Graphene in Composites – the development of industrial applications

15th Anniversary HVM 2017 & 4th Graphene New Materials Conference
2-3 November 2017 Cambridge, UK
www.cir-strategy.com/events

Peter Hansen
Engineering Manager

haydale

Haydale's positioning

Industry leader applying advanced materials, including graphene, to enhance existing products across a wide range of industries

Operating via a global footprint, Haydale's advanced materials are **designed into** clients' next generation products

Bespoke, precise, consistent products. Haydale:

Identifies everyday products that can be enhanced by the introduction of advanced materials

Works in close partnership with manufacturers' pre-existing production processes

Delivers specific, engineered products aimed at billion dollar markets

"Further to the announcement in February 2017, a production trial was held in early April using Haydale graphene nano platelets and initial tests are encouraging. Flowtite have requested a second trial to repeat and corroborate the first set of results and this is scheduled for early 2018."

Nick Crofts CEO - Amiblu Holding GmbH

"Our work with Haydale has shown that significant performance improvements can be achieved whilst maintaining processibility of the resins, overcoming a key challenge."

Dr David Hatrick, VP of Innovation, Huntsman Advanced Materials

"We believe the Haydale plasma reactor presents a cost effective way to functionalise graphene, and other 2D materials in a reproducible and controlled way."

Tom Taylor, Director of CPI

Global footprint

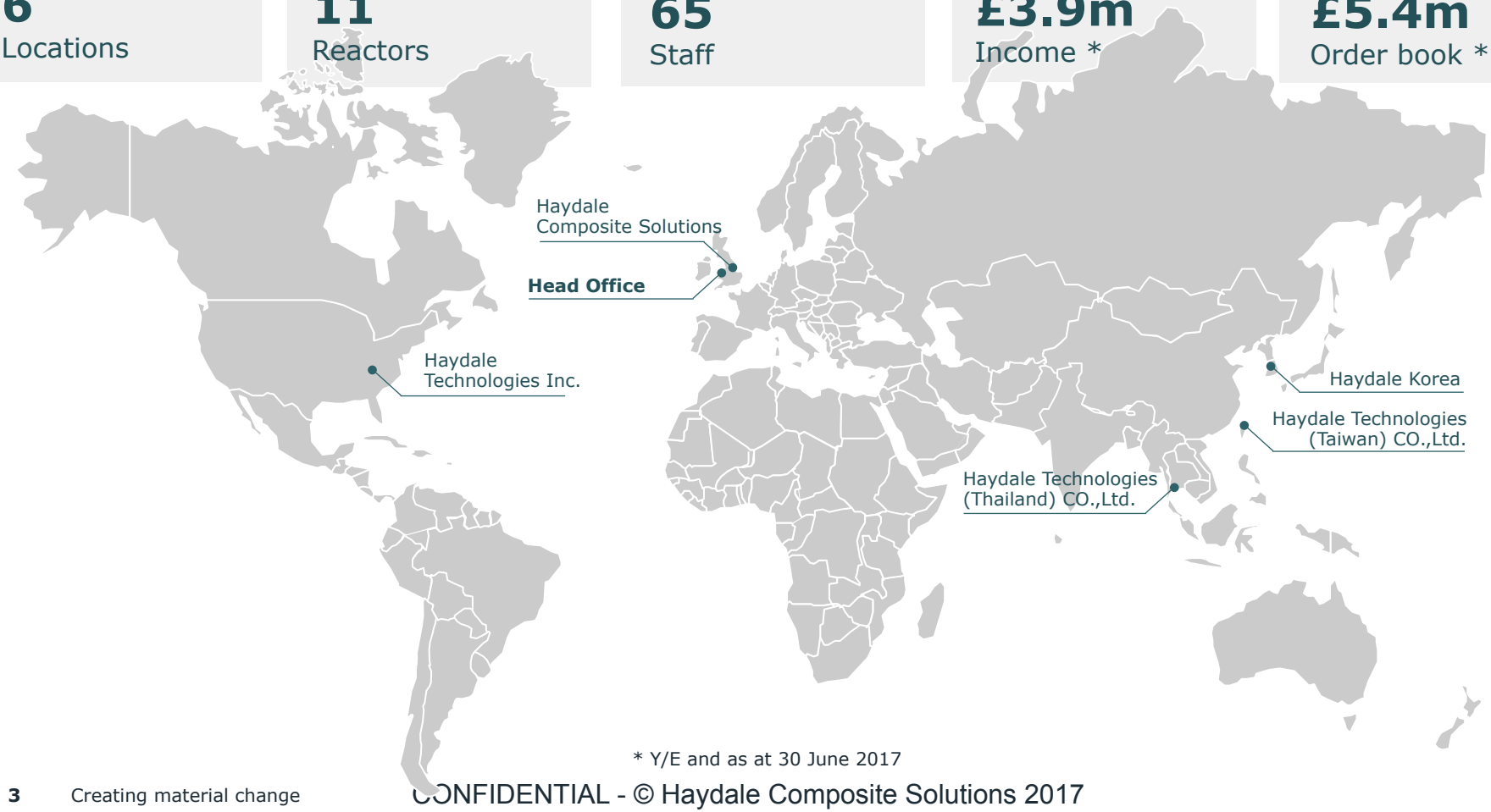
6
Locations

11
Reactors

65
Staff

£3.9m
Income *

£5.4m
Order book *



* Y/E and as at 30 June 2017

Sales focused

Facilitating fast, cost-efficient supply of material applications to a growing customer base

Created two sales divisions from 1 July 2017

RPC
Resins, Polymers and Composites

Composites

Enhanced electrical conductivity

Enhanced thermal conductivity

Improved strength and longevity

Uses include:

- Electronics
- Aviation
- Wind turbine blades
- Pipes
- Automotive

AM
Advanced Materials

Printing (e.g Inks)

Increased processing speed

Specific formulations

Masterbatch

Uses include:

