 presents the experimental work, testing methods, results, and discussion. The final, fifth chapter contains proposals for further work. The thesis draws on 55 literature sources relevant to the topic.

The final part of the thesis presents the author's research outputs. The author is the first author of two articles published in impacted professional journals, the author of one book chapter, and the author of four conference contributions. In addition, three manuscripts are currently under consideration in journals. I must point out several issues that are uncommon in this type of work.

First, the literature list includes citations to all three of the author's manuscripts currently under review in journals. This may be misleading, as the review process can substantially change not only the manuscript content but also the title. Therefore, citing manuscripts under review in this manner is not appropriate.

Second, the Results and Discussion chapter is divided into three separate parts, each titled "Results and Discussion" with an additional specification, such as "Conductive Composites." It would be more appropriate to combine these sections into one main Results and Discussion chapter with clearly defined subchapters.

The doctoral thesis is written clearly and uses relevant technical English with appropriate terminology.

Regarding the scientific content of the work, the study generally uses two commercially available intercalated materials and three expanded samples, which were subsequently modified. The observations made during the research are presented in a relatively simple manner; however quantity of various observation is high and broad. Many characterisation results are also described only briefly. For example, in the case of XRD, no diffraction patterns are provided. Table 1 includes information about the second and third peaks; however, it is impossible to determine what these peaks represent. There are also inconsistencies in the units used, such as mixing nm and Å. In addition, the FWHM values of very broad peaks are reported to four decimal places, while the calculated crystallite size is the same for all samples, which raises questions about the reliability and interpretation of the data.

It is also surprising that figures containing the term "Raman diffraction," presented as Fig. 8 in the thesis, were published in Scientific Reports, since Raman spectroscopy is based on inelastic scattering rather than diffraction.

Many analysis and testing are described in text only, this makes difficult to evaluate correctness of statements.

Questions for thesis:

1. How does the laser fluence shown in Figure 2 affect the expansion behavior of the samples? Why does H_2SO_4 -activated graphite show only a limited response to increasing laser power?
2. Based on Table 1, please explain the meaning of the higher crystallite size reported for the second and third peaks of the HNO_3 -GIC sample.
3. Which technique was used to determine the N, C, H, and S content? Also, what does the nearly 6% remaining fraction in the EG1 sample represent?
4. How many repetitions of the elemental analysis measurements shown in Figure 10 were performed to obtain the reported 100% removal of the studied element value?
- 5.

Overall evaluation of the work:

The presented thesis is application-oriented research that offers a new perspective on the advanced utilization of expanded graphite. The experimental work provides a useful starting point for deeper investigation of graphite expansion, especially regarding intercalant chemistry, processing conditions, and material morphology. The preliminary results however should have stronger scientific background. The results may support further optimization for environmental, protective, and conductive applications.

Final evaluation:

Submitted thesis Ing. Divan Coetzee, B.Sc. met the planned goals, and its content meets the requirements recommended for the dissertation, and I classify the work as "passed". I recommend the dissertation for the final defence and the award of the adept with the title "philosophiae doctor" (Ph.D.) after successful defence of thesis.

V Ostravě 1.7.2026

prof. Ing.
Gražyna Simha
Martynková,
Ph.D.

Digitally signed by
prof. Ing. Gražyna
Simha Martynková,
Ph.D.
Date: 2026.07.02
23:50:30 +02'00'

prof. Ing. Gražyna Simha Martynková, Ph.D.
CNT, CEET, VŠB-Technical University Ostrava



Review of the Ph.D. thesis of Mr Divan Coetzee

This dissertation addresses a timely and scientifically relevant topic that combines a number of still unresolved fundamental questions with considerable potential for practical applications. Realising this potential, however, requires a thorough understanding and technological control of the underlying processes. The dissertation focuses on the process-controlled production of expanded graphite (EG), particularly by laser-induced expansion of graphite intercalation compounds (GICs), and on tailoring its microstructure for specific applications. More specifically, it investigates how the type of intercalant (H_2SO_4 or HNO_3) and laser fluence affect graphite exfoliation, morphology, crystallinity, thermal behaviour, and bulk density, and establishes relationships between processing conditions, material structure, properties, and final performance.

The hypotheses and research questions related to the stated objectives address both fundamental aspects and potential practical applications in several selected areas. However, there is no detailed explanation of why these particular applications were selected or what specific added value results from connecting them within the framework of the dissertation.

The dissertation is clearly divided into individual chapters; however, it lacks an overall concluding chapter. The introduction and the state-of-the-art/theoretical section are relatively brief but generally clear and well structured. However, the complete absence of schematic diagrams, graphs, or other illustrative material represents a notable weakness. Given the nature of the topic, figures illustrating the structure of graphite intercalation compounds, the mechanism of graphite expansion, or the differences between conventional thermal and laser-induced expansion would substantially improve the clarity and educational value of the theoretical part.

The experimental section of the thesis is very extensive and, in some parts, lacks clarity and a sufficiently explicit connection to the stated objectives. Some important data are missing and, as mentioned above, there is no overall conclusion summarising the principal findings and the scientific contribution of the work. Further selected comments are provided below.

In the experimental section of Chapter 4.1, schematic diagrams and summary tables are again absent, making parts of the text unnecessarily difficult to follow. I consider this a weakness. The chapter also lacks sufficient explanation and justification for the selection of some of the input materials, which makes it difficult for the reader to place the experiments in context. Some materials are insufficiently specified; for example, the sources of the polymers used for the production of nanofibre yarns are not provided. The absence of such information compromises the reproducibility of the experiments.

