High temperature optical fibre coatings (HiT OFCs)

for next generation gas emission monitoring

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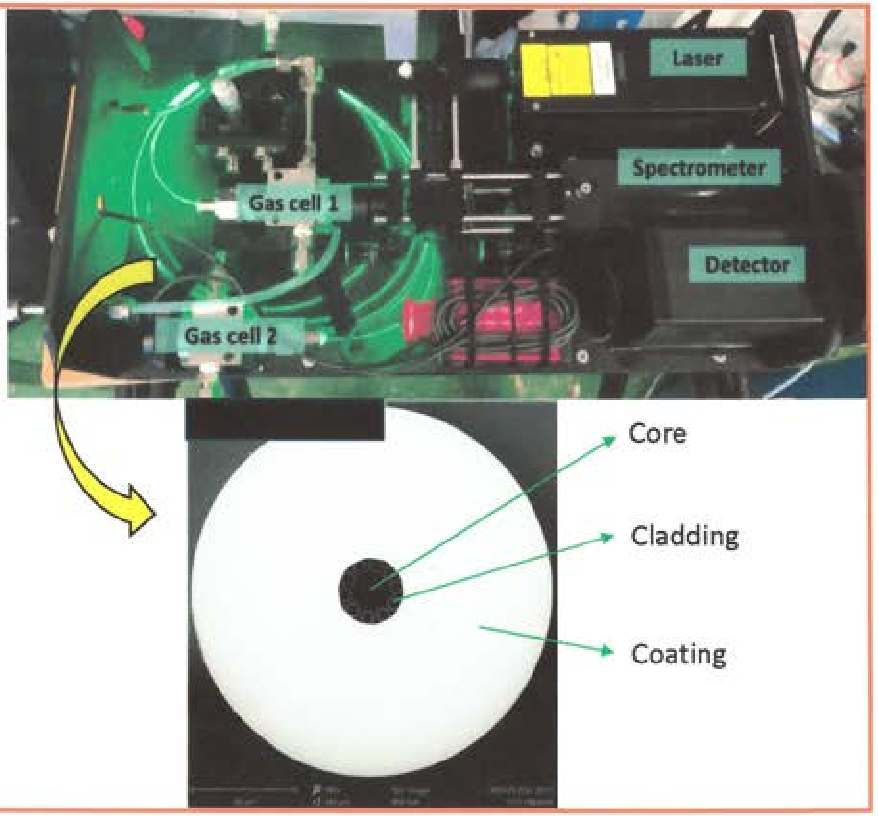
- Foundation Industries (FIs) contribute significantly to the overall UK CO_2 emissions.
- Sensitive real-time gas emission monitoring is prerequisite to the step-changes necessary in FIs processes for reductions in environmental emissions and energy consumption to achieve net zero.
- Continuous Emission Monitoring Systems (CEMS) are commonly used in Foundation Industries (FIs) for process monitoring and to ensure compliance with permits.
- Commonly used techniques for emission monitoring in the FIs are:

Gas Chromatography Mass Spectrometry (GC-MS)	**Fourier Transform Infrared Spectroscopy (FTIR)**
✓ High efficiency ✗ Not a real-time technique	✓ Quick and Reliable ability to monitor multiple gaseous compounds simultaneously ✗ Inability to detect homonuclear diatomic molecules (e.g., O_2, N_2, H_2).

- The evolving UK regulations and legislations in relation to real-time emission monitoring, demand systems with enhanced sensitivity and reliability capable of detecting a wide range of gaseous species.

Innovate UK

- hot Gas Raman Identification and measurement For Foundation INdustries (GRIFFIN), an Innovate UK project valued at > £500k (95372).
- Began in March 2021 and was led by IS-Instruments.
- Aimed to deliver a transformative new instrument for the glass, cement and ceramics, utilising analytical Raman gas.
- This instrument uses a microstructured hollow-core optical fibre to increase the interaction volume between laser light and the gas sample.
- To prevent acid condensation, an operating temperature of 180°C was selected.