- Medical sensors
- Wearables
- Automotive

Silicon carbide whiskers

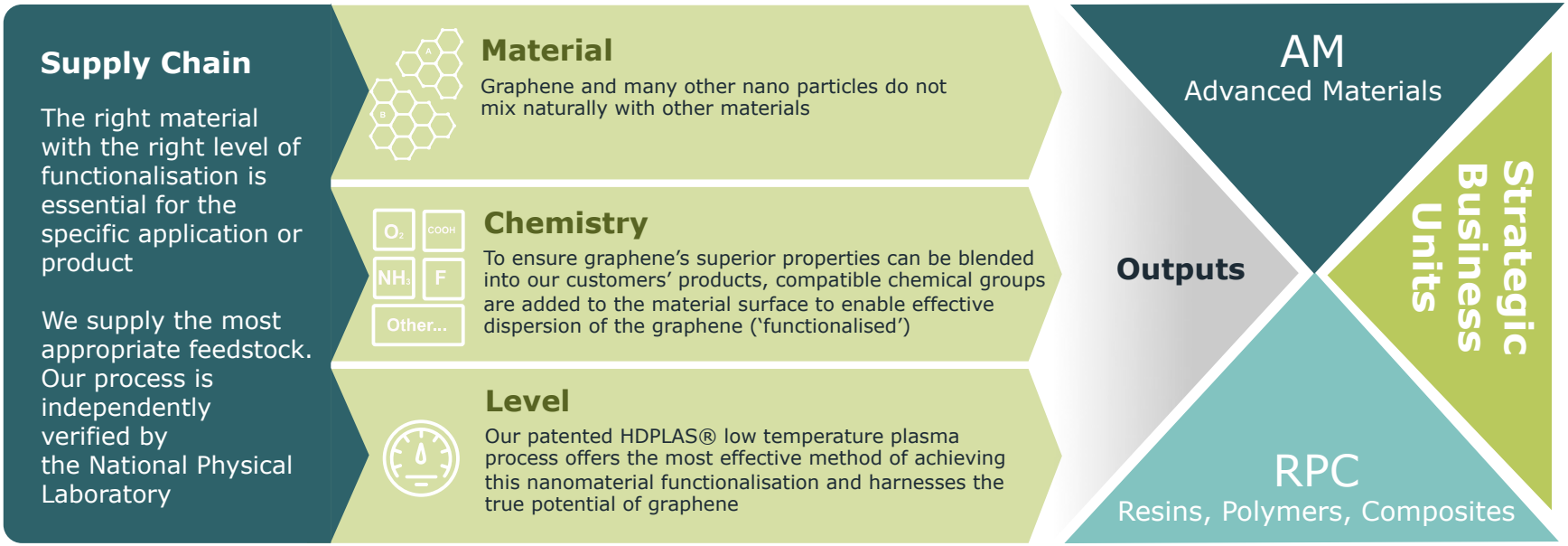
Tough and durable

Uses include:

- Ceramic cutting tools
- Technical ceramics
- Protective coatings

Our process

Our HDPLAS® process is delivering a growing portfolio of products with unprecedented performance



Advanced materials & graphene markets

Significantly improves material properties including mechanical, electrical and thermal attributes

Here, and here to stay.

These materials have moved through an R&D cycle:

13 years ago, identification & research

extraordinary attributes led to wide ranging and sweeping claims

6 years ago, focus on development

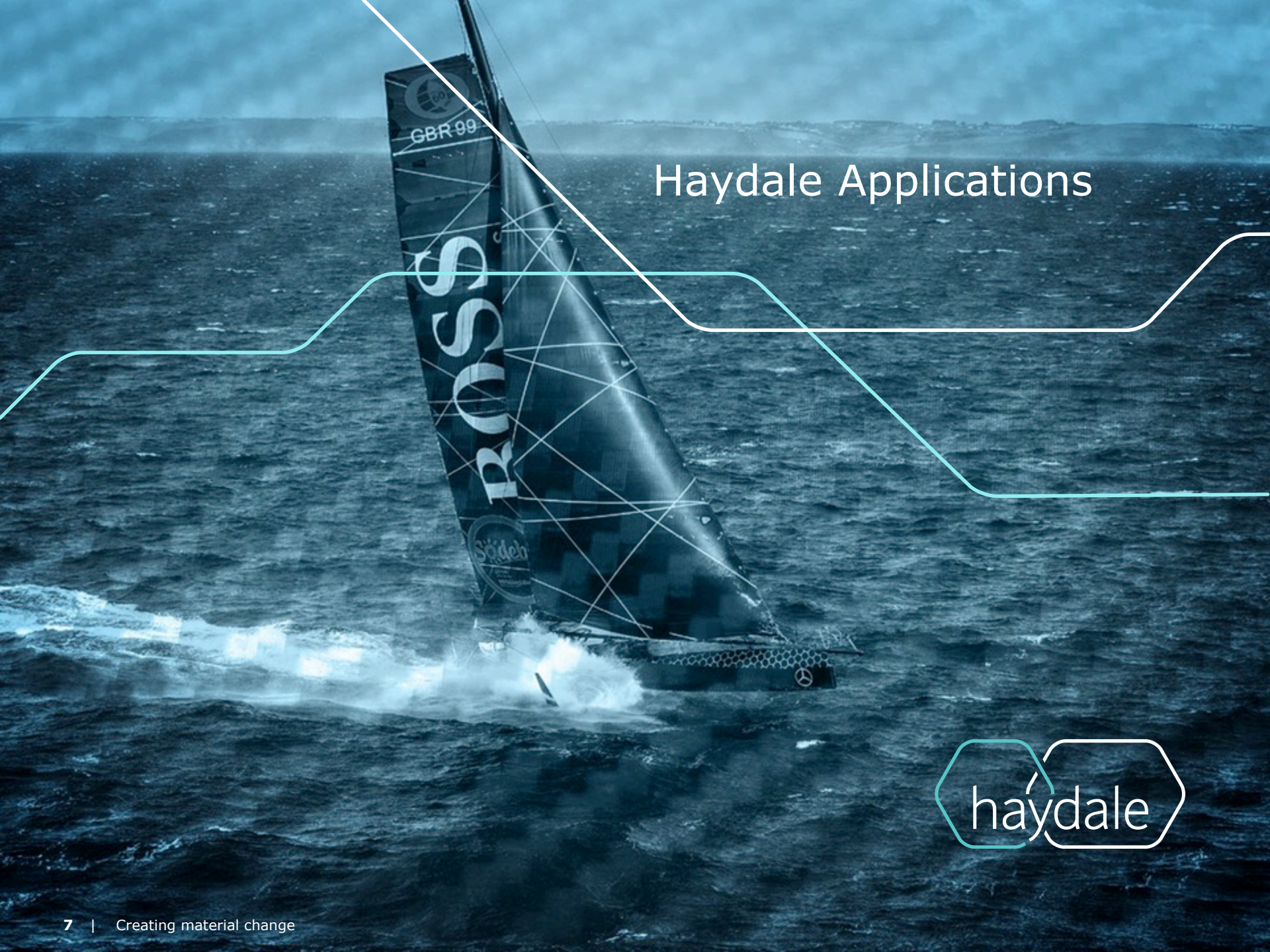
targeting those attributes and understanding where and how they can be applied

now users actively engaged on practical targeted applications

deployment has started

Graphene is now, following many years of testing, starting to be deployed across a number of industries

Significant UK government and public investment to research graphene and other 2D materials, identifying commercial opportunities



Haydale Applications

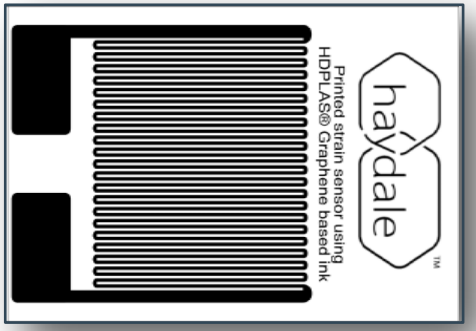
haydale

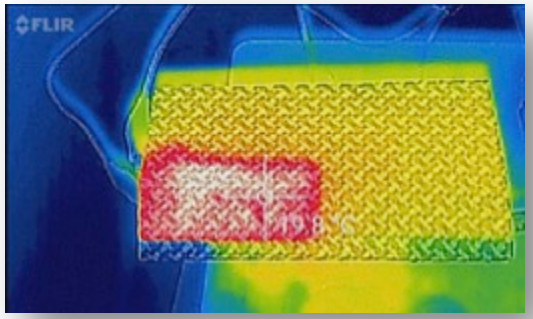
Haydale Graphene Applications - 1

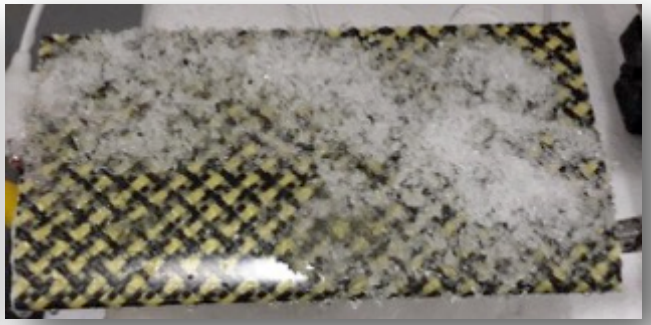
Pressure Sensors
- Wearable systems e.g. shoes, clothing
- Industrial equipment measurements e.g. gaskets
- Impact monitoring e.g. helmets

