From polymer precursors to high performance fibers and ceramic matrix composites

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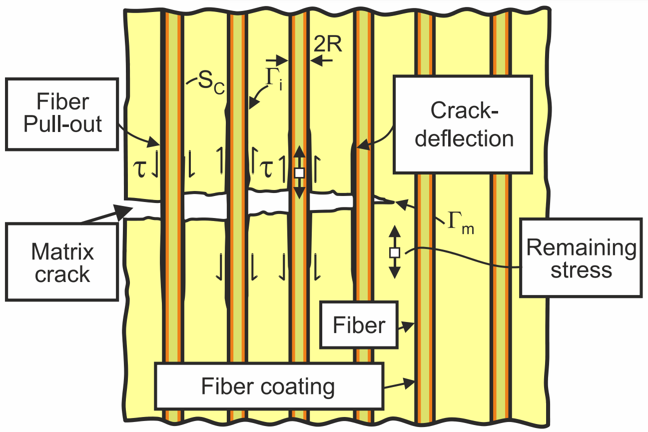
Ceramic matrix composites

- Mechanical reinforcement of ceramics with carbon or ceramic fibers
- Energy dissipating effects during crack propagation
- Larger strain at fracture and higher crack propagation resistance

Different types of textile preforms

- Rovings
- Nonwovens
- Weaves
- Braids

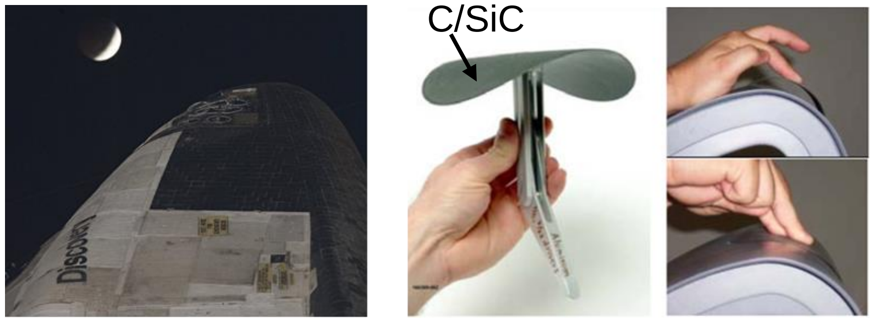
Mechanisms of fiber reinforcement



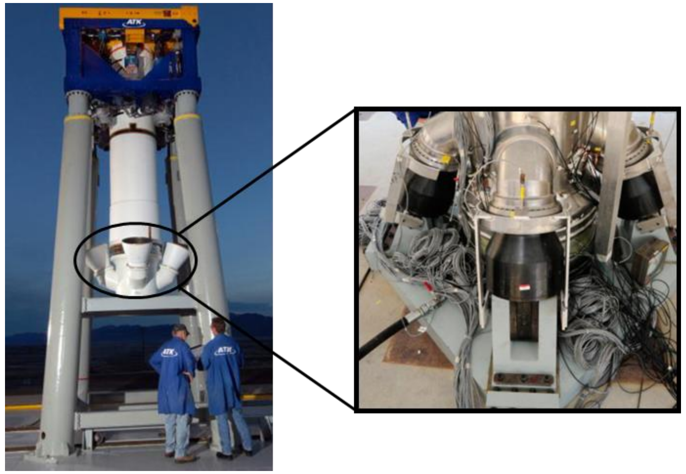
Introduction

- C/C-SiC[1]: Non-oxide ceramic matrix composite
  - Reinforcement phase: Carbon fibers
  - Matrix phase: SiC, residual silicon, amorphous carbon

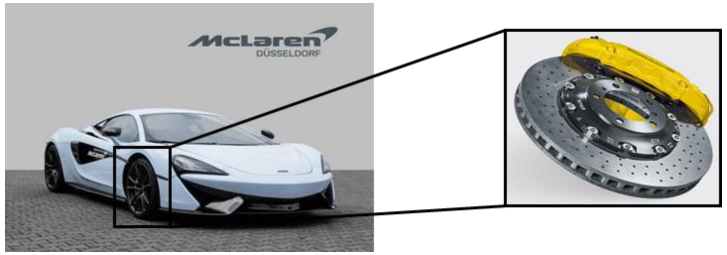
- Applications:



Space Shuttle: Wing leading edge repair [2, 3]



Orion LAS: Nuclear thermal propulsion nozzle extension [4]



Automotive industry: Brake discs [5, 6]

[1]: W. Krenkel, Keramische Verbundwerkstoffe, Wiley, 2003
[2]: https://www.nasa.gov/multimedia/imagegallery/image_feature_1827.html
[3]: D. Glass, 15th AIAA International Space Planes and Hypersonic Systems and Technologies Conference, Dayton, USA, 2008
[4]: D. Jones et al., 48th AIAA/ASME/SAE/ASEE, Joint Propulsion Conference and Exhibit, Georgia, USA, 2012
[5]: https://www.sglcarbon.com/loesungen/anwendung/bremstechnik/
[6]: https://preowned.mclaren.com/eu/de/de/fahrzeuge/mclaren-570s-qualified-kjcun8n8

Introduction - Requirements for the CFRP matrix material for C/C-SiC production

- Manufacturing of a C/C-SiC via the liquid silicon infiltration process

Raw materials
- Carbon fibers as reinforcement phase
- Thermoplastic or thermoset matrix

Shaping
- CFRP manufacturing
- RTM, hot pressing, additive manufacturing, etc.

Pyrolysis
- C/C manufacturing
- Transition of polymer matrix material to carbon
- Volume shrinkage
- Evolution of characteristic crack pattern

Siliconization
- C/C-SiC manufacturing
- Infiltration of crack pattern with liquid silicon
- Reaction of silicon with carbon to silicon carbide

- Requirements for successful C/C-SiC manufacturing
  - Good infiltration of carbon fiber bundles with matrix polymer during shaping process
  - High char yield after pyrolysis

Specific thermoset and thermoplastic polymers meet the requirements for **CFRP matrix materials**

[7]: N. Bansal, Ceramic Matrix Composites – Materials, Modeling and Technology, Wiley, 2015
[8]: Patel et al., Bulletin of Materials Science, 35(1), 2012

State of the art – Thermosets as CFRP matrix material

State of the art: Thermosets as CFRP matrix material [9]

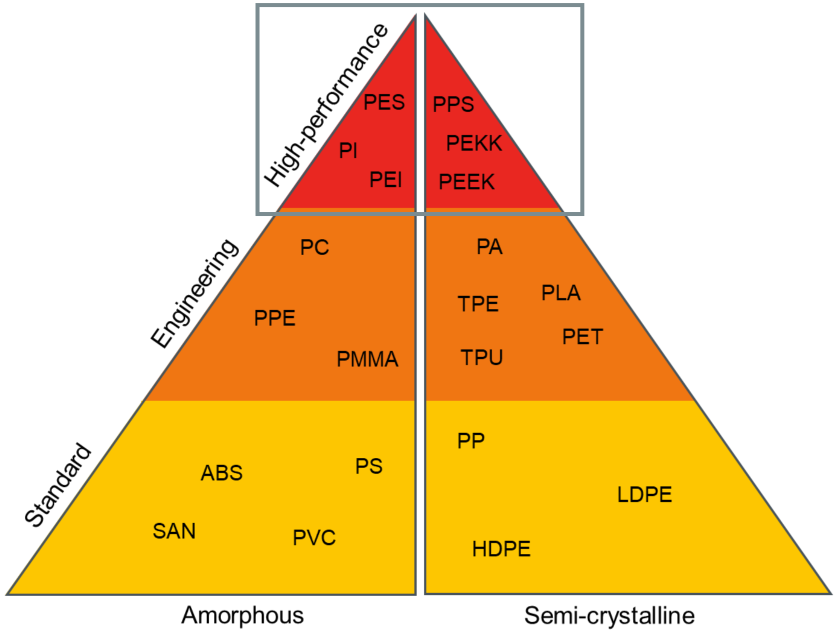
- Experience in C/C-SiC manufacturing based on thermoset materials
- No re-melting processes during pyrolysis → form stability
- Low viscosity (η = 0,7 Pas) → good fiber bundle infiltration

- Condensation reactions → health issues
- Long processing times
- No recyclability
- Curing necessary → Long process cycles

Solution: Use of thermoplastics as CFRP matrix material

[9]: G. W. Ehrenstein, Faserverbundkunststoffe, Carl Hanser Verlag, 2006

First aim – Additive manufacturing and carbon fiber hybrid yarn using thermoplastics