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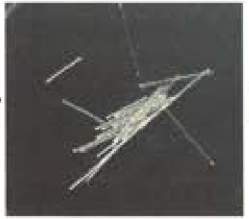
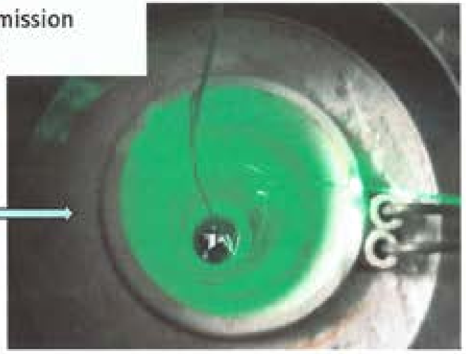


As-received

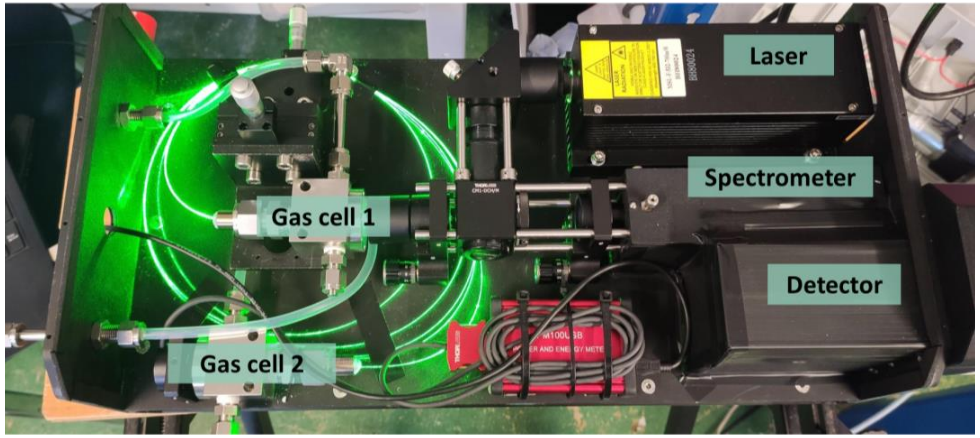
5 hours at 180°C under air

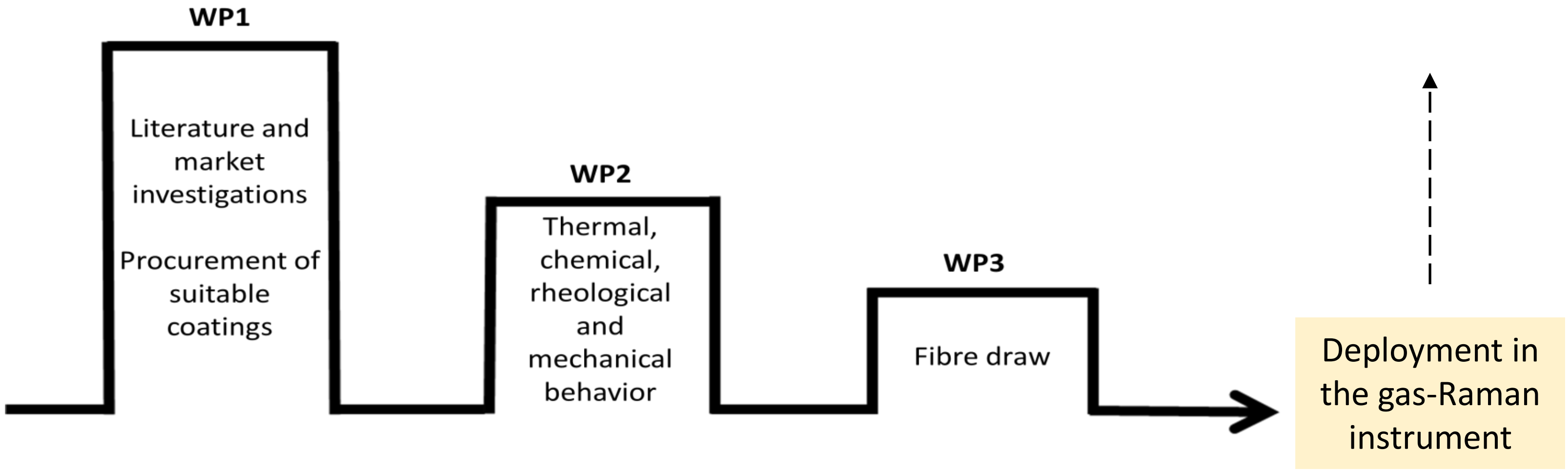
Setup at GTS for simultaneous laser transmission measurements under varied temperature



Optical transmittance of the fibre can be affected by the oxidative degradation of the fibre coating used by ORC, University of Southampton.

