

# WHITE PAPER

## GRAPHENE-ENHANCED TOUGHENED VINYL ESTER KIT

January, 2020

---

G6-EPOXY



G6-EPOXY™

---

# ABSTRACT

The product series, G6-GVE37, is a lightweight graphene-enhanced toughening vinyl ester, intended to be used as laminating resin for applications in aerospace, marine, automotive and defense. The addition of graphene, a nanoscopic reinforcing material (atomically thin carbon platelets), effectively improves performance of the laminating resin and the laminate composite as a whole. The Company observed that graphene fillers significantly improve the mechanical properties of laminates. Graphene increases impact resistance and fracture toughness, as well as fatigue and corrosion resistance, thereby resulting in safer, lighter weight composite structures with a longer service life.

---

## FAILURE IN FIBRE LAMINATES: IMPACT SUSCEPTIBILITY, FATIGUE AND ENVIRONMENTAL DEGRADATION.

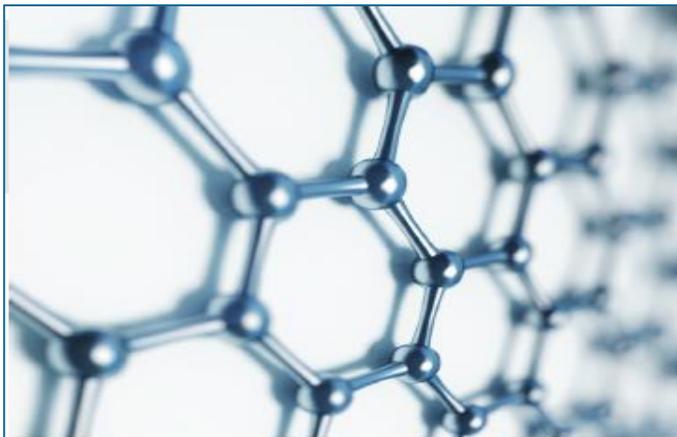


There are many microscopic mechanisms of material deterioration that contribute to the damage and ultimate failure of laminate structures, e.g., fiber breaking, debonding of a fiber from the resin (interface failure), cracks or crazes in resins, and void growth (separation of layers forming the laminate, also known as delamination). For these reasons, to ensure the long service life of the composite, the selection of the materials

used for making the composite is critical. The choice of reinforcement is important if stress corrosion is to be mitigated, while resin chemistry must be optimized to limit matrix damage. Fiber-matrix interface properties are also critical when composites are immersed for long periods. The failure mechanism in composite materials strongly depends upon the type of fibers used for reinforcement. Glass fibers tend to perform well under impact loads, while carbon fibers are relatively more brittle. An effective strategy for improvement of impact resistance is the use of additives that improve resin-fiber adhesion and ductility of the laminate. Glass fiber laminates tend to suffer from fatigue that can be strongly accelerated by environmental degradation. Therefore, introduction of graphene additives into the resin to reduce brittleness, promote ductile non-destructive energy absorption and inhibit crack formation is highly desirable for longer service life and reduced repair costs.

---

## GRAPHENE MATERIALS AS A REINFORCING AGENT FOR FIBRE LAMINATES



Graphene, the thinnest material in the universe, has transformative potential and applications in multiple industries. The 2010 Nobel Prize in Physics was awarded to A. Geim and K. Novoselov for their discovery of the unique properties of graphene. Graphene is readily visualized as a hexagonal lattice of carbon atoms in a honeycomb-like structure. Layers of graphene are stacked to form

graphite having an interplanar spacing of 3.35 Å. Graphene's crystalline structure affords its unique optical, thermal, mechanical and electrical properties. Graphene is the strongest material ever tested, having an intrinsic tensile strength of 130.5 GPa and a Young's modulus of 1 TPa. [1]

The graphene nanoplatelets are small particles with a lateral size of 0.2-25 µm and a thickness varying from one to several dozen atomic graphene layers. Graphene nanoplatelets take the form of a low-density black powder that can be utilized as a reinforcement agent in various polymer composite materials including but not limited to thermoplastic resins. With its high surface area, the addition of less than 1% graphene to a polymer is enough to significantly improve the properties of neat resin.

### ROUTES FOR IMPROVEMENT OF FIBRE LAMINATES WITH GRAPHENE NANOPATELETS

Despite that glass and carbon fiber laminates are widely available and produced in a variety of formulations, there continues to be demand for the improved performance of such laminate composites. Fatigue and microcracking endurance are physical characteristics recognized as needing to be improved. Fiber-based materials have incredible mechanical strength, but often lack stress and impact resistivity. The Company's toughened vinyl ester, G6-GVE37, formulated as a laminating resin for use in the manufacturing of innovative, light-weight, graphene-enhanced materials and composites shows marked improvements compared to typical fiber laminates.

