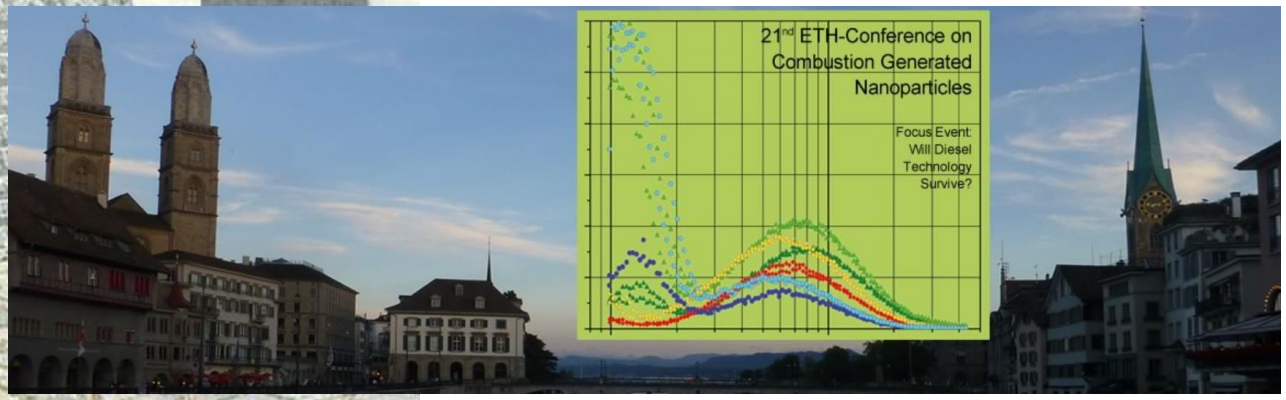
Wehrwissenschaftliches Institut
für Werk- und Betriebsstoffe
(WIWeB)

# Formation of Respirable Carbon Fiber Fragments in Carbon Composite Fires

**21st ETH Conference on**
**Combustion Generated Nanoparticles**
**Zürich, 19.-22.06.2017**

**S. Eibl**




Bundeswehr
Wir. Dienen. Deutschland.

# Outline

- Introduction
  - basics to composites
  - thermal properties
- Formation of respirable carbon fibers
  - influence of temperature and time (lab experiments)
  - legislation
- Real fires
  - large scale fire test and mishaps
  - hazards and protective measures (flame retardants, binder coatings etc.)
- Summary / Outlook