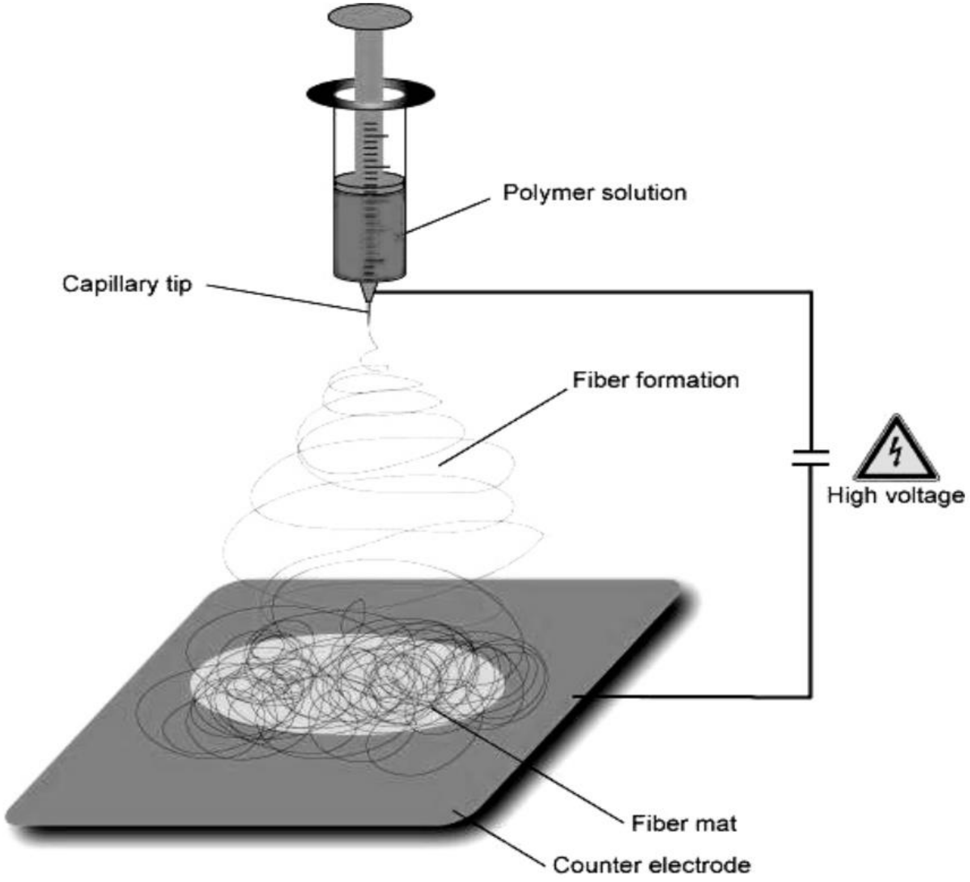


- Not all thermoplastics suitable as matrix materials
- High char yield nescessary → high-performance thermoplastics
- High melt viscosity of suitable thermoplastics → problems with fiber bundle infiltration

Aim: New methods to generate CFRP using additive manufacturing and well infiltrated fiber bundles
→ Two routes for CFRP fabrication: **(I) fused filament fabrication, (II) hybrid yarn**
→ Production of C/C-SiC via LSI process and analysis of the processing steps

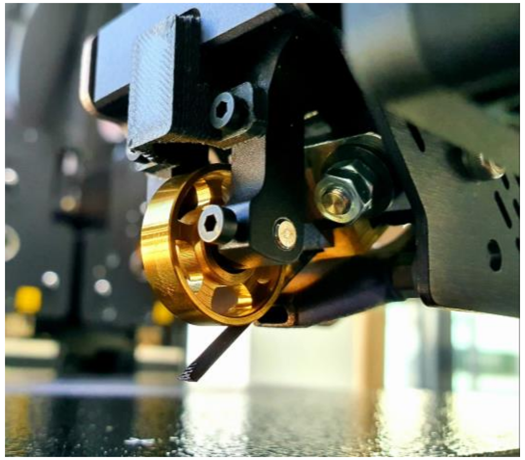
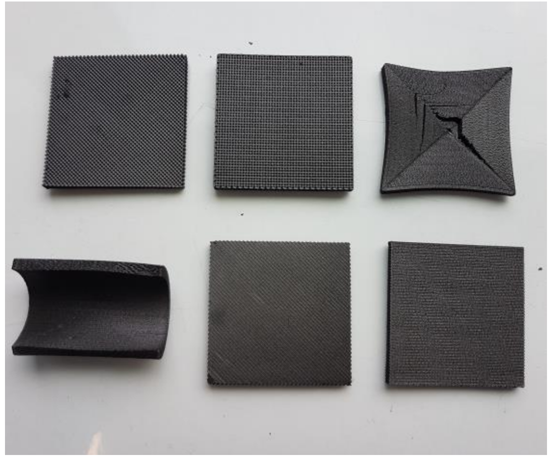
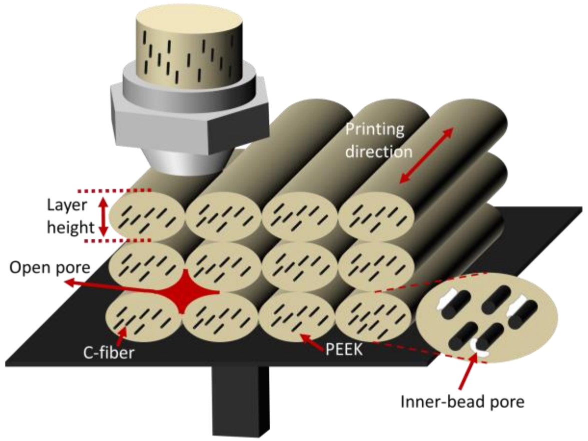
Second aim – Oxidation resistant carbon fibers

- Development of C/SiCN(O) ceramic fibers with improved oxidation resistance from polyacrylonitrile (PAN) and organosilazanes (OSZ)
- Carbon fibers oxidize at 400 °C, SiC fibers are expensive
- Limitation: PAN cannot be melt-spun, thick ceramic fibers are not flexible
- Electrospinning leads directly to nonwovens with diameters in the nanometer range and can be used for PAN and OSZ



S. Agarwal, A. Greiner, J. H. Wendorff, *Chemie Ingenieur Technik* **2008**, *80*, 1671.
Larrondo, L. & Manley, R. S. J.. J. Polym. Sci. Part A-2, Polym. Phys. 19, 909–920 (1981).

I Additive manufacturing of CMC

"Additive manufacturing of carbon fiber reinforced ceramic matrix composites based on fused filament fabrication"
Freudenberg et al., *J. Eur. Ceram. Soc.* **42** (2022) 1822.

"Processing-microstructure correlations in material extrusion additive manufacturing of carbon fiber reinforced ceramic matrix composites"
Best et al., *Addit. Manuf.* **79** (2024) 103888.

Additive manufacturing

CFRP manufacturing via additive manufacturing (FFF)

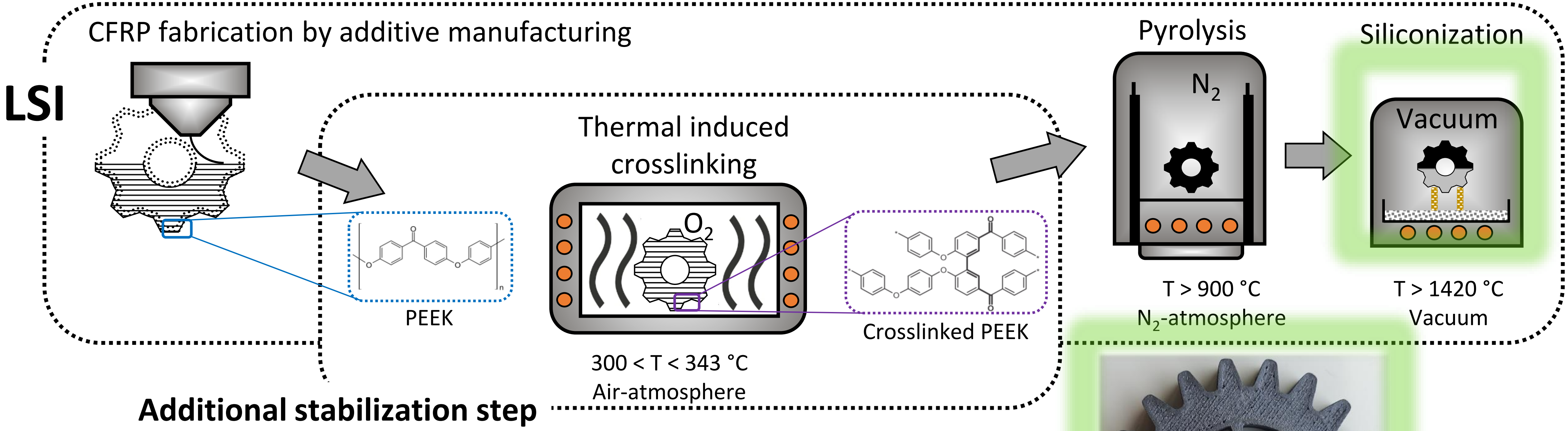
Short carbon fiber
reinforced PEEK filament

© Toray

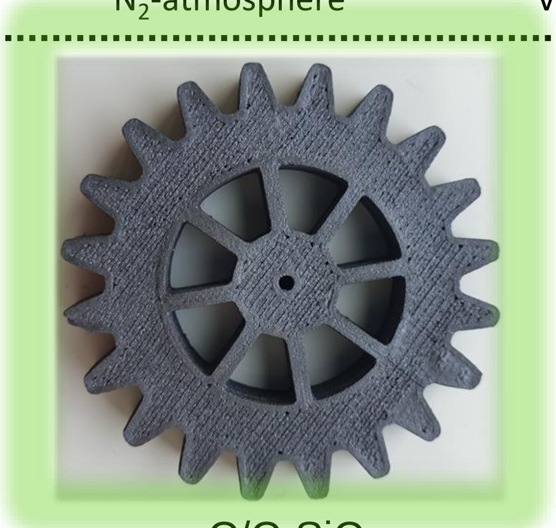
Continuous carbon fiber
reinforced PEEK tape