**Fatigue Resistance:** The enhancement of over three orders-of-magnitude in the flexural bending fatigue life of G6-GVE37/glass fiber composite translates into significant performance, cost, safety and reliability benefits in a wide range of structural applications.

**Crack Resistance:** Graphene materials have a clearly demonstrated ability to mitigate crack formation in resins. The incorporation of graphene as a nanofiller in the Company's formulation

---

considerably contributed to higher Mode II Fracture Toughness  $G_{IC}$  of G6-GVE37/E-glass fiber laminate, which was improved by 34%. Mode II intralaminar fracture toughness in modified ASTM D5045 arrangement [2]. Moreover, the stress intensity factor  $K_{IC}$  of vinyl ester composite improved by 31% and strain energy release rate  $G_{IC}$  - by 51%.

**Improved Barrier Properties:** Compared to metals, composite materials are much more robust against the damaging effect of the environment and moisture. Yet, the composite matrix is prone to deterioration by water damage. The most lucrative advantage of the graphene nanofiller is the impressive barrier resistance that it offers. Being impermeable to water molecules, the graphene nanoplatelets substantially slow down water penetration inside the matrix, thereby protecting the matrix material against hydrolysis. The composite's capability to withstand corrosion is correlated with the water absorption rate. This parameter was improved by 32% for the enhanced vinyl ester.

**Better Thermal Stability:** Temperature significantly affects the behavior of polymers and laminates, and as such must be carefully considered especially when designing vessel components because of direct surficial sunlight exposure. Polymers have an amorphous structure with a distinctive glass transition temperature ( $T_g$ ) at which the material shifts from a glassy (rigid) to rubbery behavior. Laminates lose effectiveness when they operate at temperatures above the transition temperature. The glass transition temperature is strongly dependent on the cure schedule. The matrix being cured at room temperature, without applying external heat, has the lowest possible glass transition temperature.

The Company's graphene-enhanced vinyl ester resin, G6-GVE37, optimizes the transition temperature by 7-10°C, significantly expanding the operating range of the laminates. Moisture absorption markedly reduces the glass transition temperature. Thus, the aforementioned improvement in water resistance is another factor to be considered when composites are to be used in a humid environment. An example is the composites used for making marine vessels. These composites are employed in highly humid environment and could potentially be exposed to high temperatures during vessel operation.

**Improved Interfacial Adhesion Strength:** When the composite is under a load, most of the stress is carried by the fiber structure. But first, the stress must be transferred from the matrix to the fiber structure. Thus, the composite's performance is strongly dependent on the bonding strength between the matrix resin and the fiber. The short beam strength test as discussed in ASTM D2344 [3] is an indicator of fiber adhesion to the resin, as determined by the Interlaminar Shear Strength (ILSS) parameter. The Company observed that the introduction of the graphene nanoplatelets to the resin leads to 12% improvement of the ILSS as compared to the composite made with a regular unmodified vinyl ester.

**Increased Tensile Strength and Stiffness:** The tensile and flexural moduli are indicators of the material stiffness. These properties of the laminating composites are mostly determined by fiber reinforcement. However, toughening of the resin can improve the overall laminate performance.

The Company observed that the Flexural Modulus improved by 45% and Tensile Modulus also showed a 27% improvement. The Company attributed these improvements to better adhesion of the fibers to the matrix resin.

**Better UV Stability:** Infusion of the graphene nanoplatelets into the matrix resin greatly improves the UV resistance of the composite material. The penetration of UV light at a wavelength damaging to matrix resin is mostly prevented by the optical density from the graphene nanoplatelets dispersed in the matrix. Graphene naturally has a very broad optical absorption spectrum. Each layer of graphene absorbs approximately 2.7% of the incident light [4]. Absorption grows accordingly to the number of layers and this phenomenon helps explain the deep, black color of graphene nanopowder. Also, graphene nanoplatelets offer an effective mechanism of quenching the electronic excitation being imposed by the absorbed UV photon, thereby preventing photo-damage to the composite [5].