# Lightweight Design

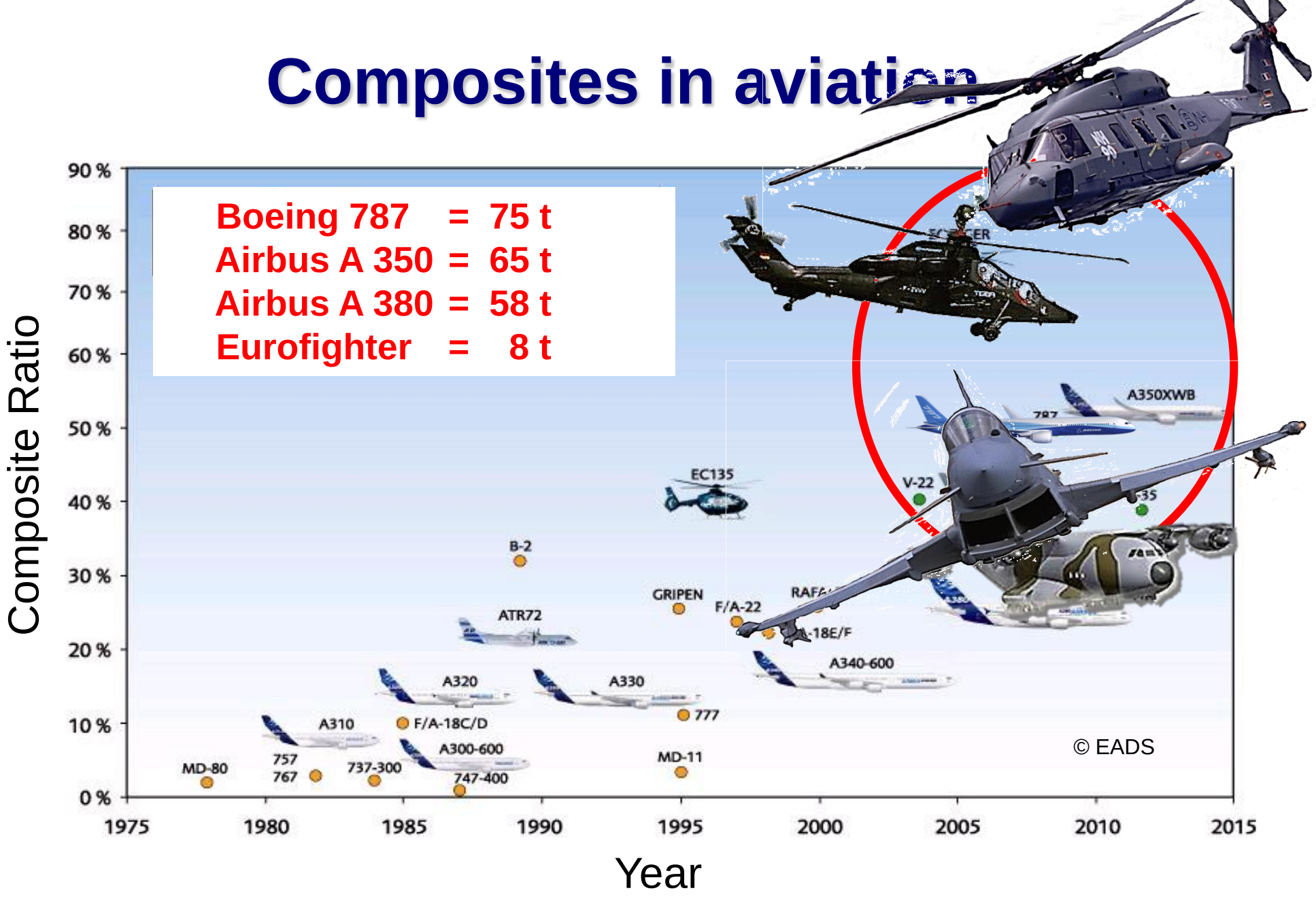
- Mechanical performance

| Material | Density [g/cm$^3$] | Max. Tensile Strength [GPa] | Max. Modulus [GPa] |
|---|---|---|---|
| **Steel** | 7,8 | ~2 | ~210 |
| **Aluminum** | 2,7 | ~0.6 | ~75 |
| **Titan** | 4,5 | ~1 | ~110 |
| **C fiber** | 1,8 | ~7* | ~700* |
| **G fiber** | 2,6 | ~3* | ~80* |