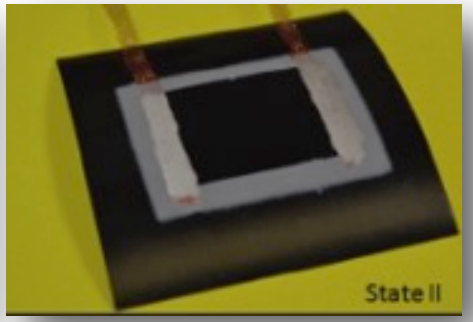
Heaters
- Composite heating e.g. de-icing
- Wearable heating e.g. elite sports

Sensors
- Self-sensing composites
- Wearable technology e.g. medical



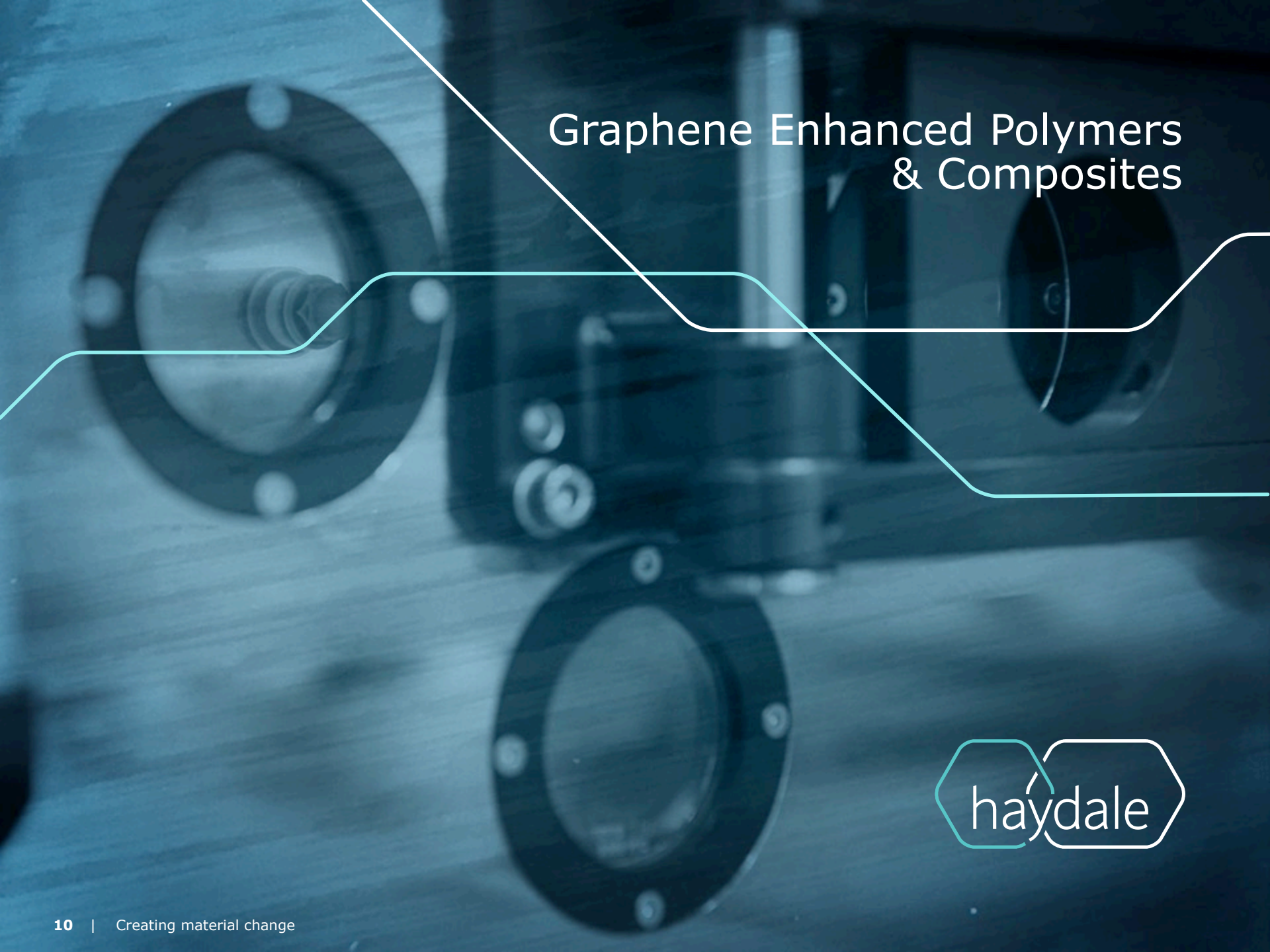






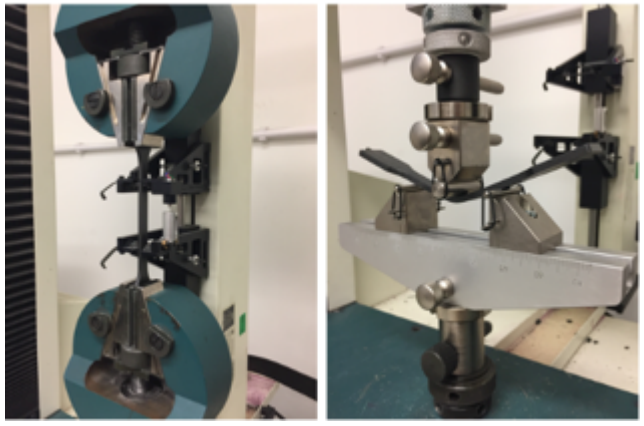
Haydale Graphene applications - 2

- Bipolar plate coatings - high conductivity carbon-based coatings
- Treated & coated plates for incorporation into fuel cell stacks
- Biocompatible, electrically conductive graphene ink for rotogravure printing
- Marine anti-fouling coatings
- Permeation barrier coatings
- Elastomers - improved properties such as barrier properties, mechanical properties and thermal and electrical conductivity
- Composite prepregs (resin modification)
  - Mechanical Performance - e.g. Compression after Impact. Strength, Stiffness, Shear
  - Electrical Performance - e.g. Lightning Strike, EMI/EMC, Anti Static etc…
  - Thermal Performance - e.g. Thermal Conductivity, Heat Dissipation, reduced exotherm, tooling…
  - Physical Performance - e.g. Permeation, Shrinkage, Surface Finish, Lubricity, Corrosion
- Electrically conductive adhesives
  - EMI shielding for electronics and avionics
  - Antistatics