- High Temperature Optical Fibre Coatings for Next Generation Gas Emission Monitoring (HiT OFCs), a TFIN+ funded project valued at ≈£30k.
- Began in July 2022, led by SHU.
- This project aimed to advance the TRL of the developing gas-Raman instrument by expanding its operating temperature (beyond 85°C).





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WP1

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Review

From acrylates to silicones: A review of common optical fibre coatings used for normal to harsh environments

R. Janani [a,*], D. Majumder [a], A. Scrimshire [a], A. Stone [a], E. Wakelin [a], A.H. Jones [a], N.V. Wheeler [b], W. Brooks [c], P.A. Bingham [a]

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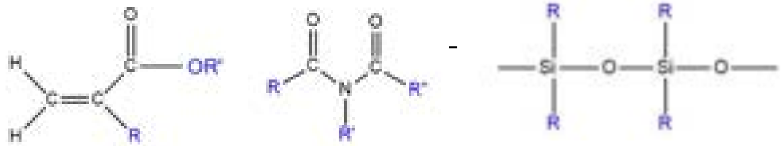
[c] IS-Instruments Ltd, Pipers Business Centre, Tonbridge, Kent TN9 1SP, UK

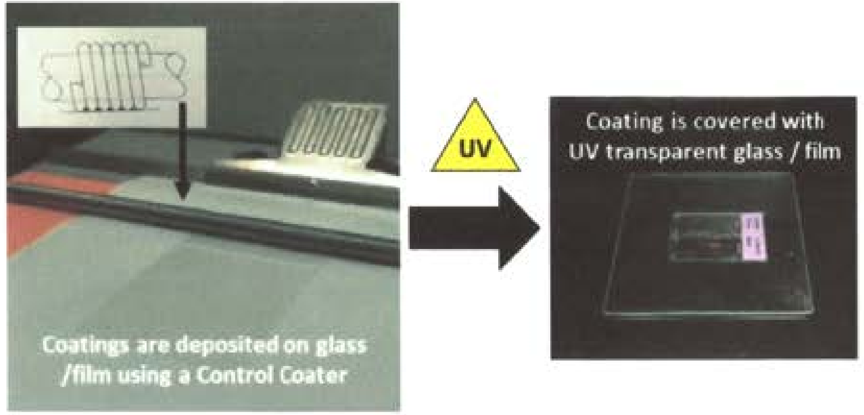
- Acrylates dominate the optical fibre coating market due to their chemical versatility and lower cost.
- Specialty acrylates, including silicone-acrylate hybrids, appear to be the most promising UV-curable coatings currently on the market.



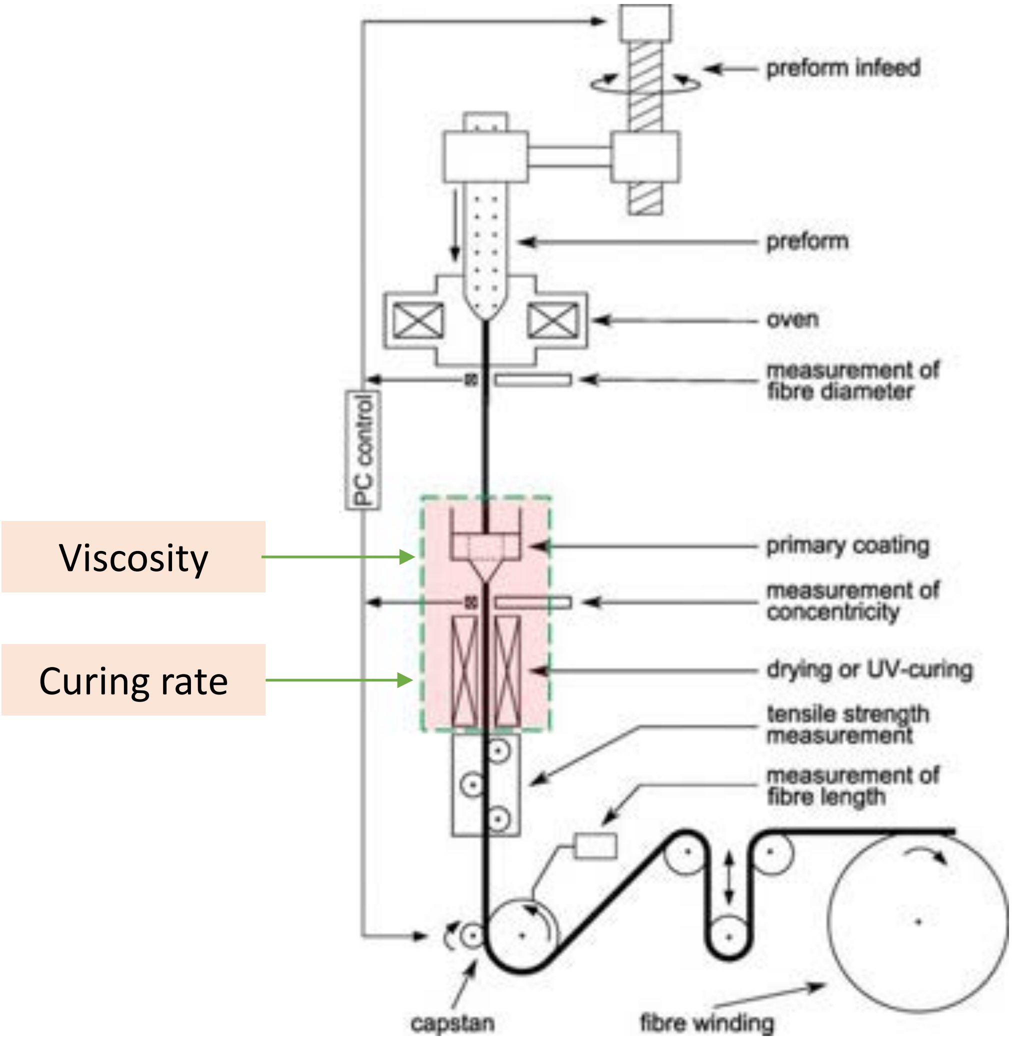
Acrylic ester   Imide functional group   Silicone