*) corresponds roughly to composite property under tensile load



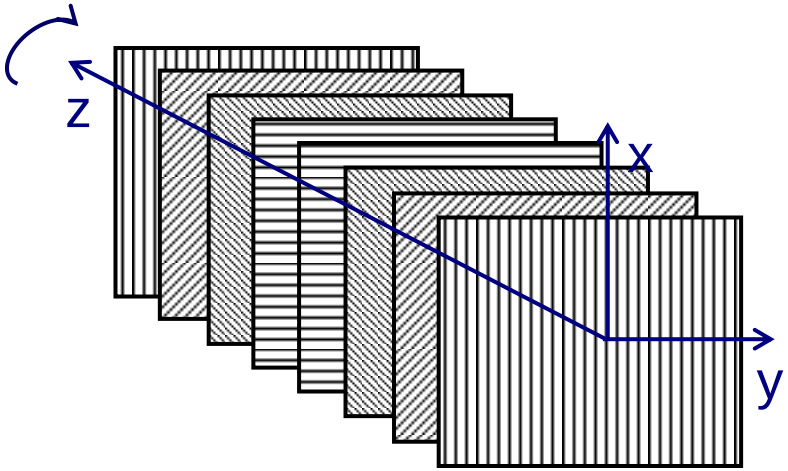

# Composites in aviation



# Manufacture of components in aviation

- Prepreg Technology

1. Pre-impregnated plies are laminated




*Quasi-isotropic laminate*

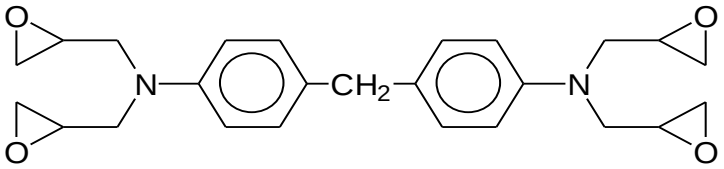
2. Resin cured at 8 bar, 180 °C

*Autoclave*

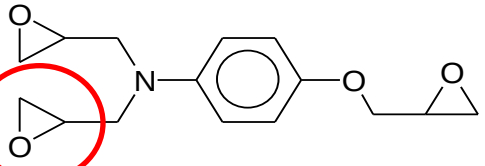
Resin infusion / transfer moulding or thermoplastics provide lower cycle times for automotive industry

# Typical resin composition for aviation

**Epoxy resin (~30%)**

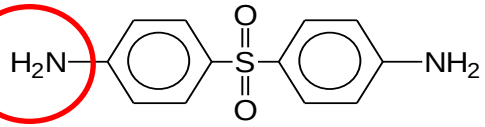


Tetraglycidylmethylendianilin (TGMDA)



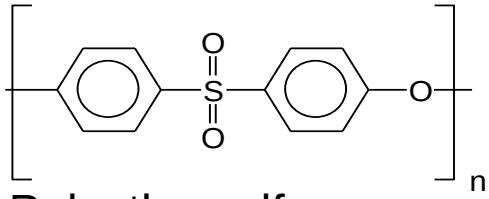
Triglycidyl-p-aminophenol (TGPAP)

curing



Diaminodiphenylsulfon (DDS)