→ FFF technology enables tailoring microstructures for the LSI-process

Thermally induced crosslinking of PEEK



- **Stabilization Step**
  - Thermally induced crosslinking
  - Oxygen atmosphere
  - Below the melting temperature of PEEK (T_m ~ 343 °C)



C/C-SiC

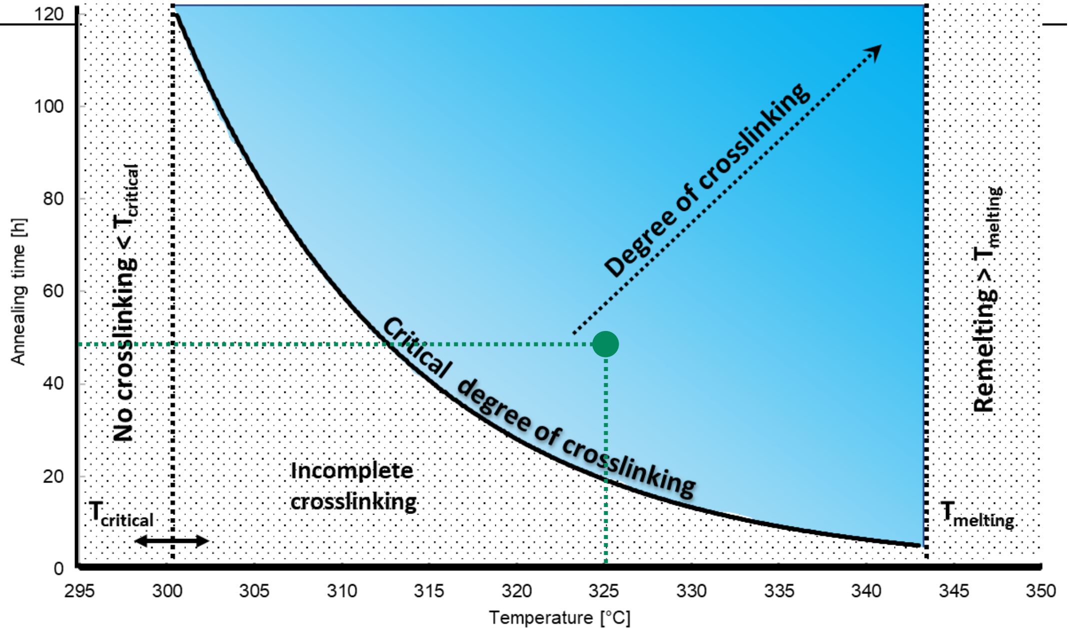
Conditions

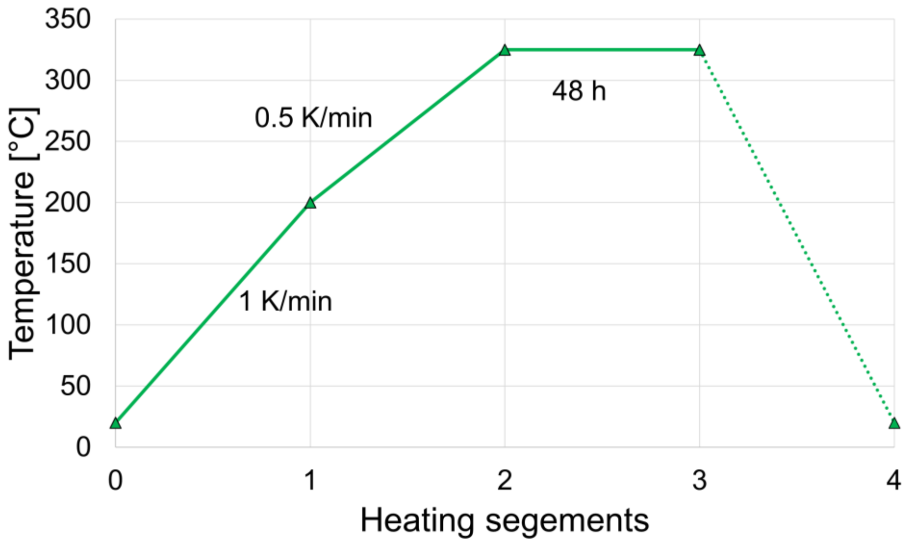
Conditions for the thermal induced crosslinking

$T < T_{melting}$: Sample should not remelt

$T > T_{critical}$: Temperature must initiate the crosslinking

Time for crosslinking should be as short as possible, but as long as necessary





Current parameters:

- Temperature: 325 °C
- Duration: 48h
- Heating rates: 0.5 K/min; 1 K/min

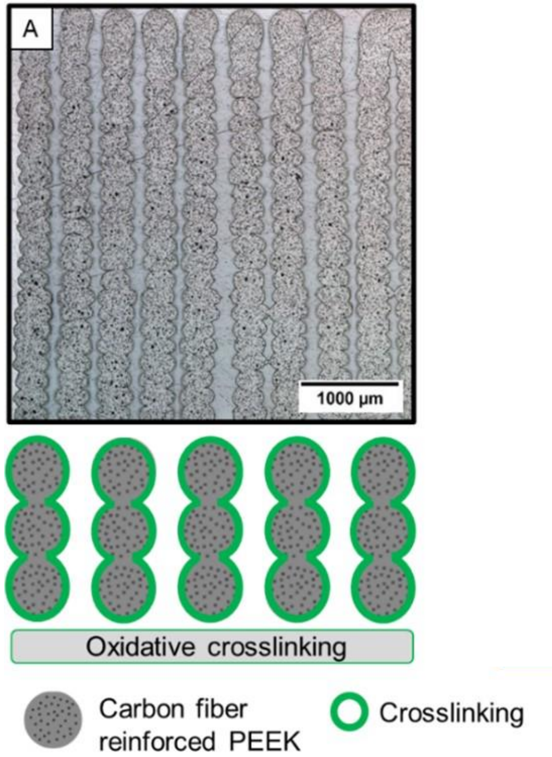
Question: Which annealing temperature and time?

Microstructure

Microstructural requirements

- Microstructure of the FFF technology with open channels

→ Crucial for successful liquid silicon infiltration process

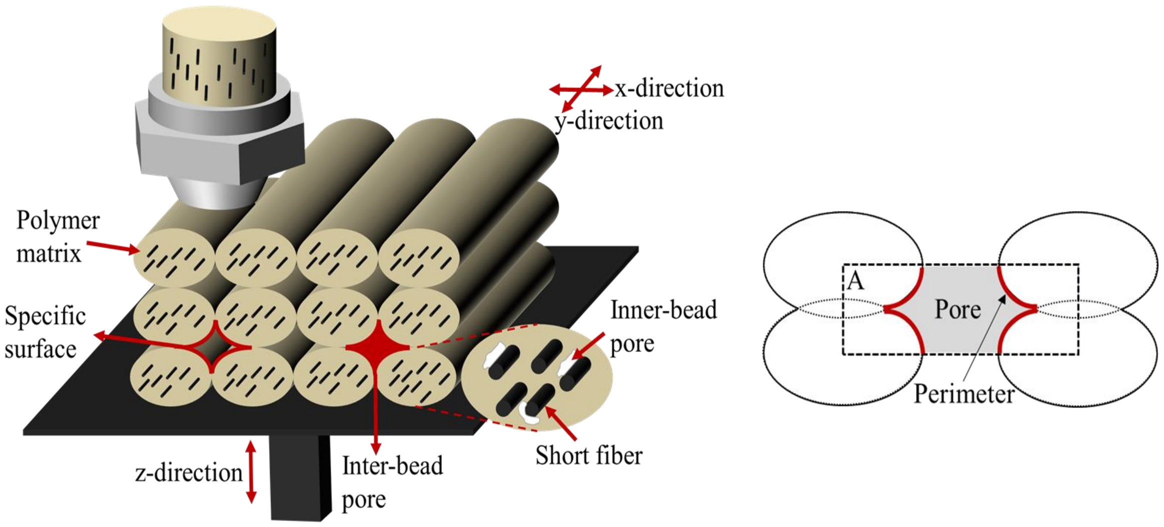


CFRP: Providing a high specific surface due to the thermally induced oxidative crosslinking