WP2

Coating ID	Manufacturer	Upper temperature limit	Type
1		150°C (3000 hours - air)	Conventional acrylates + additives
2		**up to** 200°C	Acrylic urethane elastomer
3		**up to** 300°C	Siloxane Acrylate
4		**up to** 300°C	Siloxane Acrylate
5		**up to** 300°C	Siloxane Acrylate
6		**up to** 360°C	Fluorosiloxane Acrylate
7		-	Acrylated resin

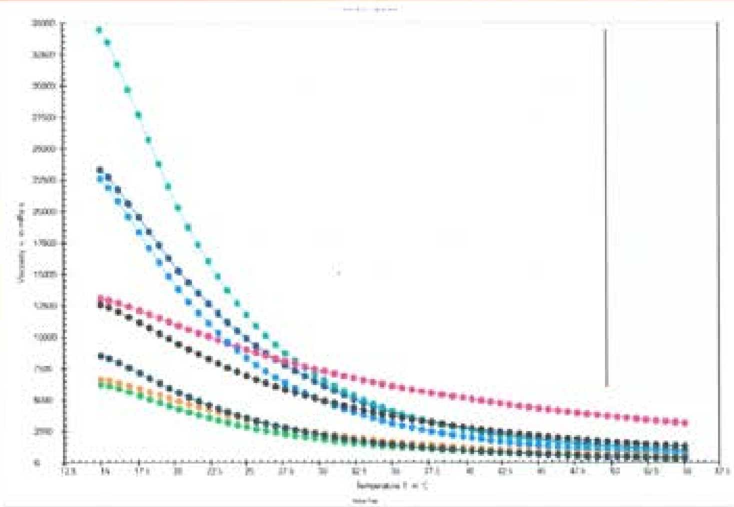


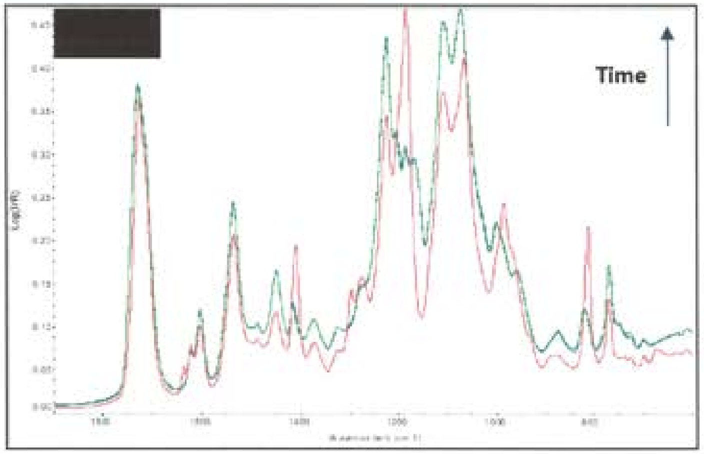
WP2

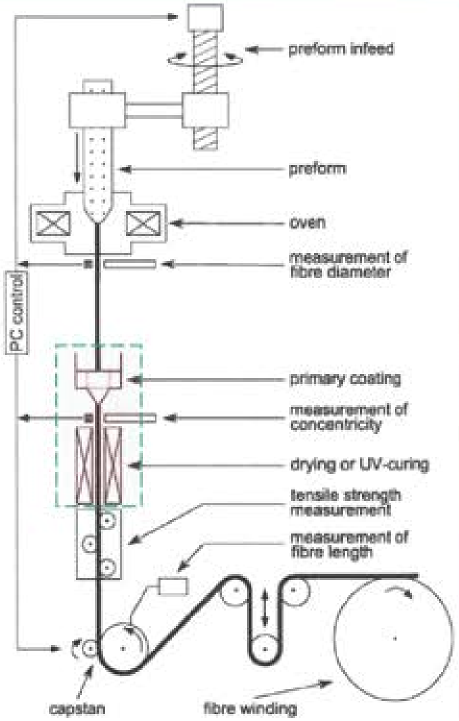


Schematic illustration of a fibre draw tower

WP2

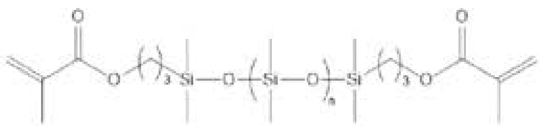






Schematic illustration of a fibre draw tower