**Thermoplastic (~5%)**



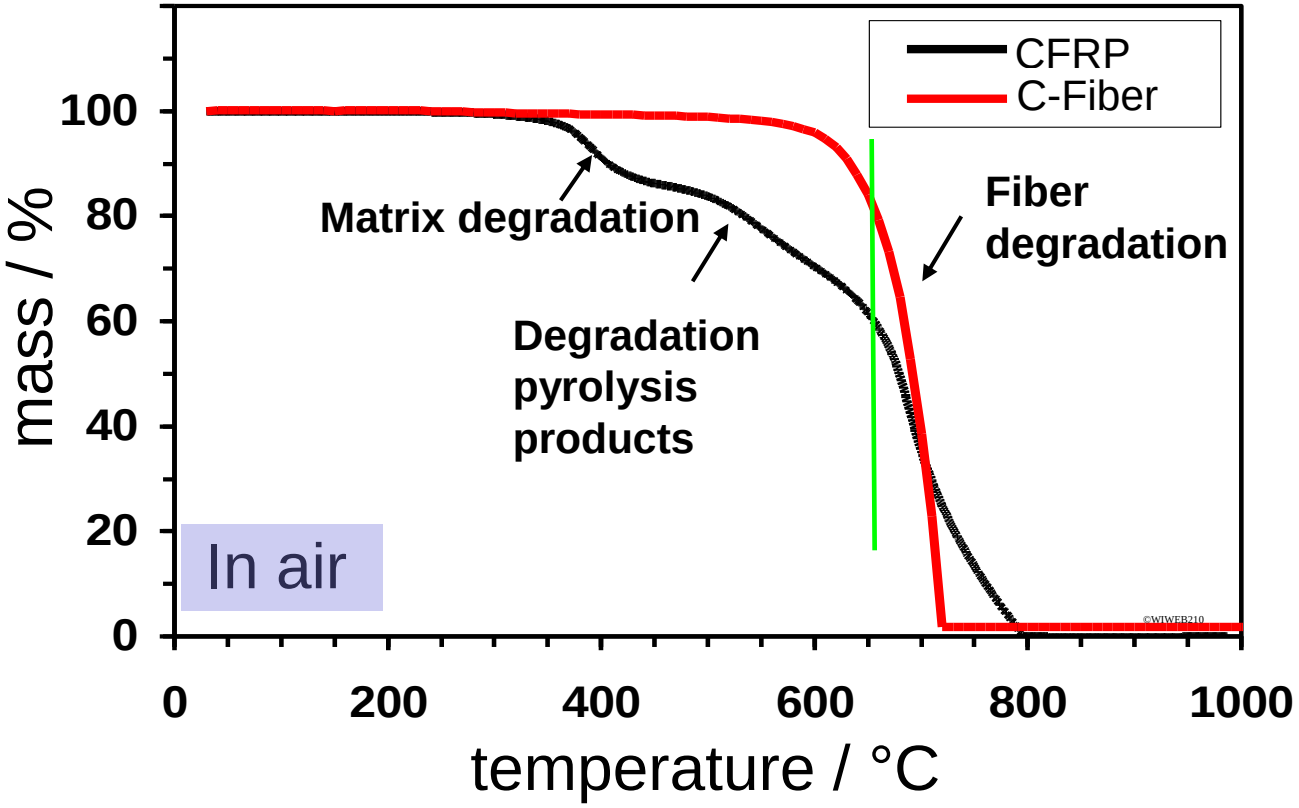
Polyethersulfone

Aromatic structure: thermally resistant (Op. temp. lim.: 121°C, (180 °C))

**+ ~65% carbon fiber (+ flame retardant (<3%))**

# Typical carbon fiber reinforced plastic (CFRP)

- Thermogravimetric analysis (TGA)