## CASE STUDY

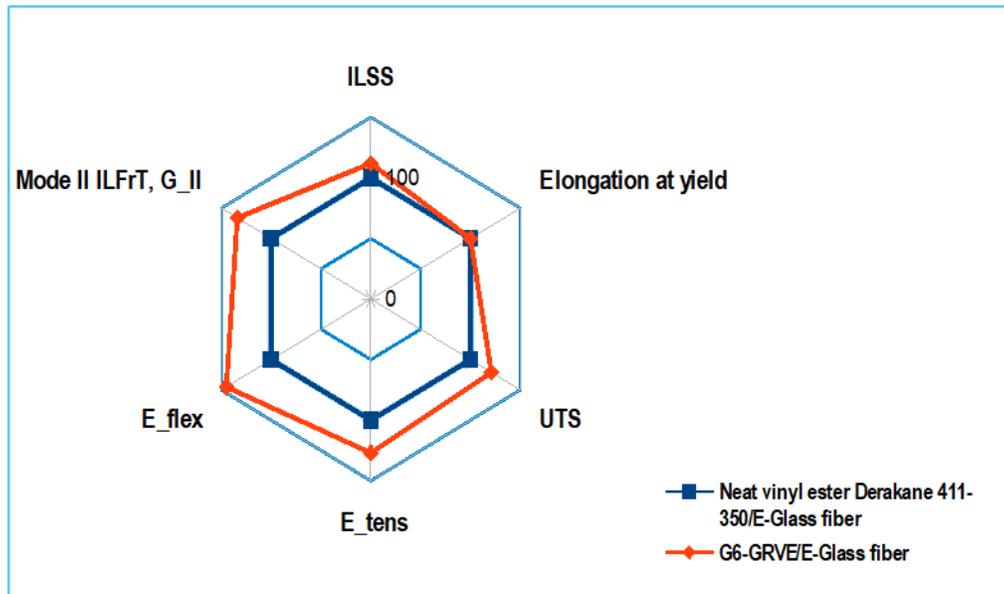
There are multiple types of laminating vinyl ester resins available on the market. Graphene additives described herein can be used for the enhancement of many types. To illustrate the performance improvement of the materials by graphene-based additives, the Company chose a generic laminating vinyl ester and analyzed the resin’s performance and E-glass fiber laminate with and without the graphene additive. The results of the analysis are presented below.

### COMPARISON IN PERCENTAGE OF THE PERFORMANCE OF THE NEAT VINYL ESTER RESIN via G6-GVE37\*

Test		Improvement, %
ASTM D5045	Fracture toughness, Stress Intensity Factor $K_{IC}$ (MPa·m <sup>1/2</sup> )	31
ASTM D5045	Fracture toughness, Strain energy release rate $G_{IC}$ (kJ/m <sup>2</sup> )	51
ASTM D570	Water absorption, %	32
Solid Rheology	Glass transition temperature, $T_g$ , °C	+7 °C
ASTM D638	Tensile Modulus, $E_{tens}$ , GPa	58
ASTM D638	Tensile Strength, MPa	19
Solid Rheology	Flexural Modulus, $E_{flex}$ , GPa	21

\*Vinyl ester was catalyzed with 1.25% MEKP

**COMPARISON IN PERCENTAGE OF THE PERFORMANCE OF E-GLASS FIBER LAMINATE OF THE NEAT VINYL ESTER RESIN via G6-GVE37\***



Test		Improvement, %
ASTM D2344	Interlaminar shear strength, (ILSS) MPa	12%
	Mode II Intralaminar fracture toughness $G_{II}$ , MPa	34%
Solid Rheology	Flexural Modulus, $E_{flex}$ , GPa	45%
ASTM D638	Tensile Strength, MPa	21%
ASTM D638	Tensile Modulus, MPa	27%

\*Vinyl ester was catalyzed with 1.25% MEKP

Disclaimer: The information provided is based on data and tests believed to be accurate. Graphene Laboratories, Inc. makes no warranties (expressed or implied) as to accuracy and assumes no liability in connection with any use of this product.

**REFERENCES**

1. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene"; Science 2008, 321, 5887, 385–388
2. ASTM D5545, [www.astm.org](http://www.astm.org)
3. ASTM D2344-14, [www.astm.org](http://www.astm.org)
4. F. Bonaccorso, Z. Sun, T. Hasan & A. C. Ferrari "Graphene photonics and optoelectronics"; Nature Photonics, 2010, 4, 611–622
5. Amal Kasry, Ali A. Ardakani, George S. Tulevski, Bernhard Menges, Matthew Copel, and Libor Vyklicky "Highly Efficient Fluorescence Quenching with Graphene"; J. Phys. Chem. C 2012, 116, 4, 2858-2862

---

## FINAL THOUGHTS

The incorporation of nanomaterials in the fiber-polymer composite offers an exceptionally effective technique to improve the mechanical properties of composites. Fiber laminates that are currently being used in naval, automotive, military and aerospace applications can also greatly benefit from the incorporation of graphene. Graphene is a multifunctional filler that can simultaneously improve the properties of fiber laminates while addressing critical performance drawbacks. The Company created a novel material, G6-GVE37, with improved resistance to stress, corrosion, cracking and fatigue. Additional benefits of the Company's graphene-enhanced resin include increased tensile strength and stiffness, reduced flammability, and improved thermal and UV stability. Therefore, the inclusion of graphene resins is expected to reduce the overall weight and cost of laminate structures while also improving operational safety.