- A comparable viscosity to the benchmark coating can be achieved by adjusting the Coating Cup temperature by (maximum) ±16°C.
- Siloxane acrylates demonstrated the slowest curing rate and most O_2 sensitivity amongst all the coatings investigated. This implies that the speed of fibre draw must be reduced for these coatings to ensure complete curing.



Example of an acrylate-terminated siloxane hybrid molecule.

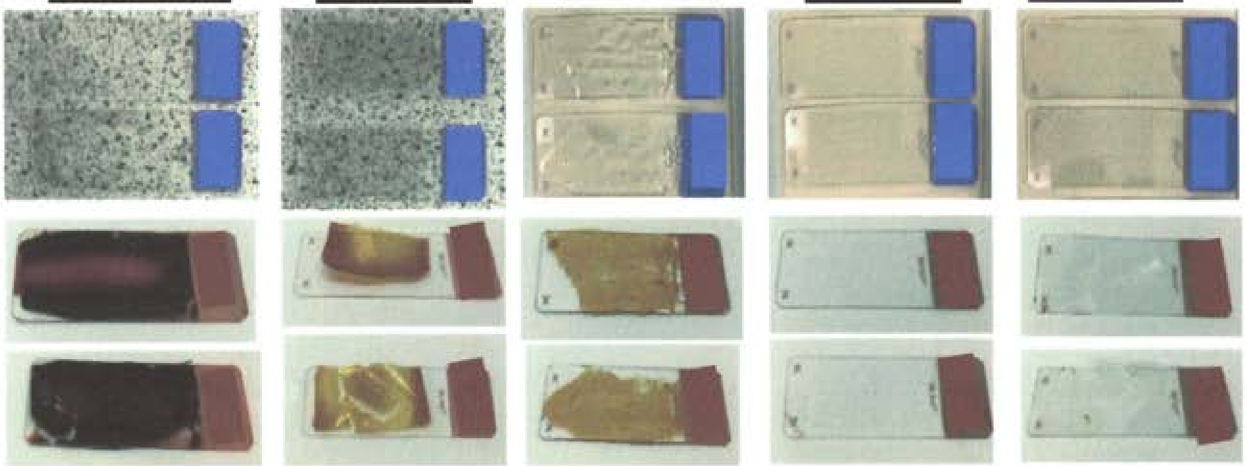
WP2

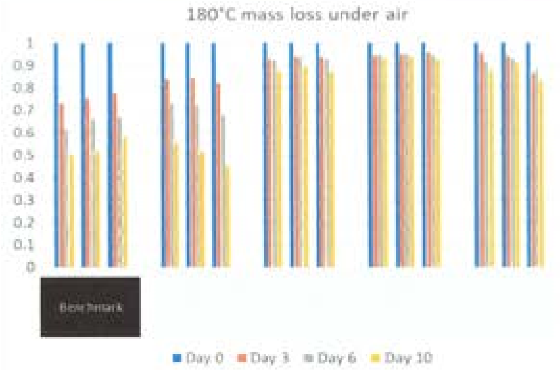
Conventional acrylate | **Specialty acrylates** (hybrid acrylates or acrylates with certain functional groups) | **Siloxane acrylates**