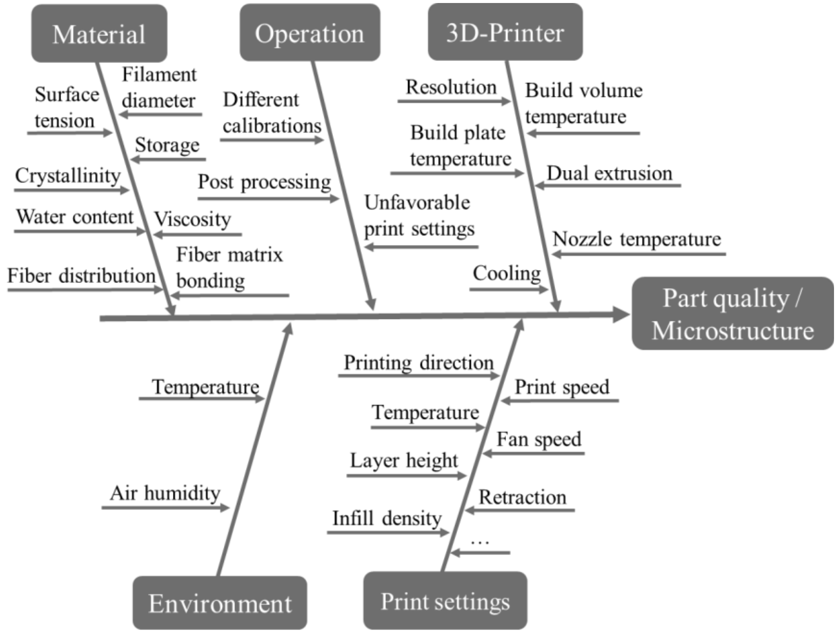
C/C: Removal of gaseous products during pyrolysis and the conversion of the polymer matrix to amorphous carbon

C/C-SiC: Capillaries for the Si-infiltration

Processing-microstructure-property relations



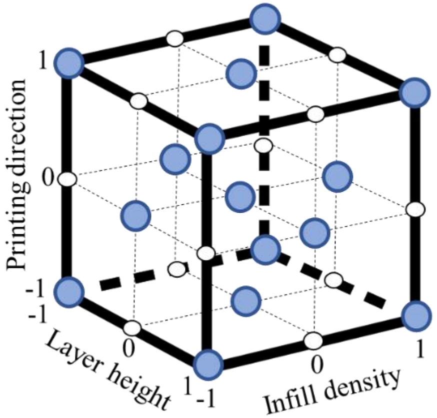
Overview of the FFF technology with inter-bead (open) and intra-bead (closed) pores; calculation of the specific surface area

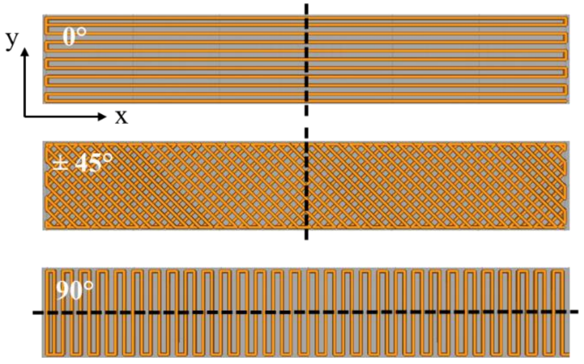


Cause/effect diagram of the FFF technology

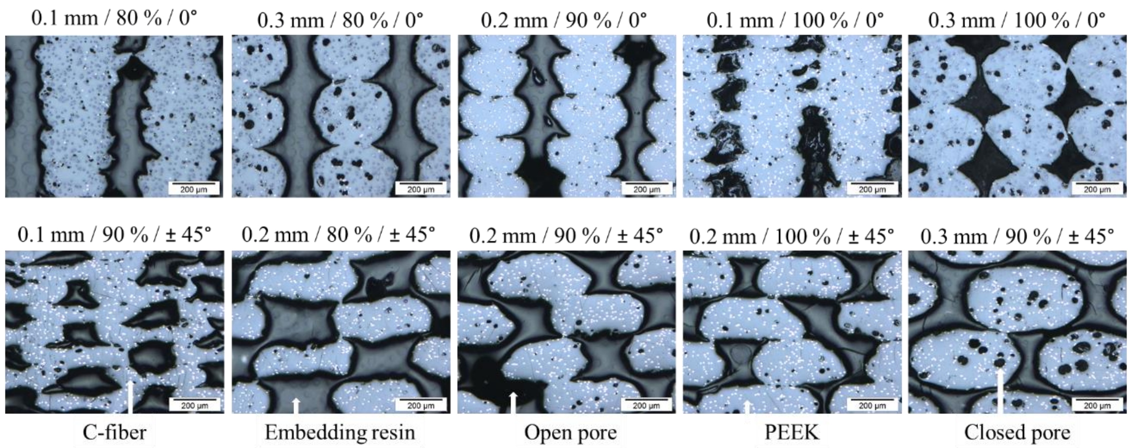
Design of experiments to reveal processing-microstructure-property relations

Factor	Level -1	Level 0	Level 1
Layer height (LH) [mm]	0.1	0.2	0.3
Infill density (ID) [%]	80	90	100
Printing direction (PD) [°]	0	± 45	90

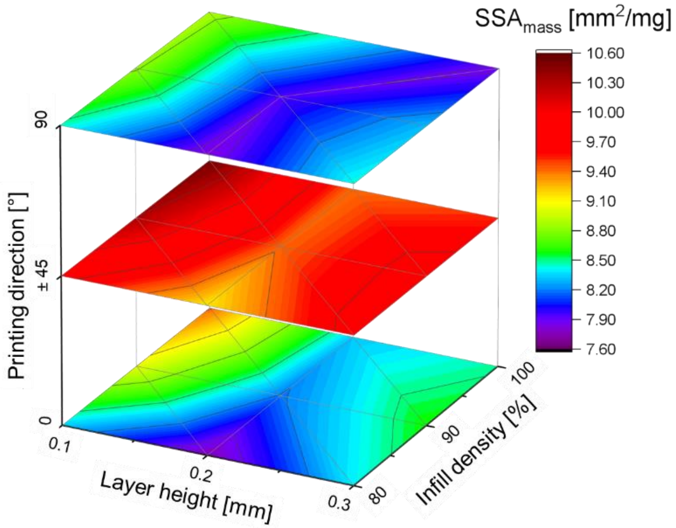




Face centered central composite design (left) and printing directions with illustration of image analysis of the specific surface area (right)

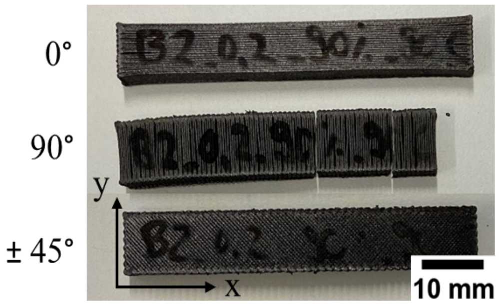


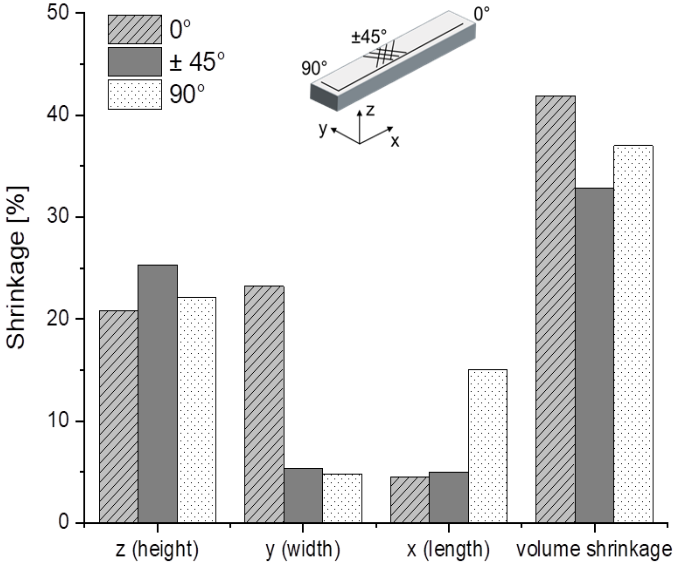
Optical microscopy images of CF-PEEK with different process parameter combinations (layer height / infill density / printing direction) showing the specific surface area at the interface between material strands and pores or as embedding resin



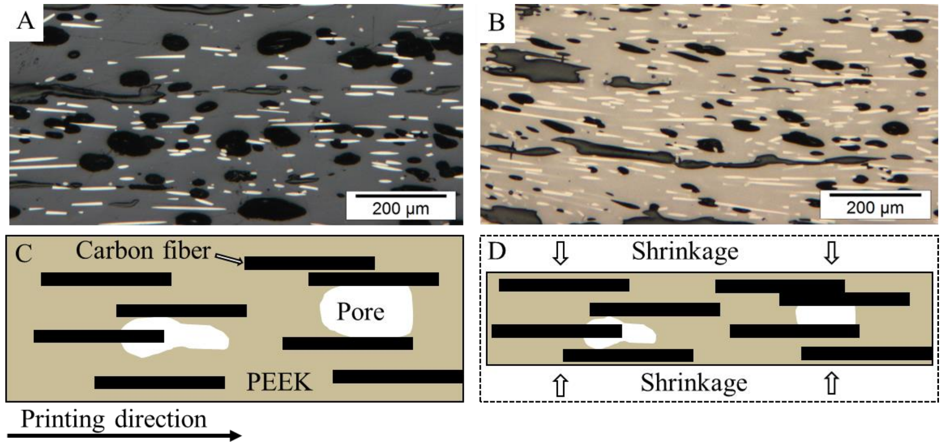
Specific surface area (mm^2/mg) as a function of the three investigated factors