Graphene Enhanced Polymers
& Composites
haydale

THERMOPLASTICS

- Range of processes of nano materials and polymers – processes and parameters are VERY influential
- Nano enhanced PP, ABS, PA6 and PLA, short chopped glass fibre PP, continuous carbon fibre PA6
- Tensile modulus increases up to 65% at 10wt% nano in ABS
- Tensile strength increases up to 35% at 5wt% nano in PP
- Thermal conductivity increases up to 20% at 10wt% nano in PP
- Electrically conductive PA6s have been produced with 1wt% nano (0.5wt% is anti static)
- For 20wt% glass filled PP the addition of 1wt% nano increases the tensile modulus by 20%



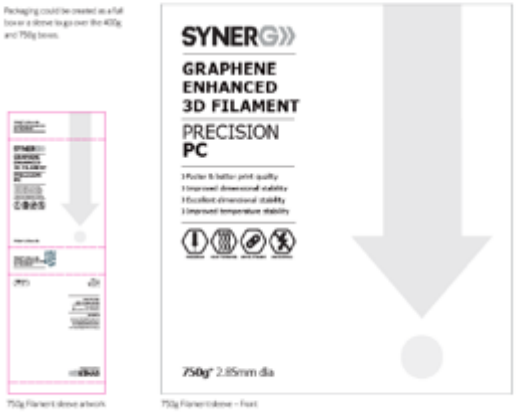
3D printing filament

INVESTCAST PLA

INVESTCAST
PLA

hydrophobic icon

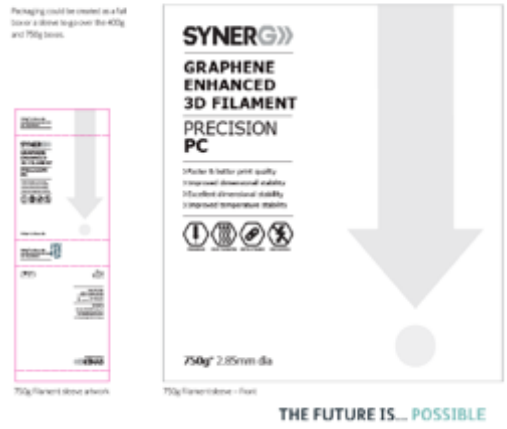
- Engineered to print patterns for casting
- Clean burnout and hydrophobic
- Faster and better print quality
- Excellent first layer and z axis bonding



CONDUCTIVE PLA

CONDUCTIVE
PLA

- Printed Electronics
- Faster and better print quality
- Excellent first layer and z axis bonding
- Can be customised



Material	PLA Polymer/Functionalized Graphene
Color	Black
Filament diameter	1.75 ± 0.10 mm
Volume resistivity	0.60 ± 0.03 Ohm.cm
Print temperature	200 – 230 °C
Platform Temperature	75 – 80 °C

Current Developments in prepregs

HCS are working with a range of industrial, commercial and academic collaborative partners to enhance, on industrially relevant scales:

- Thermal conductivity
- Electrical conductivity
- Mechanical properties
- Reducing exotherm
- Increasing fracture toughness
- Adhesives development
- Lightning Strike protection
- De-icing

In Sectors:

- Aerospace
- Space
- Automotive
- Industrial Materials
- Coatings
- Composite Materials
- Thermoplastics
- Thermosets




Composite Tooling – thermal enhancement

Objectives:

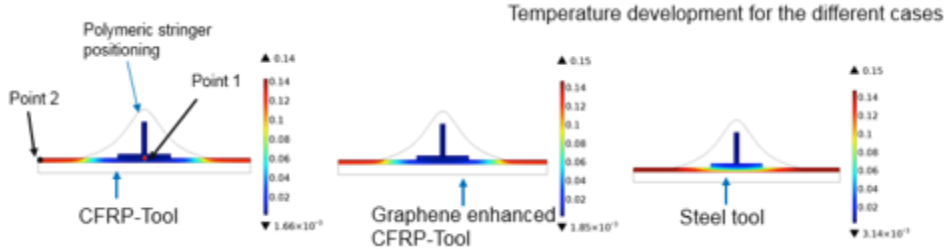
- Preserve the advantage of CFRP tools vs steel tools: low expansion coefficient
- Bridge the thermal performance gap of CFRP tools and steel tools
- Reduction of exotherm in thick section components

Today's improvement:

- 50% better heat conductivity in through thickness direction

Benefit in tooling applications:

- Reduced time for temperature equilibration (in example up to 20%)
- Increased homogeneity of cure especially in complex part arrangements (up to 25%)



Graphene Composites Evaluated in Lightning Strike (GraCELS)

Haydale Composite Solutions
SHD Composites
Cobham Antenna Systems
Airbus
BAE Systems

Aerospace Growth Partnership

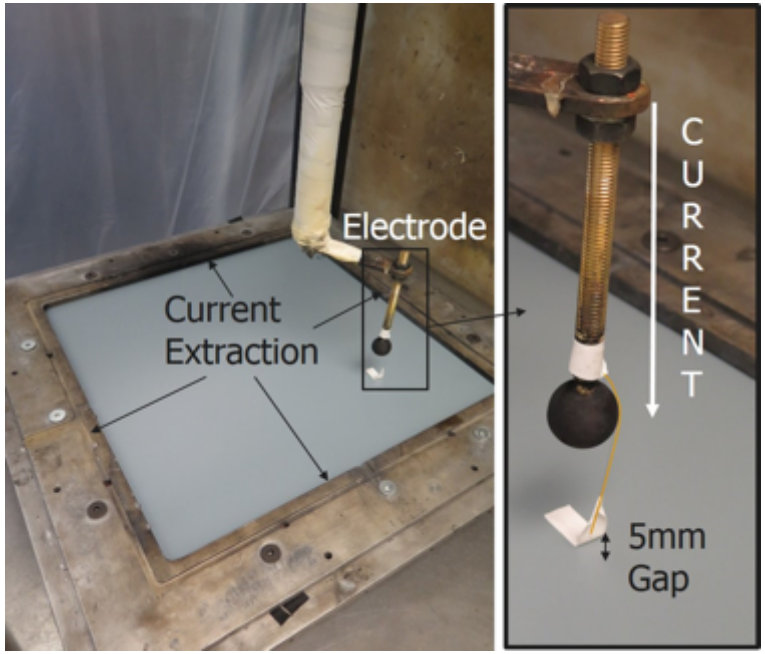
Electrically enhanced prepregs

Problem: CFRP is low electrical conductivity, particularly through-the-thickness

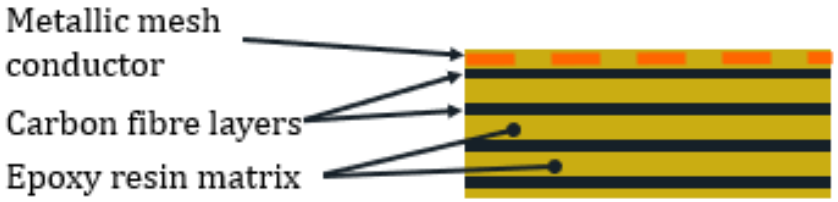
- Lightning strike prevention aircraft
- Electronic cases and enclosures
- Conduits and cables
- Antennas
- Reflectors