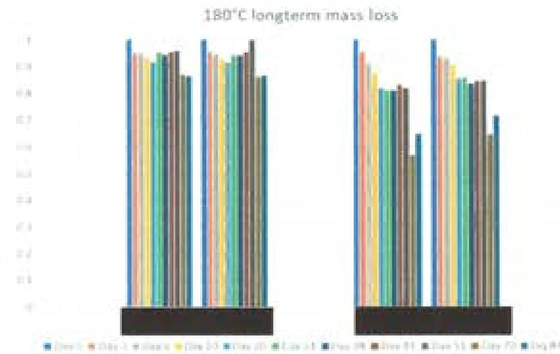
Benchmark | [redacted] | [redacted] | [redacted] | [redacted]

Day 0

Day 10





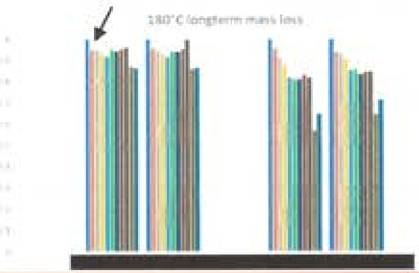


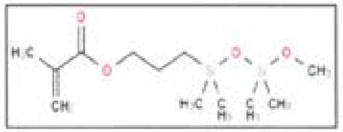
- The empirical results indicated that the siloxane acrylates are the most resistant to oxidative degradation at 180 °C.
- The two hybrid coatings showed more than 85% and 70% weight retention after ≈3 months of exposure to 180°C under air.
- Unlike the other siloxane acrylate coatings investigated, [redacted] showed no signs to shrinkage throughout the heat treatment experiment.

[redacted] [redacted]

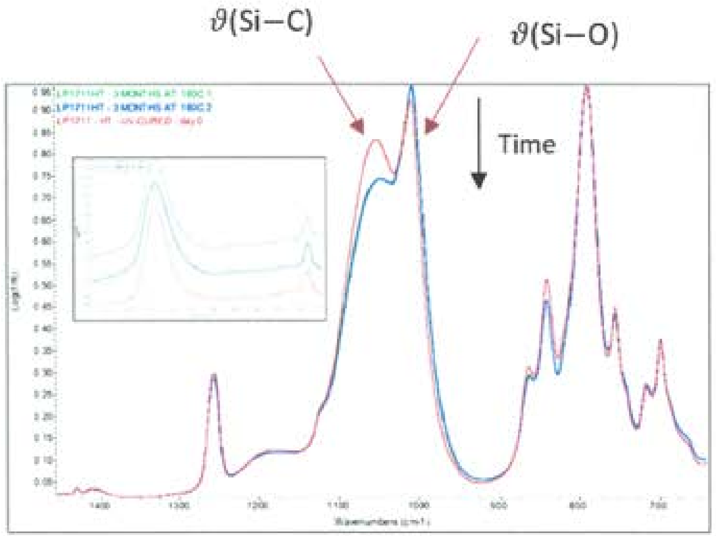
WP2

- Headspace GC-MS was conducted on the emitted gases within the first 24 hours of heating.
- Based on the results, the initial mass loss in siloxane acrylates are (mainly) associated with the loss of unreacted oligomers, antioxidants, initiators, etc.
- The IR data indicates subtle signs of chains scission across the organosiloxane backbone in the [redacted] only after ≈ 3 months of exposure to 180°C.

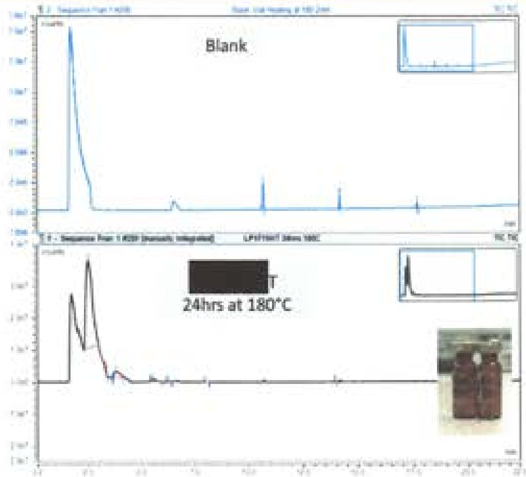




Main component of [redacted]



IR spectrum of [redacted] coating before and after 180°C exposure under air.