Shrinkage during pyrolysis as a function of the printing direction



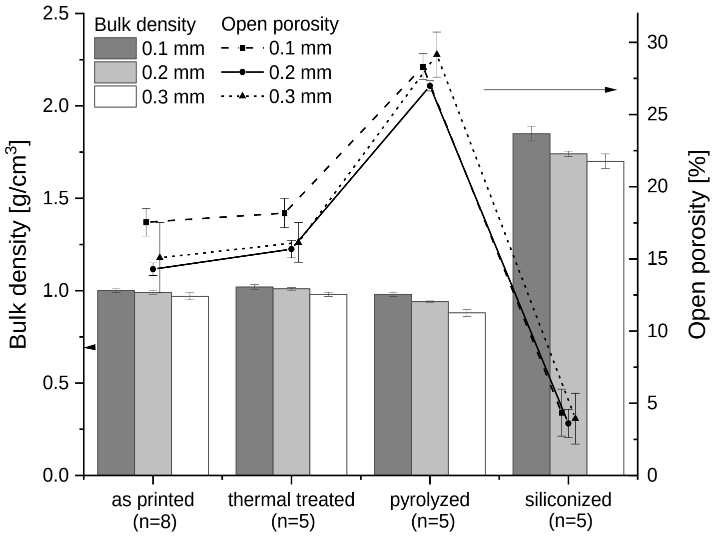


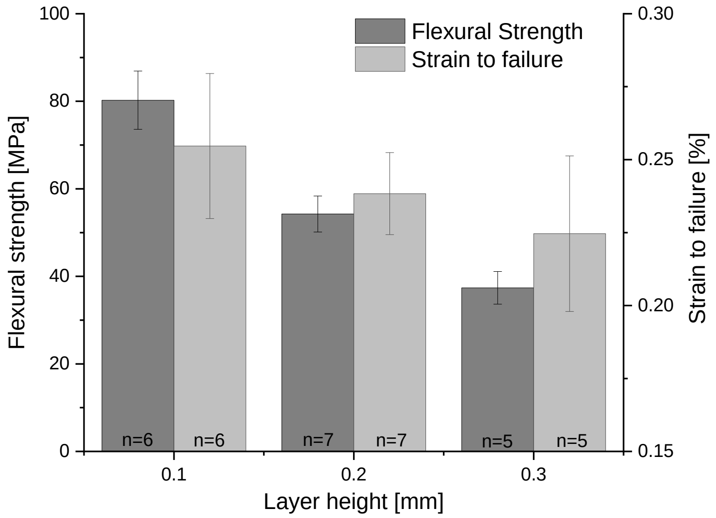
Pyrolyzed C/C with different printing directions and layer height of 0.2 mm and infill density of 90 % (left) and shrinkage after pyrolysis in comparison to “as printed” (right)

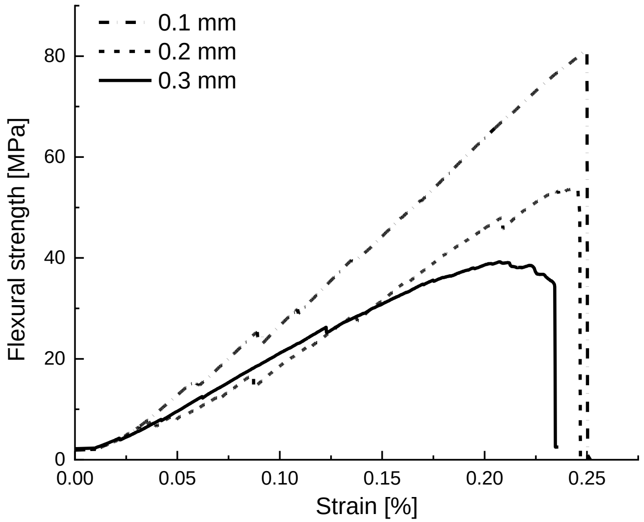


Optical microscopy images (A, B) and schematic illustration (C, D) before pyrolysis (left) and after pyrolysis (right) aligned in printing direction

Physical and mechanical properties



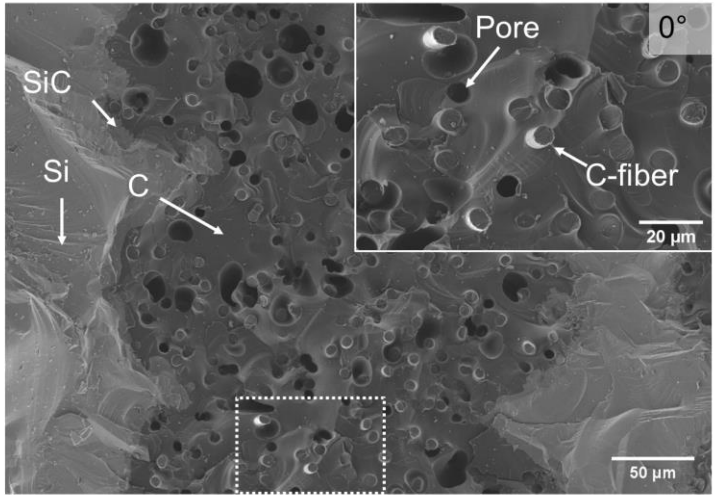




Bulk density, flexural strength, strain to failure and stress-strain curves of C/C-SiC samples with an infill density of 100 % and a ± 45° printing direction for each layer height

Fused filament fabrication (FFF) for C/C-SiC

Scanning electron microscopy

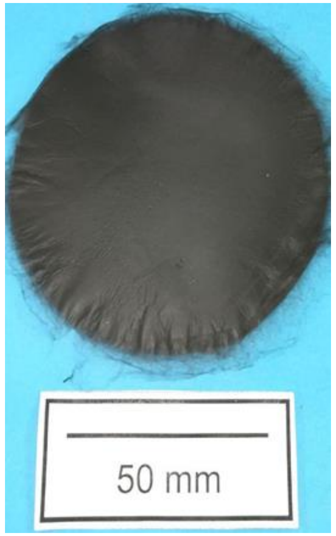


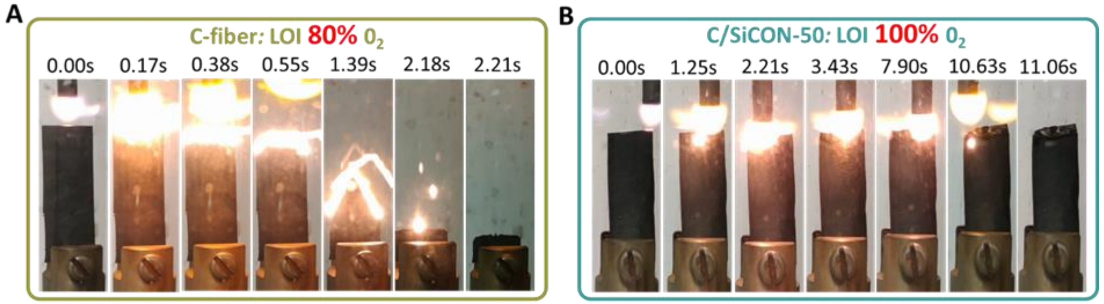
- SEM images show fiber-pull-out within the fiber length limit
- Upscaled, high complex shaped CMC parts (right figure)

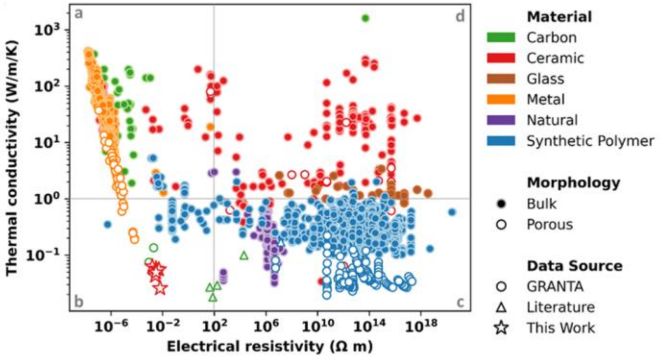
Benefits

- Freedom of design
- Highly complex geometries
- No post processing
- Material saving process
- Easy scalability
- Near net shape
- Tool-free manufacturing process
- Easy joining due to the use of PEEK
- Gradient material compositions

II Electrospinning of hybrid carbonceramic nonwovens



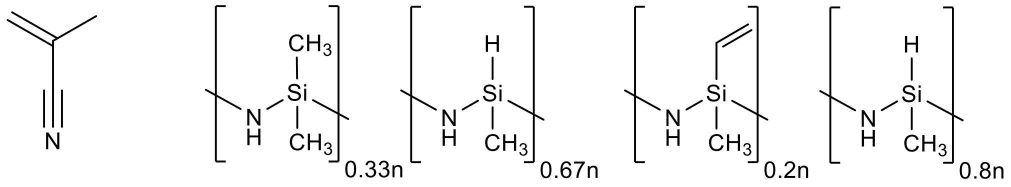




”Extremely low thermal conductivity and high electrical conductivity of sustainable carbon-ceramic electrospun nonwoven materials”
Liao et al., *Sci. Adv.* **9** (2023) eade6066.