- Aerospace
- Telecoms and Power Utilities
- Medical
- Defence

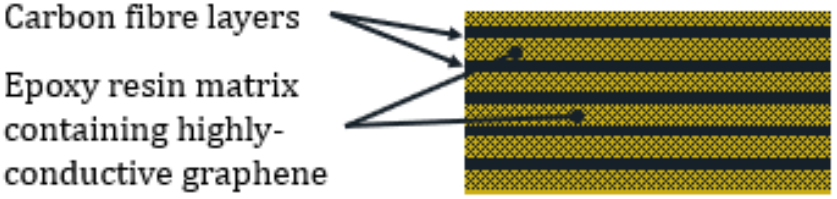
Lightning Strike - Test Setup (courtesy of Cobham)



Current approach to lightning-strike protection

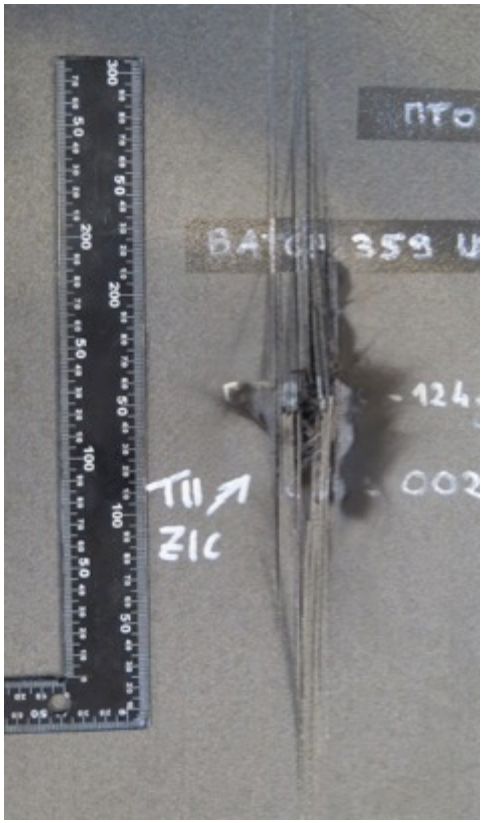


Proposed approach to L-S protection

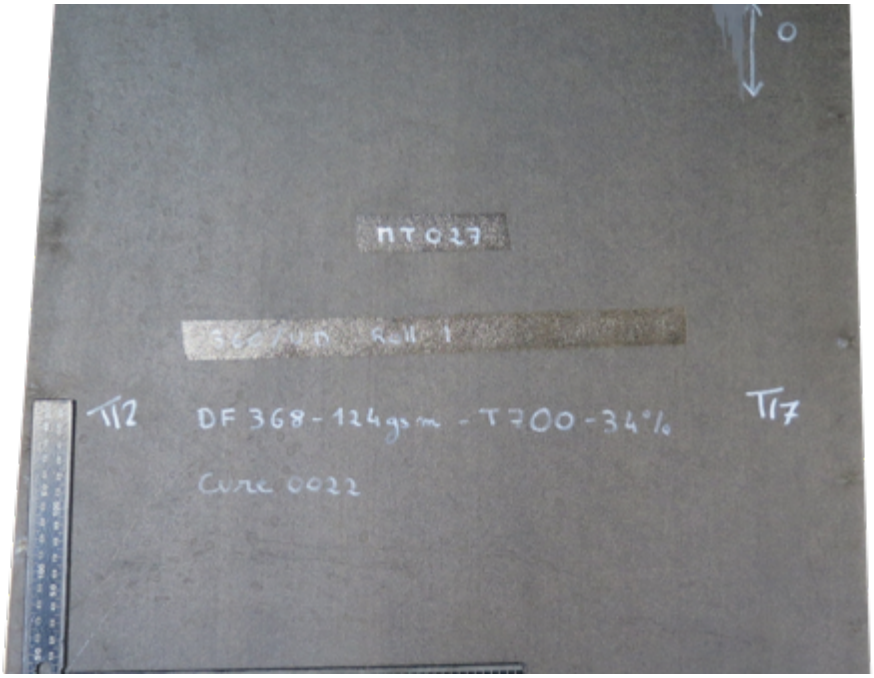


Electrically enhanced prepregs – lightning strike tests

Rear Face Damage after testing – Control Vs Haydale formulation DF368 (no copper mesh – weight reduction)



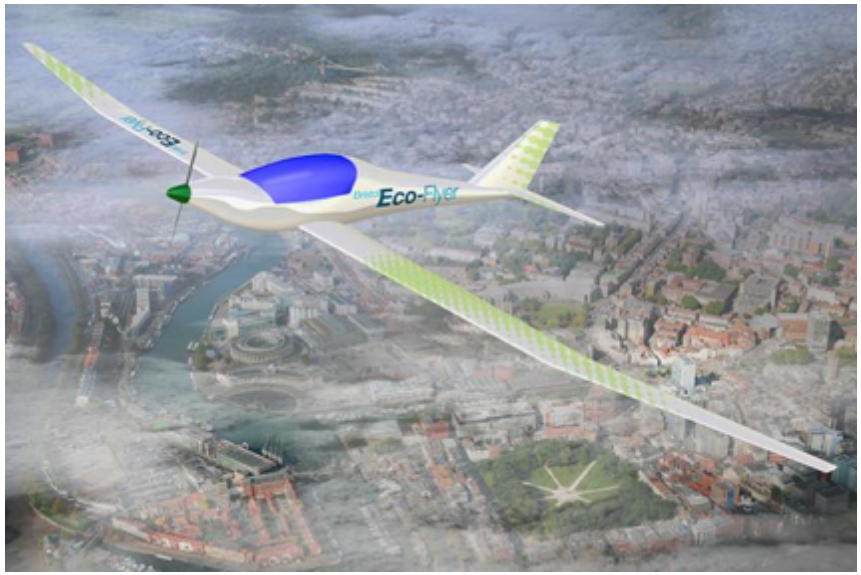
Standard Epoxy Control
Damage = 4

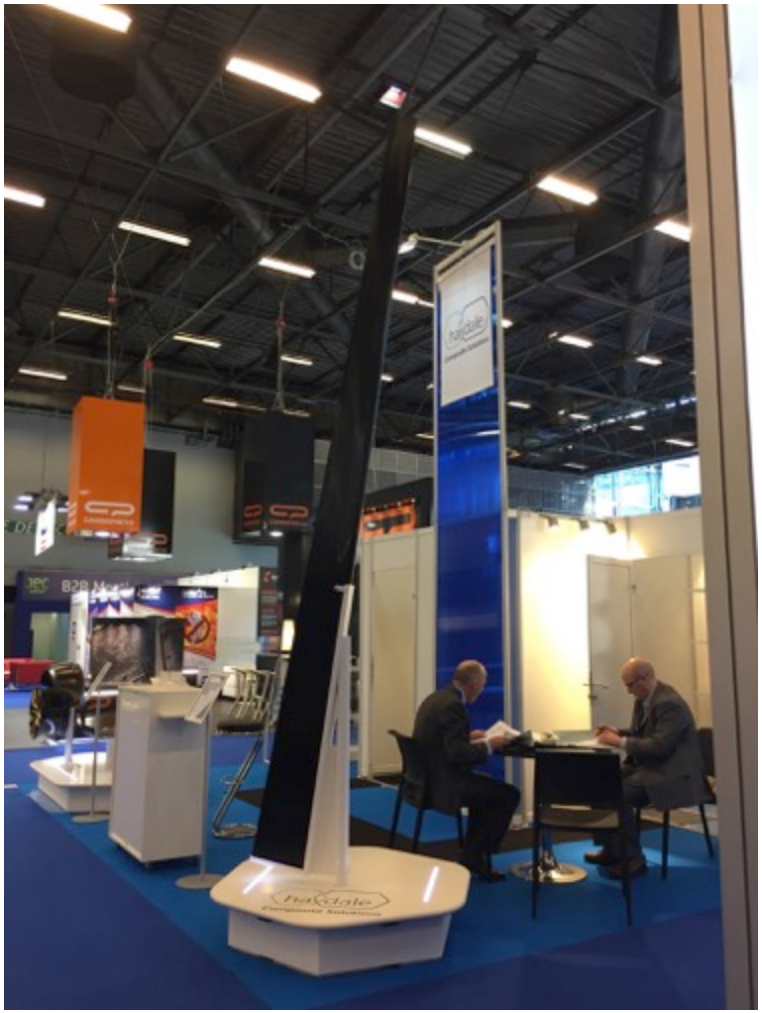


DF368
Damage = 0

Electrically enhanced prepregs – demonstrator

4m Aileron from the Airbus Eco-Flyer on display at JEC, March 2017





End-users in this development:

- Airbus
- BAE Systems

Summary - Electrically conductive composites

Lightning strike composites

- Nano additives have greatly improved lightning-strike performance with the removal of rear face damage
- 8 orders of magnitude increase in through-thickness electrical conductivity of laminates with scope to increase by several orders of magnitude more
- Strength properties equivalent or better than control material
  - 20%+ increase in compression modulus;
  - 5%+ increase in in-plane shear modulus;
  - 20%+ increase in flexural modulus;
- Applications in anti-static and ESD areas
- Application in layered materials – conductive paths in laminated composite structures

- The aim is to get materials on UAVs/airships/space applications in the next year or so

Mechanical Prepreg Development

Initial Prepreg Data:

- 7 prototypes developed – different fillers and loading levels
- Data as tested and not normalised for FVF
  - Complex, some further data required
- Independent test data provided by UKAS approved test organisation
- Comparison to standard 0/90 carbon fibre industrial prepreg control
  - Moulded and tested to same conditions
- Working with NPL to better understand the dispersion of fillers in laminated composites

		Commercial Epoxy Prepreg	HCS Developmental Product		
		T300 , 2x2T, 42% RW, 0 Dir	T300, 2x2T, 42% RW, 0 Dir	% Diff	
Property		**Results**			**Standard**
Flexural Strength	**MPa**	736	856	16%	ISO 178
Flexural Modulus	**GPa**	45.3	54.1	19%	ISO 178
Tensile Strength	**MPa**	509	594	17%	ISO 527-4
Tensile Mod	**GPa**	51.6	62.6	21%	ISO 527-4
Elongation	**%**	0.94	0.93	-1%	ISO 527-4
Compressive Strength	**MPa**	540	600	11%	ISO 14126
Compressive Modulus	**GPa**	46.9	57.5	23%	ISO 14126

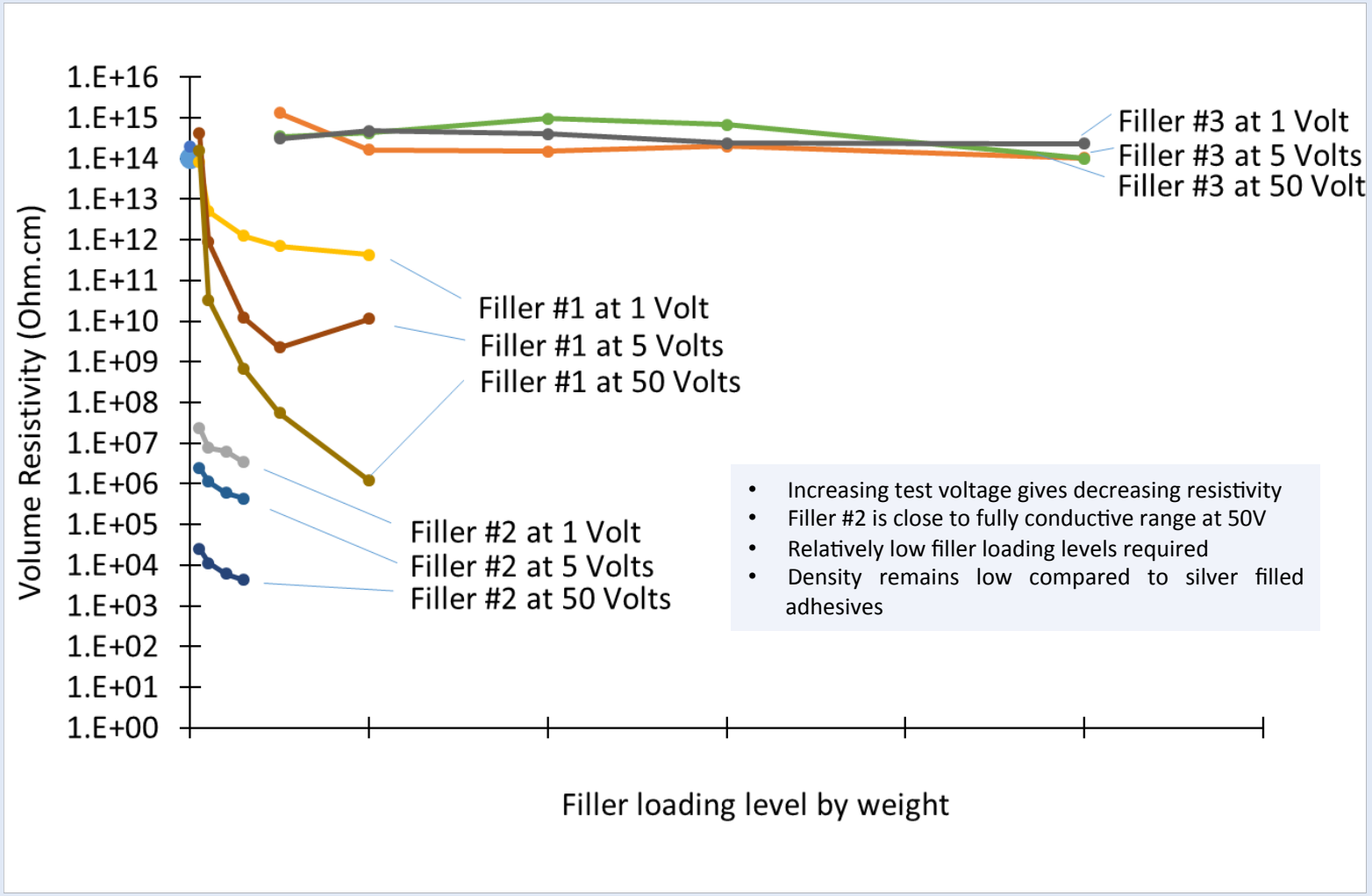
Graphene Enhanced Adhesive Technology through Functionalisation(GrEAT Fun)

Haydale Composite Solutions
SHD Composites
Element Materials Technology
Airbus
GE Aviation