Retention Time / min	Compound / CAS	Chemical structure
2.57	Methoxytrimethylsilane 1825-61-2	$H_3C-Si(CH_3)_2-OCH_3$
3.80	Hexamethyldisilane 107-46-0	$H_3C-Si(CH_3)_2-O-Si(CH_3)_2-CH_3$
5.62	Bis(trimethylsilyl) Peroxide 5796-98-5	$CH_3-Si(CH_3)_2-O-O-Si(CH_3)_2-CH_3$
7.99	Octamethyltrisiloxane 107-51-7	$CH_3-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-CH_3$
34.49	1,3-Pentadiene, 4-(trimethylsilyloxy)- 72237-32-2	

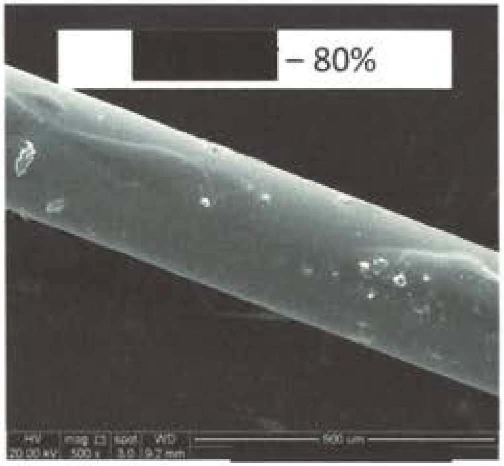
Headspace GC-MS analysis of [redacted] after 24hrs 180°C exposure

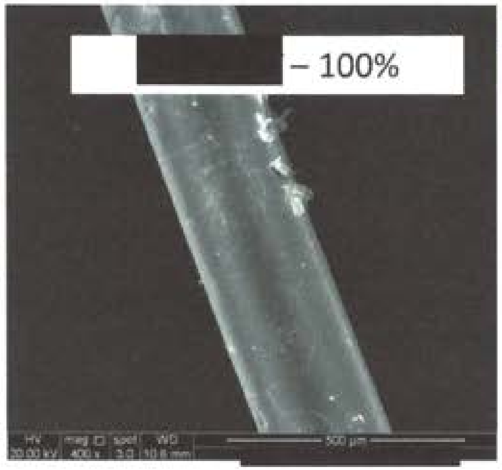
TRANSFORMING THE FOUNDATION INDUSTRIES

Motivation | GRIFFIN | Challenge | **HiT OFCs** | Beyond HiT OFCs

WP3

- Based on the results gathered, [redacted] was recommended as a suitable high temperature optical fibre coating to ORC.
- In Feb-March 2023, the first round of fibre draw was conducted at ORC facilities.
- Different lamp powers were tested (57.5%, 70%, 80%, 95% and 100%) while keeping the drawing speed the same. At 100% lamp power, the coating appeared smooth.
- Alternative fibre draw settings, including drawing speed, uncured coating temperature and alternative UV lamps are yet to be explored.





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Ultimate goal: Deployment of the optical fibre with high temperature coating in the gas-Raman instrument.

Lifetime determination using TGA

- Using a dynamic / non-dynamic TGA approach to determine lifetime-temperature dependencies of the investigated coatings.
- This may be used to find out the upper temperature limit for continuous use for a specific length of time (for example).
- Current reported methods tend to over or underestimate the Arrhenius parameters when compared to experimental data.

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) = A \exp\left(-\frac{E^*}{RT}\right) f(\alpha)$$

α → extent of reaction (0< α <1)
A → Arrhenius frequency factor
E^* → activation energy
R → gas constant
T → absolute temperature
f(α)→ kinetics model function

The parameters in red can be calculated using different TGA approaches.