Hybridpolymers of polyacrylonitrile and silazanes

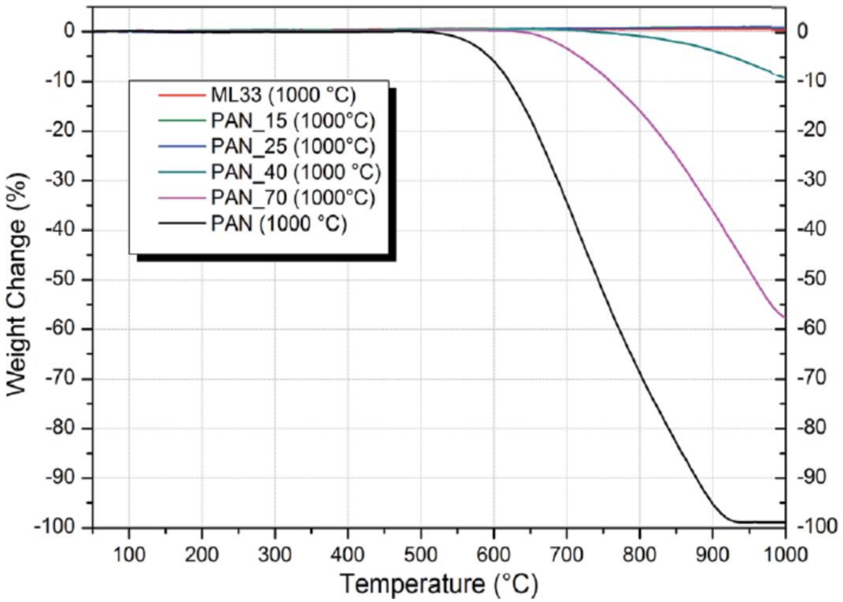
Structural formula of arcrylonitrile and commercial polysilazanes



Acrylonitrile (AN) **Durazane 1500** **Durazane 1800**

L. F. B. Ribeiro, O. Flores, P. Furtat, C. Gervais, R. Kempe, R. A. F. Machado, G. Motz, *J. Mater. Chem. A* **2017**, *5*, 720.

Oxidation resistance (5 K min^{-1}; synth. air)

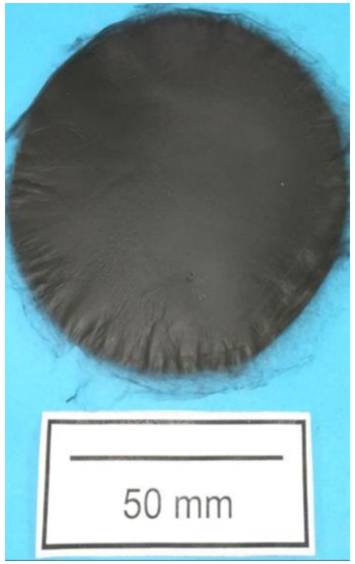


- Crosslinking reaction between Si-H and -CN leads to Si-N bonds
- During pyrolysis formation of C/Si_3N_4 nanocomposites => high oxidation resistance

Manufacturing of nonwovens by electrospinning

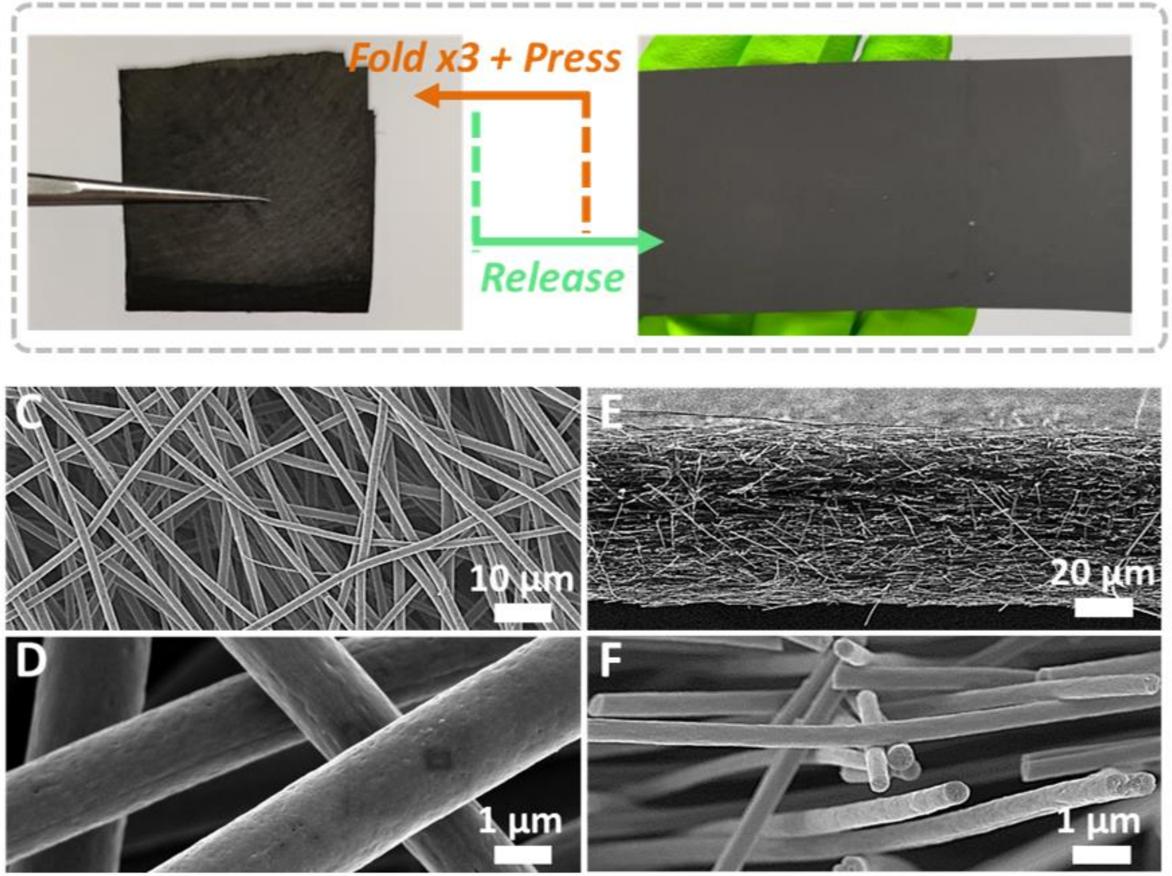
Electrospinning → Precursor fibers → Oxidation (air, 300 °C) → Pyrolysis (N_2, 1000 °C)

PAN/silazane (OSZ)



C/SiCON-x: x wt.% of OSZ in PAN

Macro- and microstructure of the nonwovens after pyrolysis

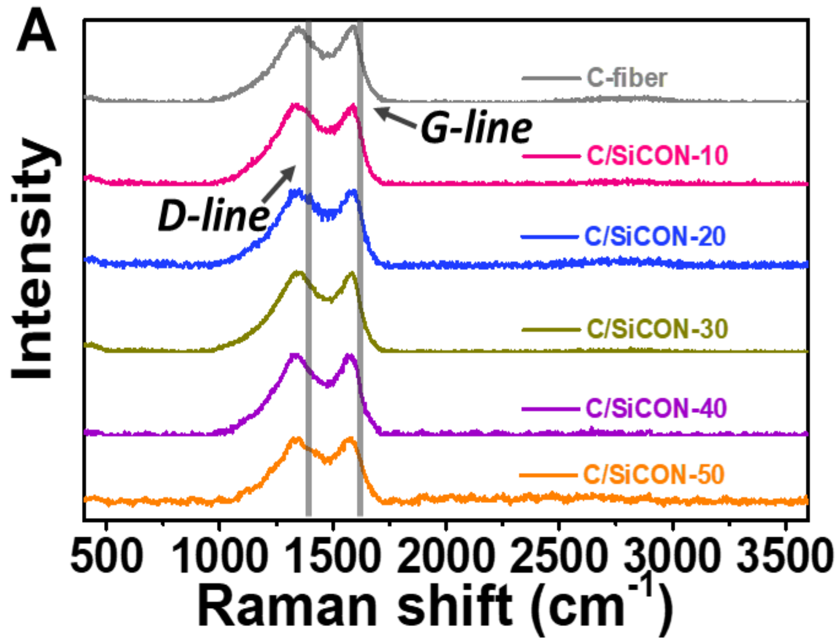


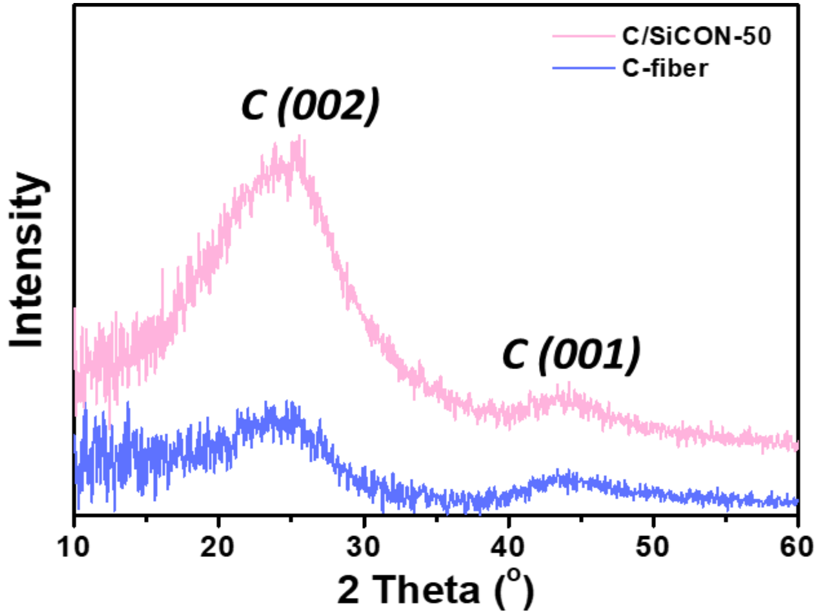
Foldability of C/SiCON-50 nonwoven compared to printing paper