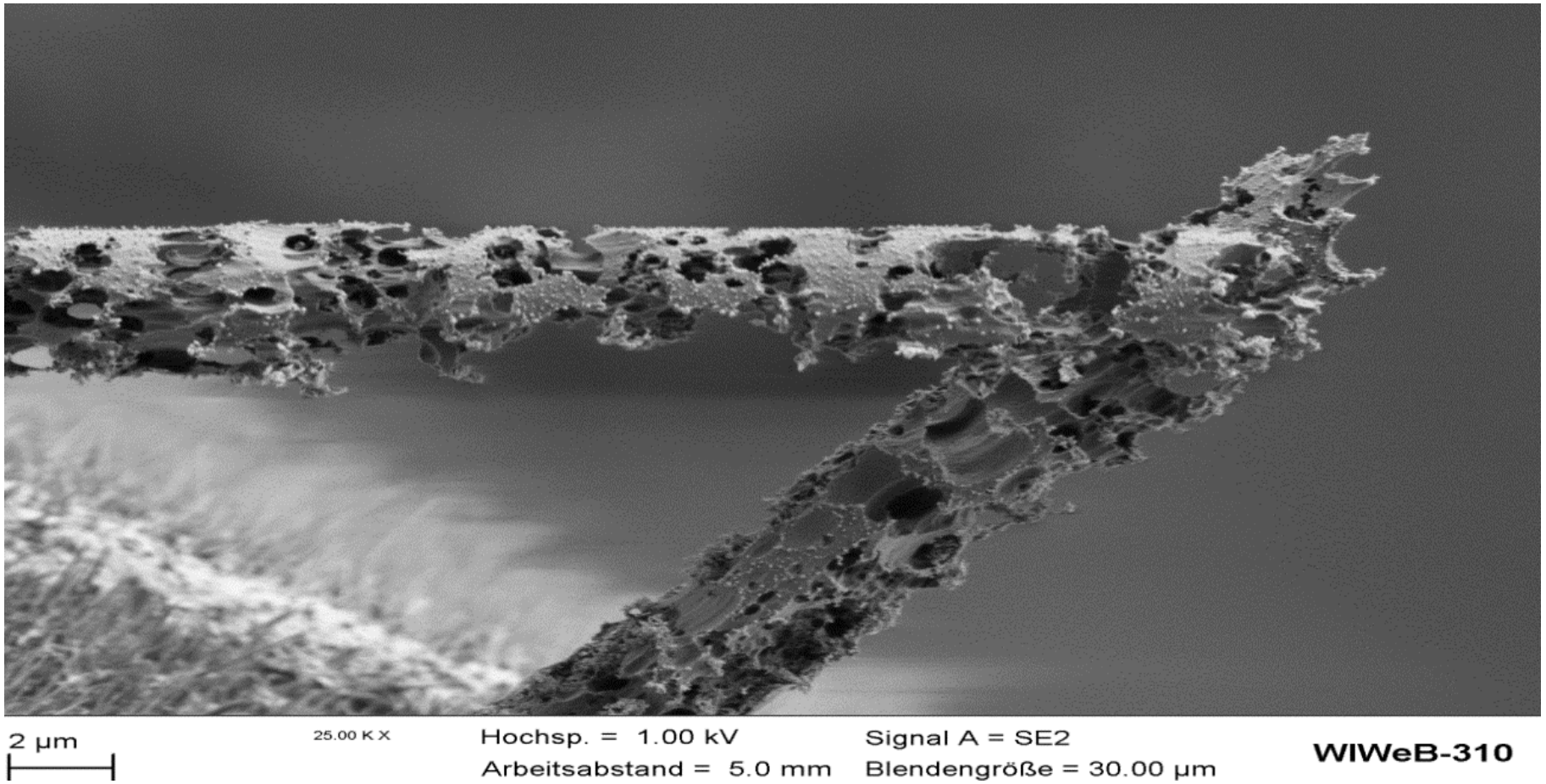

Carbon fiber is rather thermally stable

# Typical carbon fiber reinforced plastic (CFRP)

Carbon fiber is rather thermally stable