The author also does not sufficiently explain the rationale behind some of the selected processing parameters. Relevant optimisation procedures or previously published results may be described in publications cited in connection with the individual experiments. However, some of these publications are currently in press and may therefore not be readily accessible to the reader. In any case, references to external publications should not substitute for an adequate description and justification of the experimental procedure within the dissertation itself. One example is Section 4.1.4.2, "Nanofiber Threads", where it remains unclear why the particular polymers, polymer concentrations, solvents, and AC electrospinning parameters were selected. It would be appropriate either to cite available publications on which these choices were based, such as Mikule et al., *High-throughput fabrication of nanofibrous yarns produced by alternating-current electrospinning*, *Communications Engineering* (2026), or to describe the optimisation procedure used. I acknowledge that providing such detail is challenging given the breadth of the dissertation; however, this issue should have been considered when defining the scope of the work. Furthermore, although nanofibre threads are discussed extensively, no quantitative information on fibre diameters is provided, despite fibre diameter being a key structural parameter. For a substantial part of the work, the author makes experimental data available in commendable accordance with open-science principles. However, this approach is not applied consistently across all experiments, and in



some cases the accompanying description is insufficient for proper interpretation of the published data. The production of nanofibre threads is again one such example.

The first experimental photograph appears on page 31 and shows laser-expanded material. However, it provides only a macroscopic view, while higher-magnification images that would enable a detailed assessment of the resulting structures are absent. Furthermore, no direct visual comparison with the corresponding original, unexpanded materials is provided. Similar comments apply to Figures 3–5 on pages 32–34. In Section 4.4.1.4, the author states that SEM imaging did not allow the hierarchical structural differences identified by other analytical techniques to be readily distinguished. However, the possible reasons for this limitation are not discussed. It is also unclear why the advanced SEM facilities available at CXI TUL were not utilised to investigate these structures at higher magnifications and resolution, as such measurements could potentially have provided further insight into the reported structural differences. More comprehensive microscopic documentation would significantly strengthen the dissertation.

Chapter 4.2.4.2 provides an insufficient description of the cytotoxicity assessment procedure to ensure reproducibility. While the information provided might be acceptable as a brief methodological summary in an abstract, it is not sufficient for a dissertation. Important details such as the extraction ratio, exact extraction and cell-exposure times, extract concentration, positive and negative controls, and the meaning of $n=8$ are not clearly specified. In addition, a crucial procedural step—the sterilisation of the tested materials—is not described. There is no indication of the sterilisation method used, the conditions applied, the rationale for its selection, or whether sterilisation affected the material properties.

Figure 15 on pages 72–73 shows two nanofibrous threads of pure PVA, but no corresponding PA sample is shown. The layout of the figure is confusing, and the text does not contain adequate references to figures (c)–(k), making it difficult to determine which parts of the discussion correspond to individual images. Quantitative characterisation of the thread structure in terms of fibre diameter, orientation, packing density, or twist is also lacking, although some of these parameters are mentioned in Chapter 4.1.4.2. Neither the text nor the caption of Table 9 explains the meaning of the values given in parentheses.

Formal comments:

- Units are occasionally separated from their numerical values by line breaks (e.g., pp. 12 and 27).
- The use of thesis-specific abbreviations in chapter titles should preferably be limited, particularly where the reader must consult the list of abbreviations to understand the heading. Main chapter titles are generally clearer when terms are written out in full, whereas abbreviations are entirely appropriate in more technical subchapters.
- The formatting of literature citations is inconsistent; see, for example, page 58.
- The photograph in Figure 13 on page 66 lacks a scale bar.
- Some tables are excessively long and extend over several pages, which impairs readability; see, for example, Table 8 on pp. 79–81.

Questions for the defence

1) Commercial production of expanded graphite already employs rapid high-temperature treatment and can produce highly expanded materials. What, therefore, are the principal technological and economical advantages of laser-induced expansion at an industrial scale? The added value of laser processing would appear to lie particularly in improved control over process–structure–property relationships and in applications where localised processing offers a genuine advantage. Please discuss the results of your work in this context, particularly with respect to cost, productivity, efficiency, scalability, and process repeatability. Where possible, please compare these aspects with currently available commercial technologies and products.



2) One of the potentially unique advantages of laser-induced expansion over conventional thermal expansion is its spatial selectivity. Could this approach be used to create patterned or functionally graded materials containing locally expanded and unexpanded regions? What applications could benefit from such spatially controlled structures?

3) Could the author explain why no schematic diagrams of the experimental technologies or illustrations of the relevant graphite and carbon structures were included in the theoretical part of the dissertation? Such visual material would, in my opinion, significantly enhance the comprehensibility and educational value of the presented concepts.

I consider the dissertation to represent the candidate's independent scientific work. For future work, I would recommend a more systematic and detailed description of experimental materials and individual methodological steps. I would also recommend clearer structuring of extensive sections, a more focused definition of research objectives, and more explicit synthesis of the obtained results into overarching conclusions.

The author presents two first-authored publications in prestigious journals. The first, published in 2024, has already received 19 citations (see <https://www.nature.com/articles/s41598-024-64695-0/metrics>, 20.8.2026), which represents a noteworthy achievement. In addition, the author is a co-author of a book chapter and four conference papers, two of which are classified as Type D publications. The author also lists three manuscripts currently under review. Their eventual publication would further strengthen the scientific output associated with this dissertation.

Despite the comments and reservations stated above, I consider the dissertation to constitute valuable and independent scientific work that meets the requirements for a doctoral thesis, and **I recommend it for defence.**

In Turnov 20th August 2026

*Doč. Ing. Eva Kuželová Košťáková, Ph.D.
Department of Chemistry
Faculty of Science, Humanities and Education
Technical University of Liberec*