Pyrolysis leads to highly robust and flexible fibers (N_2, 1000°C; 0-50 wt% OSZ)

X. Liao, J. Denk, T. Tran, N. Miyajima, L. Benker, S. Rosenfeldt, S. Schafföner, M. Retsch, A. Greiner, G. Motz and S. Agarwal, *Sci Adv*, **2023**, *9*

Raman spectroscopy and WAXS of the nonwovens after pyrolysis



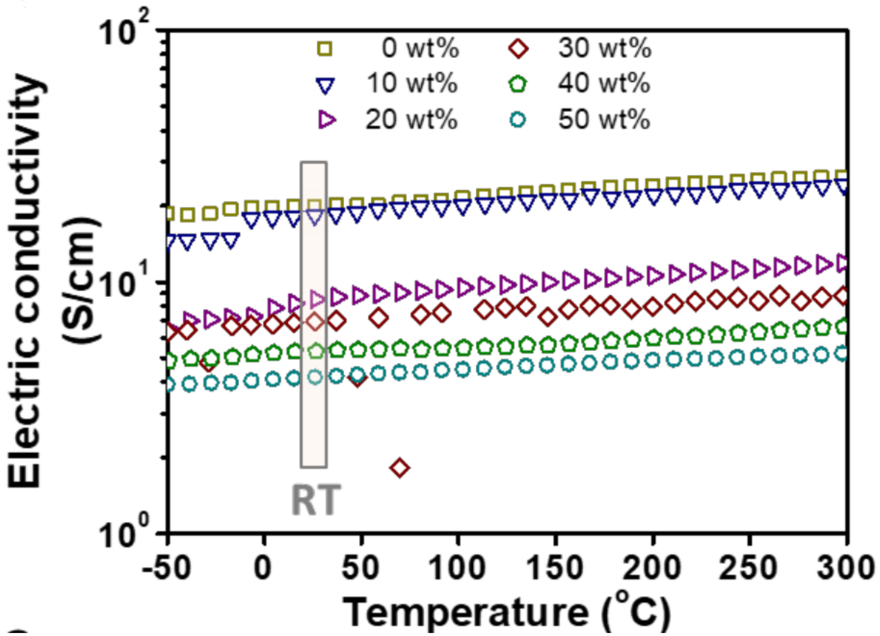


Typical G-line, D-line and 2D-line for graphitic carbon

Wide-angle X-Ray scattering: broad 25° peak (interlayer spacing) and weak 45° peak

Amorphous carbon structure was determined also for hybrid materials

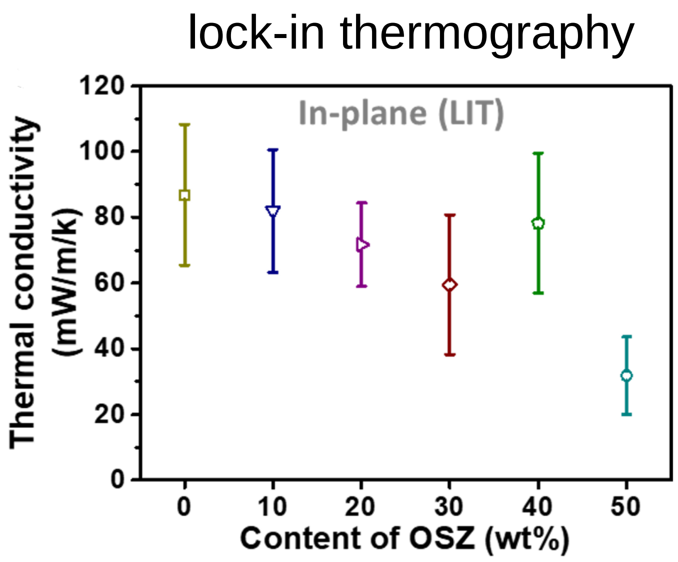
Electrical conductivity of the nonwovens

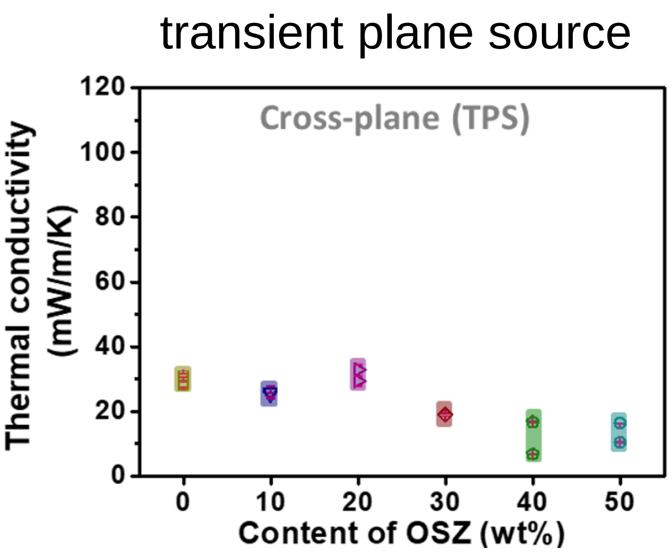


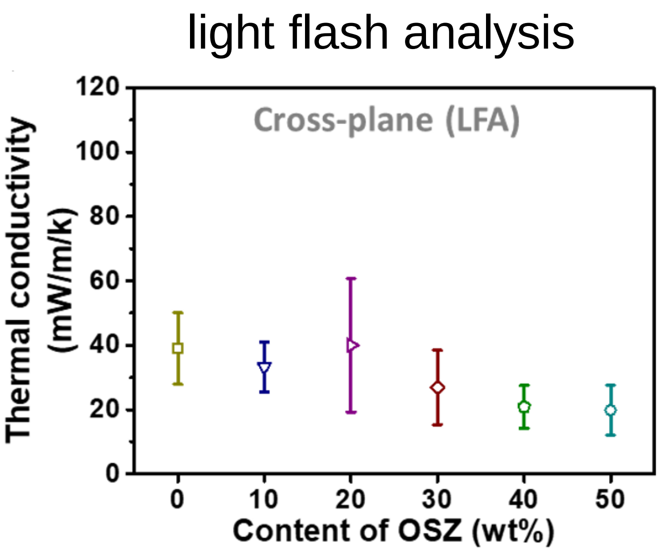
Movie S3 - negligible electrical resistance change of flexible C/SiCON-50 nonwoven during the 5000-cycle folding test

- High electrical conductivity for all different concentrations of OSZ
- Only slight decrease with higher content of OSZ
- Constant electrical resistance even after 5000-cycle folding test