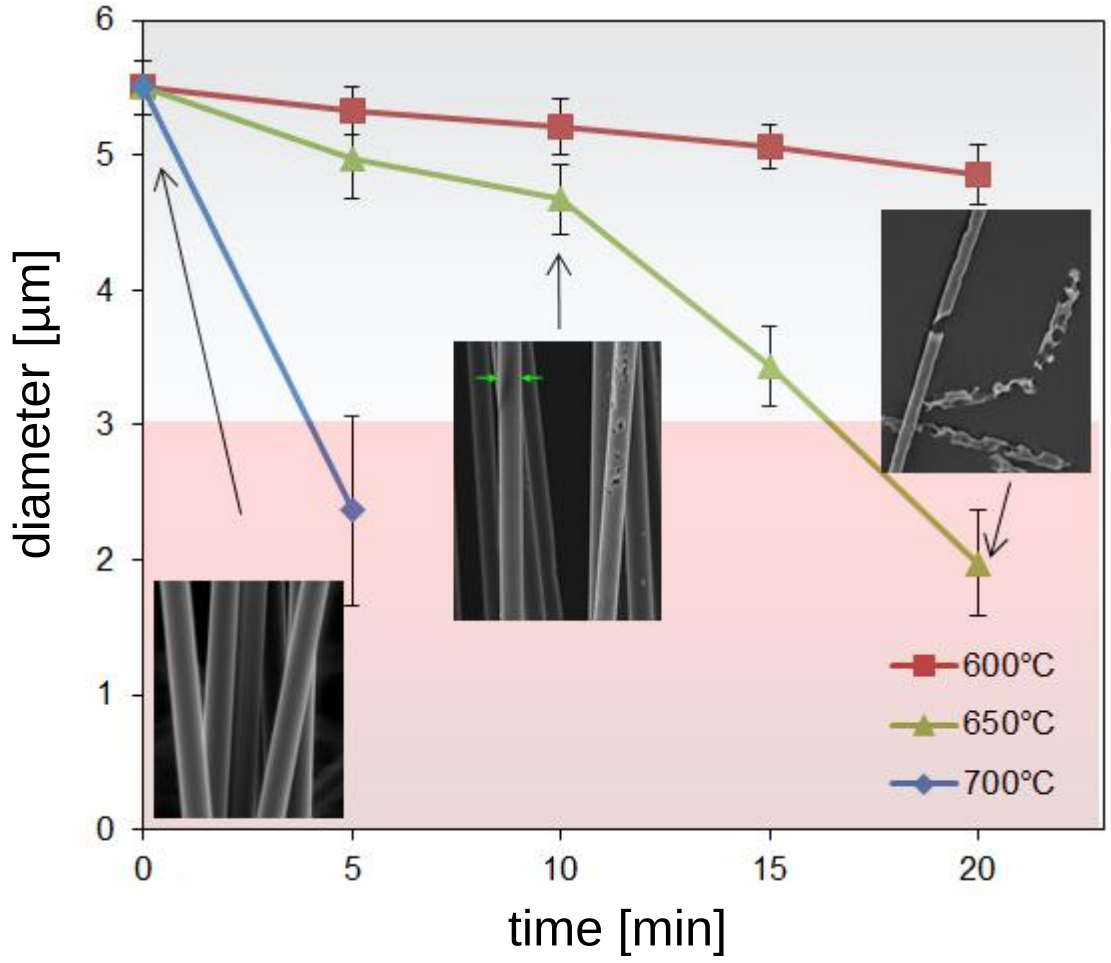
# Thermal degradation of carbon fiber

- Single carbon fibers treated at 650°C (original diameter: ~5.3 µm)