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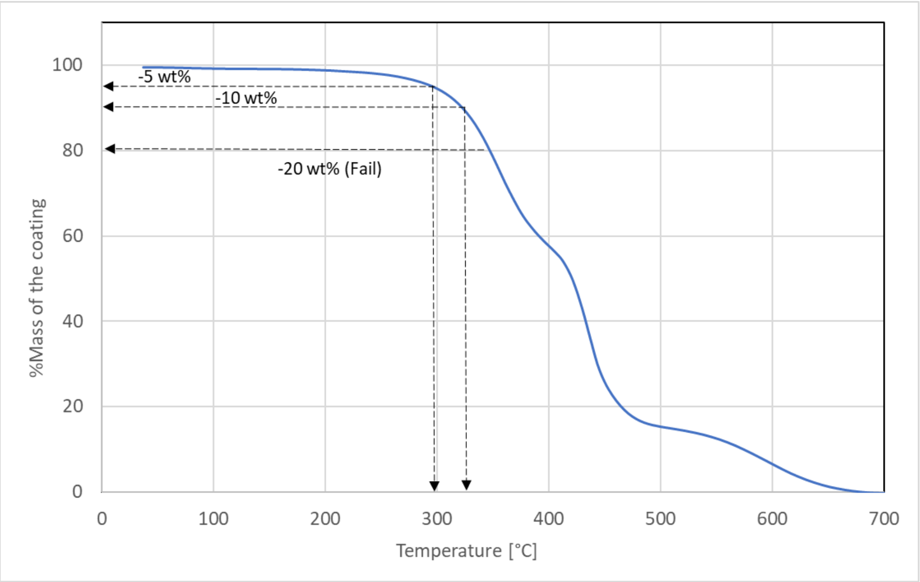
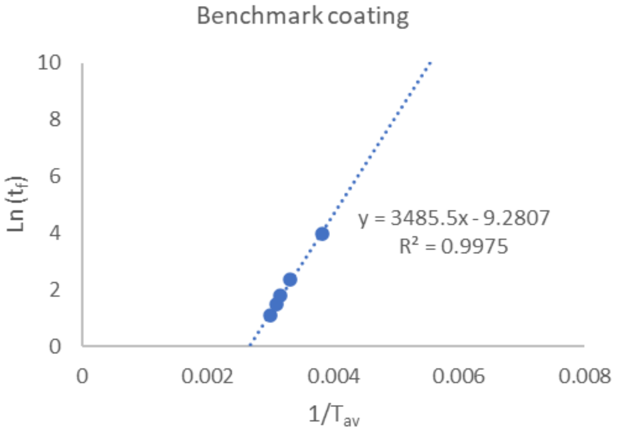
Results shown here are derived using the SSL method





Service temperature [°C]	Estimated Service life
136.96	20 years
140.80	10 years
155.24	1 year
260.60	1 hour
180.00	16.6 days

TRANSFORMING THE FOUNDATION INDUSTRIES

Motivation | GRIFFIN | Challenge | HiT OFCs | Beyond HiT OFCs

Academic and industrial development

Impacts

Review

From acrylates to silicones: A review of common optical fibre coatings used for normal to harsh environments

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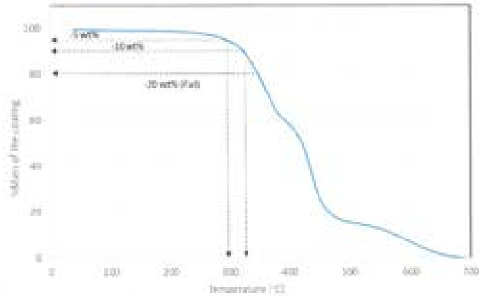
[b] Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, UK
[c] [illegible]



TGA approach for lifetime prediction

First fibre draw at ORC with a high temperature coating.

Coatings	at 35°C	
	Storage Modulus / Pa	Loss Modulus
	6.60E+08	8.6E+07
	1.70E+08	3.9E+07
	1.60E+08	7.0E+07
	1.60E+08	4.7E+07
	5.20E+07	1.5E+07
	1.50E+06	1.5E+05

Mechanical characterisations using DMA

Personal development

- Gained valuable experience as the project PI!
- Built strong academic and industrial networks.
- Expanded my supervision & teaching experience:
    - Received an internal fund and recruited a summer intern to continue the work on the high temperature coatings.
    - Designed a project focused on the realisation of a TGA method for lifetime prediction as part of a module for the Physics and Maths students.
- Gained more confidence in actively seeking opportunities to conduct independent research.

Thanks for listening

I'd like to thank everyone who contributed and enabled the delivery of this work.

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Natalie Wheeler

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Will Brooks
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Spencer Green

Newcastle University
Deblina Majumder

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Rob Werner

Wienerberger
Stephane Vissiere

TFI Network+ – Transforming the Foundation Industries

UKRI Innovate UK