Thermal conductivity

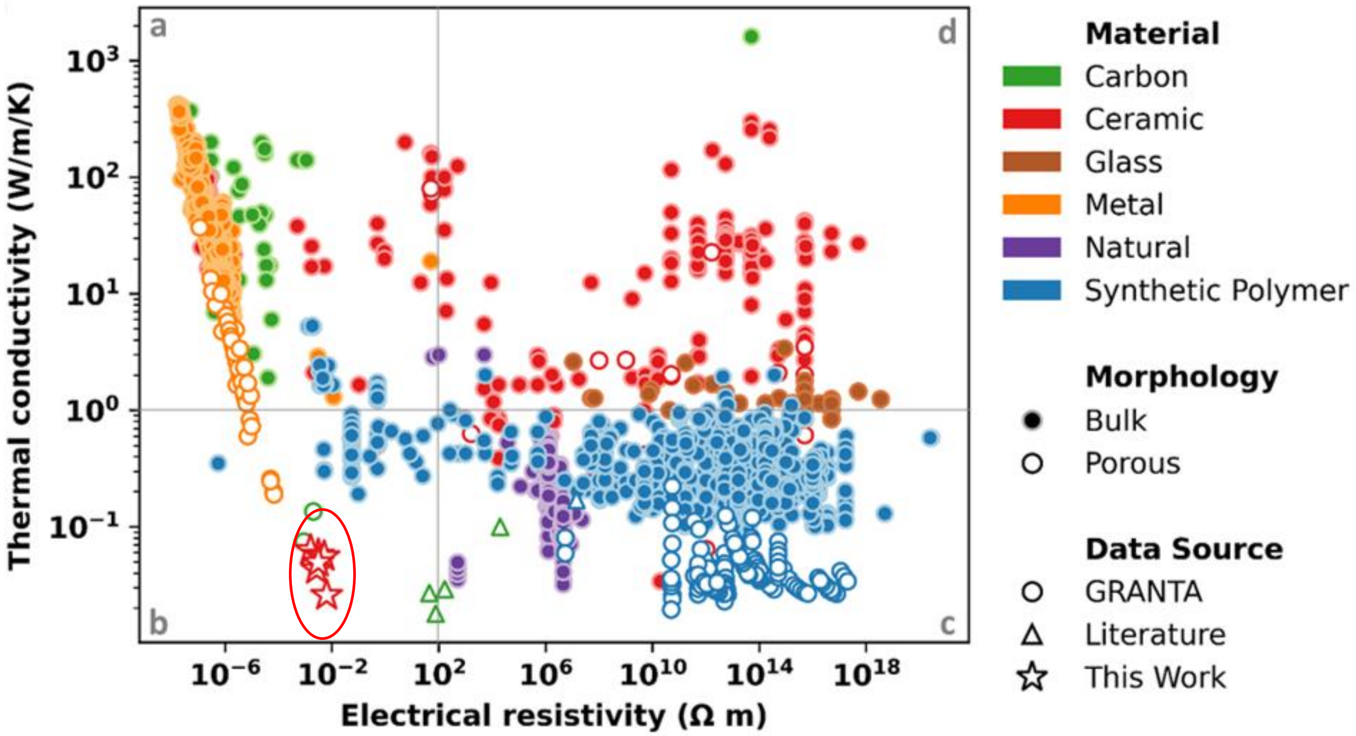






- Extreme low thermal conductivities (compareable to aerogels)
- Higher content of OSZ leads to low thermal conductivity

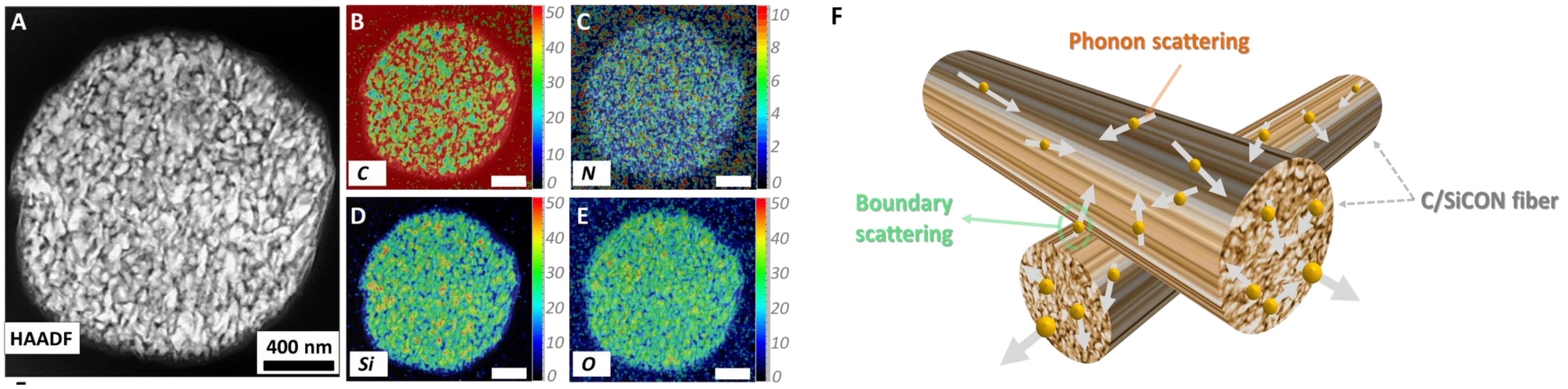
Comparison with existing materials



Cambridge Materials Selector database (www.grantadesign.com)

Comparison with other materials shows the unique combination of electrical and thermal properties

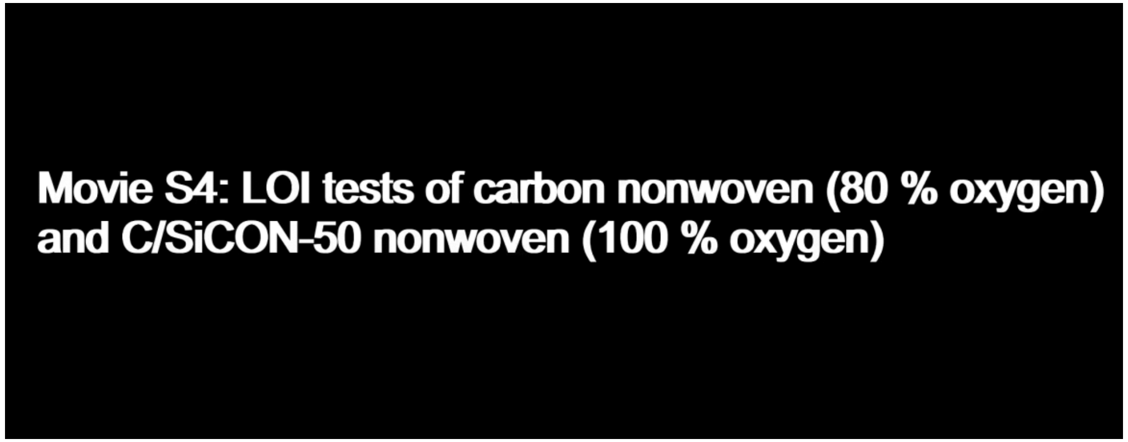
Characterization by high-angle annular dark-field STEM

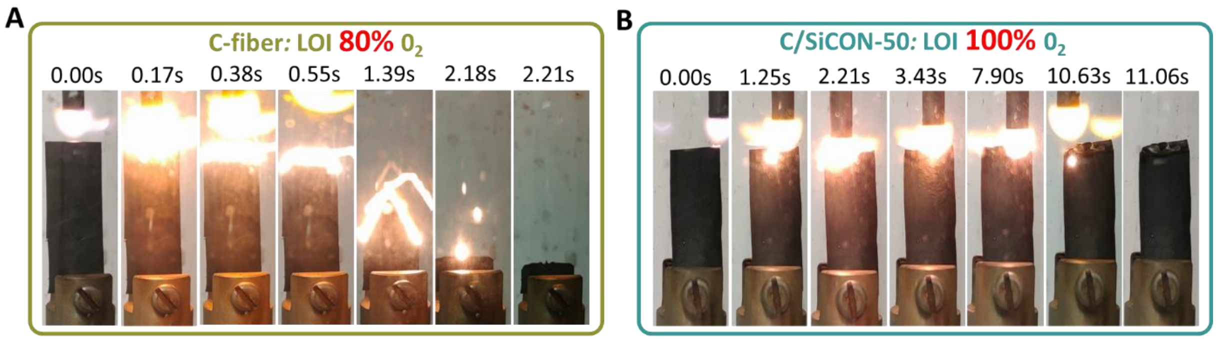


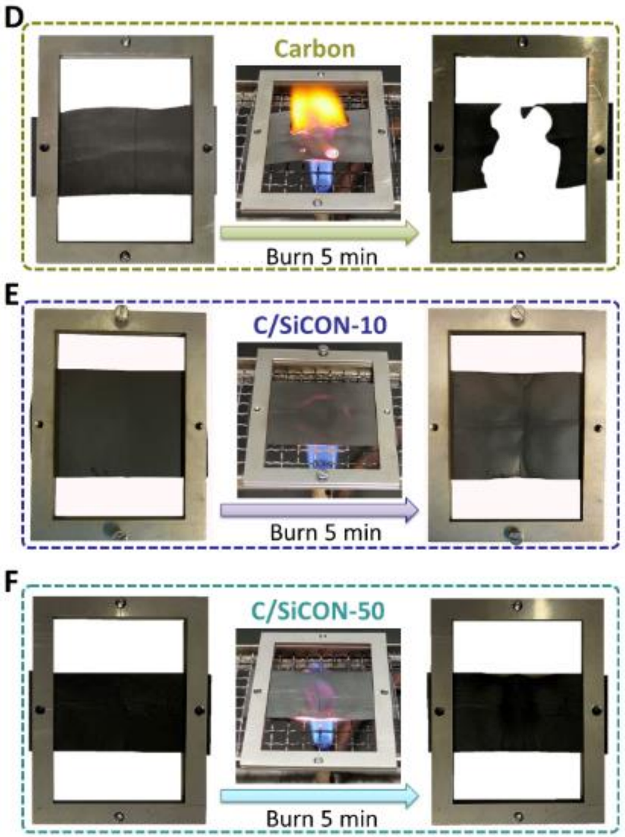
"island-in-the-sea" structure due to Si containing (e.g. SiO, SiC, SiN) and C containing (e.g. CN) phases

- Continuous amorphous C "sea" benefits electrical conductivity
- Phonon scattering due to dispersed SiCON "islands" yields superior thermal insulation

Oxidation resistance







Summary

- Thermoplastics as matrix materials for C/C-SiC ceramic matrix composites
  - PEEK filaments filled with short carbon fibers were successfully applied for additive manufacturing of C/C-SiC
  - Optimized crosslinking in air of CFRP results in shape stability and high mechanical strength
- Electrospinning of PAN/OSZ hybrid polymers
  - Successful processing of flexible ceramic C/SiCON nonwovens by pyrolysis
  - Chemical and structural characterization reveals the C/SiCON “island-in-the-sea” microstructure
  - New material with extraordinary electrical and thermal properties as well as oxidation resistance

Thank you!

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