Aerospace Growth Partnership

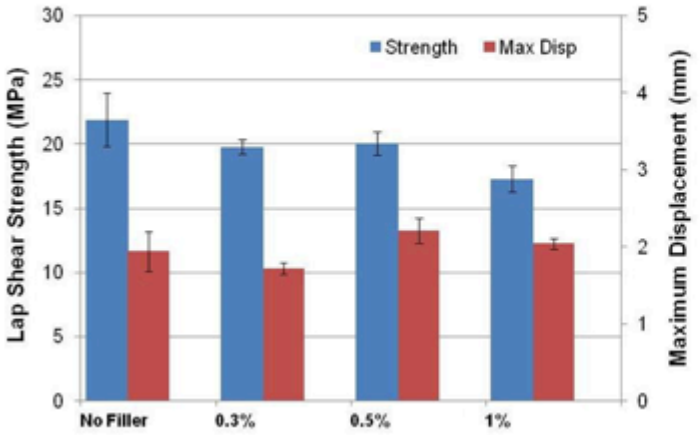
Graphene/2D enhanced adhesives

Voltage sensitivity of graphene/2D filled adhesives

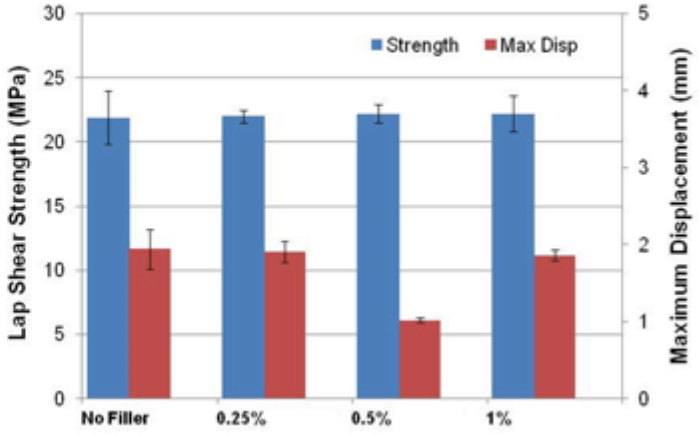


Adhesion Tests – Paste Adhesives (0.2mm thick)

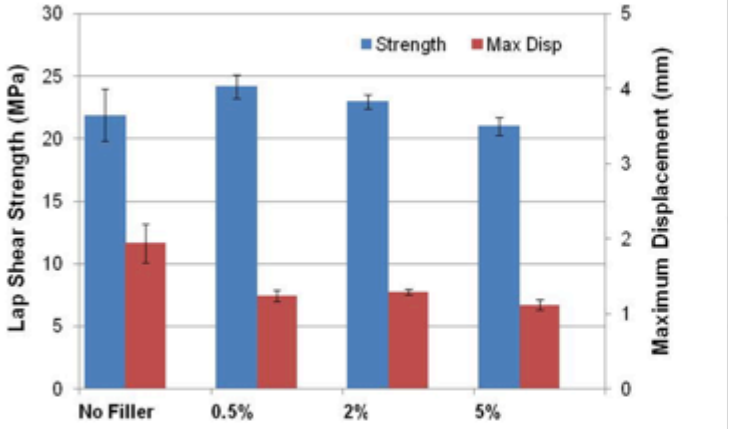
1. Araldite AW4858 Filler A



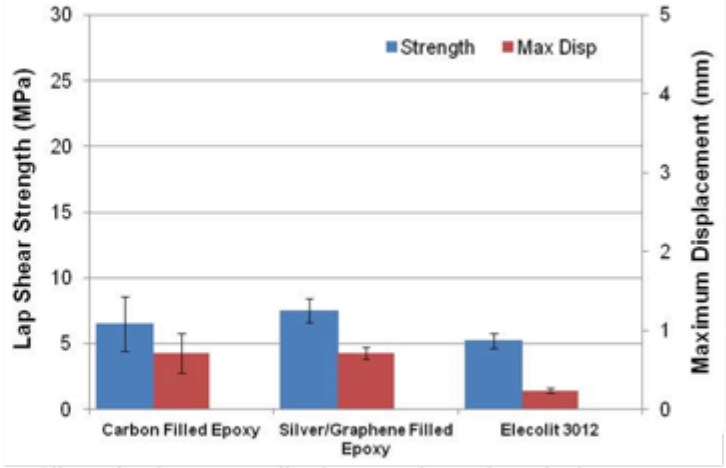
2. Araldite AW4858 Filler B



3. Araldite AW4858 Filler C

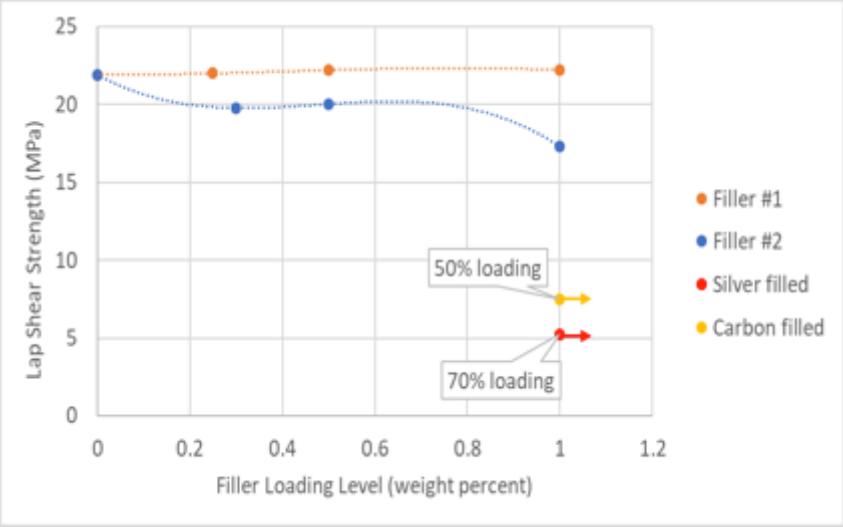


4. Conductive Paste Adhesives



- All conductive paste adhesives are dry and results in poor wetting/adhesion

Graphene/2D enhanced adhesives



Lap shear tests

- Substrates: aluminium
- Surface treatment: gritblast + solvent wipe
- Bondline thickness: 0.25mm (thinner will give higher strength)
- Test temperature: ambient
- Failure mode: cohesive (in the adhesive layer)

Summary:

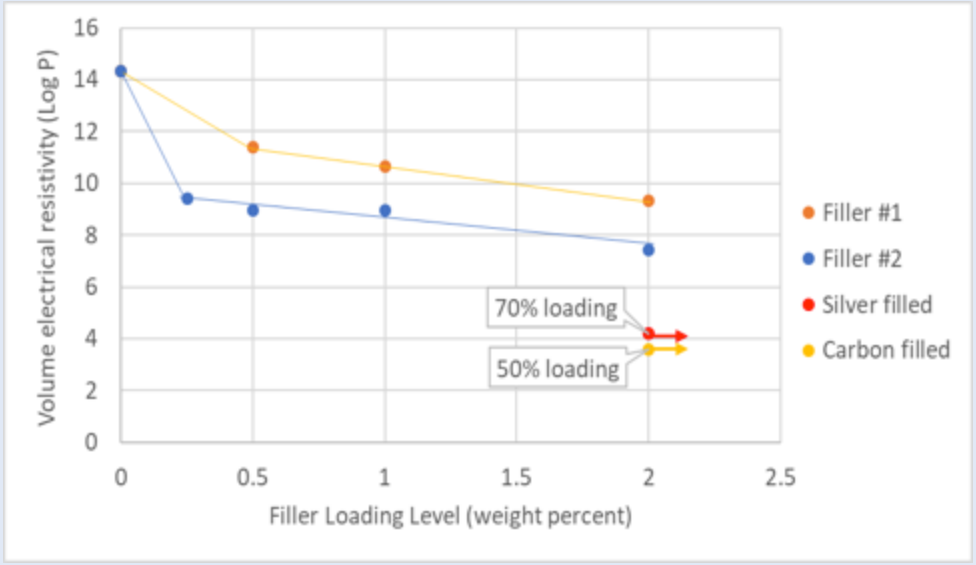
- lap shear strength maintained with increasing filler loading
- Silver filled and carbon filled adhesives have low lap shear strength and are difficult to process
- Density of silver filled adhesive is 3g/cm3 compared to 1.1g/cm3 for graphene/2D filled

Volume electrical resistance

- Test temperature: ambient
- Voltage: 2.1 volts
- Sample thickness: 4.7mm for graphene/2D samples
- Sample dimensions: 40mm x 40mm for graphene/2D samples
- Resistivity is voltage dependent (see next slide)

Summary:

- Resistivity for graphene/2D filled is higher than silver or carbon filled but graphene/2D filled have significantly higher lap shear strength
- Silver and carbon filled are less voltage sensitive
- Further optimisation of graphene/2D filled adhesives is possible



Summary - Electrically conductive adhesives

Conductive Adhesives

- 2D fillers were formulated into commercial paste adhesives – improved electrical conductivity by 11 orders of magnitude
- Electrical conductivity was not as high as silver filled adhesives but lap shear strength was significantly higher and the density was approximately half
- Current commercial conductive paste adhesives based on 70% silver exhibit good electrical properties but may not be suitable as a structural adhesive due to very low processability and mechanical results.
- Final Haydale paste adhesives with different degree of loadings of fillers are viscous but can flow and wet the substrates easily especially when warming the substrates at 40 C prior to bonding and give no detriment (and in some cases deliver improvements) in lap shear adhesion tests
- Film adhesives were also developed as well as carbon veil supported adhesives. Further work needed on impregnation, adhesion properties etc but some very promising electrical properties obtained. Aerospace prime interested for anti-static application

End-users in this development:

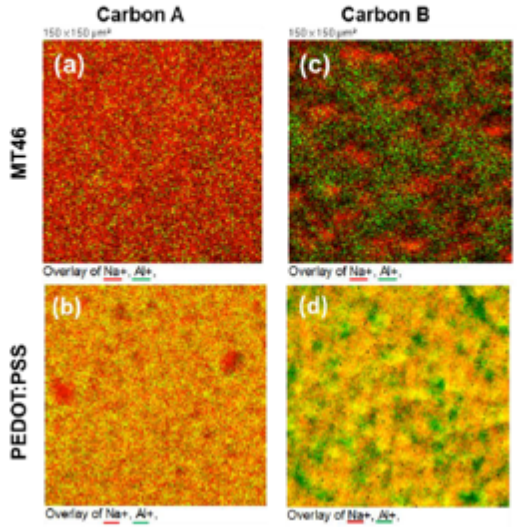
- Airbus
- GE Aviation

Dispersion analysis

SIMS of Graphene Composites

- Secondary Ion Mass Spectrometry (SIMS) for chemical characterisation
- Utilise several ion guns
  - Bismuth (Bi^+ and Bi_3^+) for Analysis
  - Cs^+ and Ar_n^+ for 3D depth profiling , and FIB cross sectioning
- Characterisation carried out on the initial graphene and polymer materials, followed by 3D depth profiling to determine the graphene distribution.

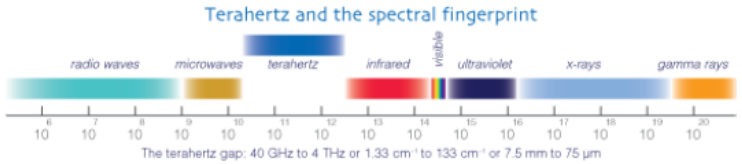
Example of GNP material in composites

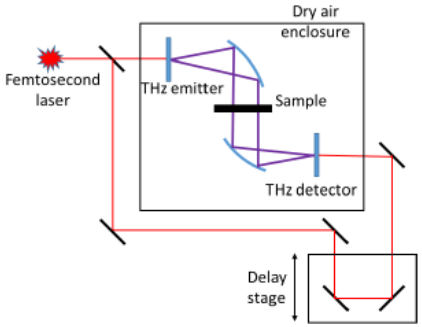


Dispersion analysis

Introduction to THz TDS

NPL National Physical Laboratory



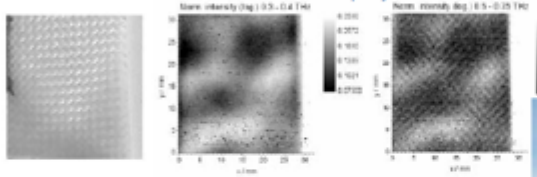


- Transmission or Reflection
- Coherent detection
- Wide bandwidth (0.1 THz – 10 THz)
- High signal-to noise ratio

Implications for dispersion

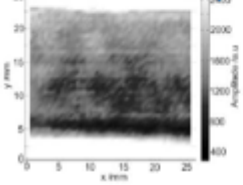
NPL National Physical Laboratory

Glass-fibre reinforced polymers



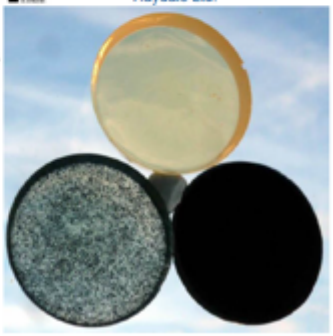
F. Rutz, *et al.*, in *9th European NDT Conference (Berlin, 2006).*

Carbon nanotube-epoxy



Ole Peters, Bernd M. Fischer, and Martin Koch, in *36th International Conference on Infrared, Millimeter and Terahertz Waves (IRMMW-THz), Houston, USA, (2011).*

Haydale Ltd.



Summary

- Haydale are a commercial organisation developing commercial applications for graphene and 2D fillers
- HCS are in the unique position to be able to select the best performing fillers (cost, quality, performance) from across the supply chain, to functionalise then if required and to disperse them into masterbatches
- All materials are designed to use traditional composite manufacturing methods and not to require special treatments
- 2D fillers have been shown to add electrical conductivity to thermoset prepregs and adhesives without detriment to mechanical properties and in some cases enhancing mechanical performance
- Electrically enhanced laminates did not have any backface damage following Zone 1 lightning strike tests performed independently
- Simulations on thermally enhanced prepregs have indicated significant potential time savings in production times. HCS have applied for IUK funding to demonstrate these benefits in the production of real composite tools and components
- Funding applications have been submitted for electrically conductive prepregs and adhesives developments to take the promising 'proof of concept' studies closer to commercialisation

Summary - Challenges

- Main challenge – to get graphene/2D enhanced materials to market to deliver real engineering benefits
- Develop ways to transfer the innovation generated in SMEs into primes/OEMs, Tiers 1's etc to the benefit of all – to vault over the 'valley of death'
- Increase SME engagement with Catapults etc under beneficial terms to the SME – cost and IP
- Government funding to help SMEs access the knowledge and expertise in the Catapults – Analysis for Innovators – A4I with NPL etc
- To work with end users with joint developments (preferably funded!) so that we can deliver some of the benefits that we are seeing

Creating Material Change

Thank You

peter.hansen@haydalecs.com

www.haydale.com