*Scanning electron microscopic images (SEM) of two fibers*

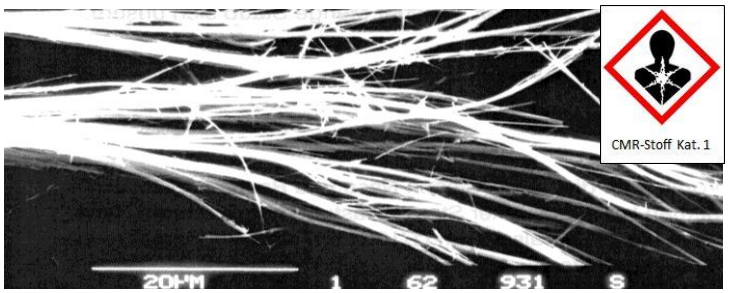
# Thermal degradation of carbon fiber



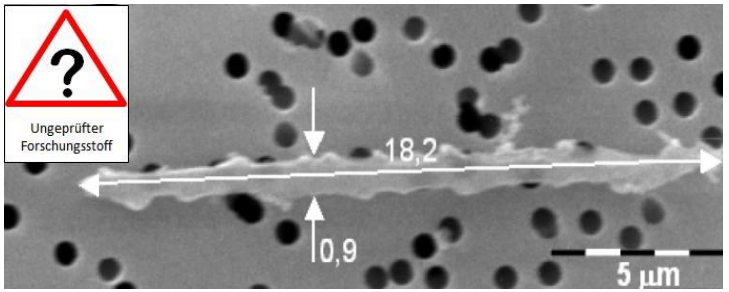

Real fires: critical fiber degradation efforts rather high heat load

# Classification

**Asbestos**




**Carbon fiber fragment**
**(on filter)**



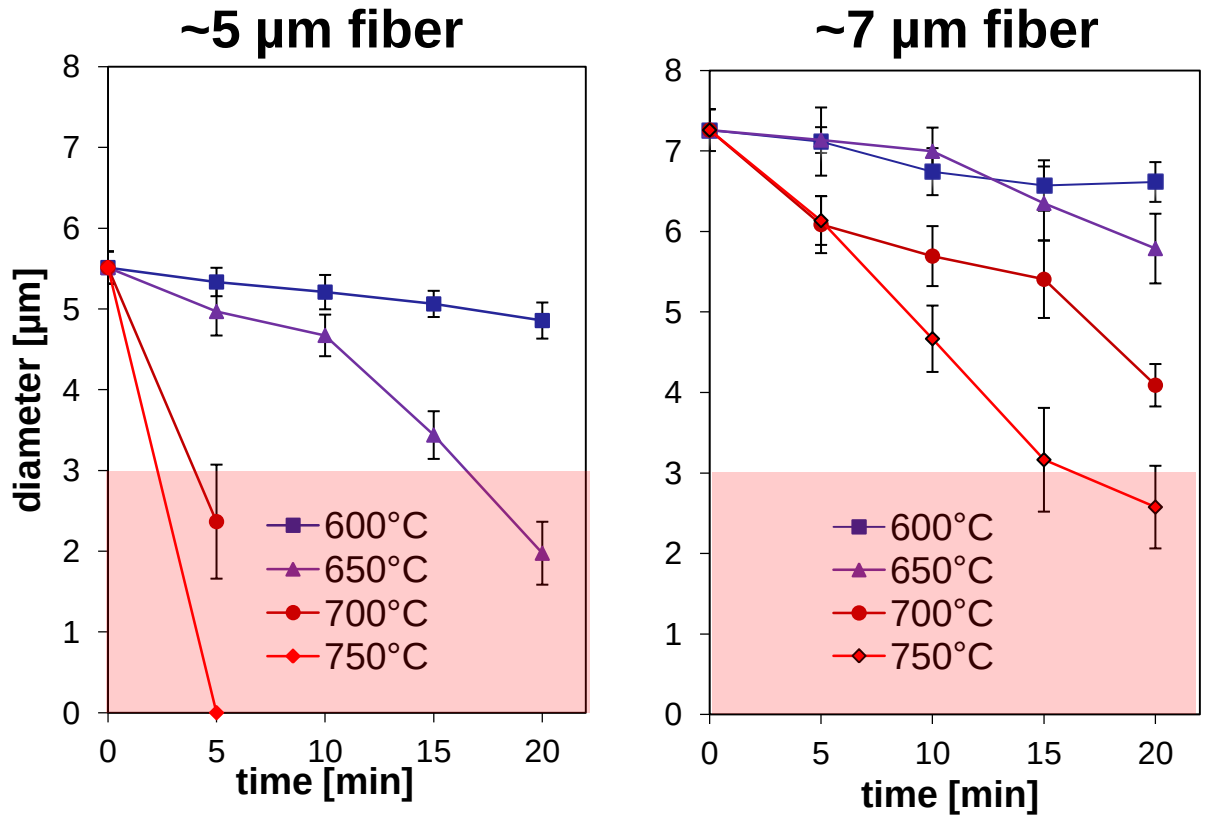

Fibers may cause cancer if:

**D < 3 µm** and **L > 5 µm** and **L:D > 3:1**
(according to WHO, TRGS 905)

**TRGS 905 (03/2016)**: Fiber type: „inorganic fiber dust….“: **cancerogenic category 2:** („....*suspicion of carcinogenic effect to men….”)*

# Influence of initial fiber diameter

- Diameter of thermally treated carbon fibers




Thin fibers reach critical diameter earlier

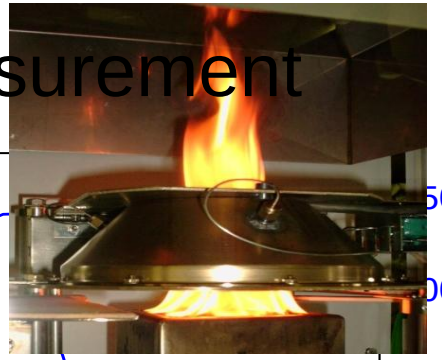
# Laboratory Combustion of CFRP

## Cone Calorimeter

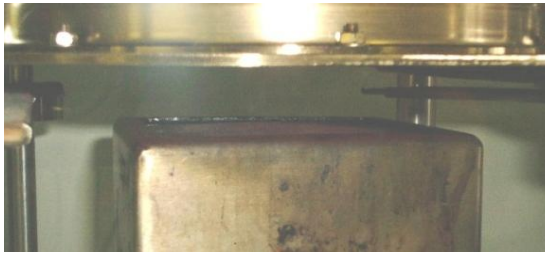
- Time to ignition
- Heat release rate
- Mass loss
- Smoke density and temperature
- Oxygen-, CO-, $CO_2$-concentration
- Filtered soot  etc.

Sample size: 100 mm x 100 mm x 1 - 50 mm
Heat flux: 10 - 100 kW/m²; Electric cone shaped heater

## Typical measurement



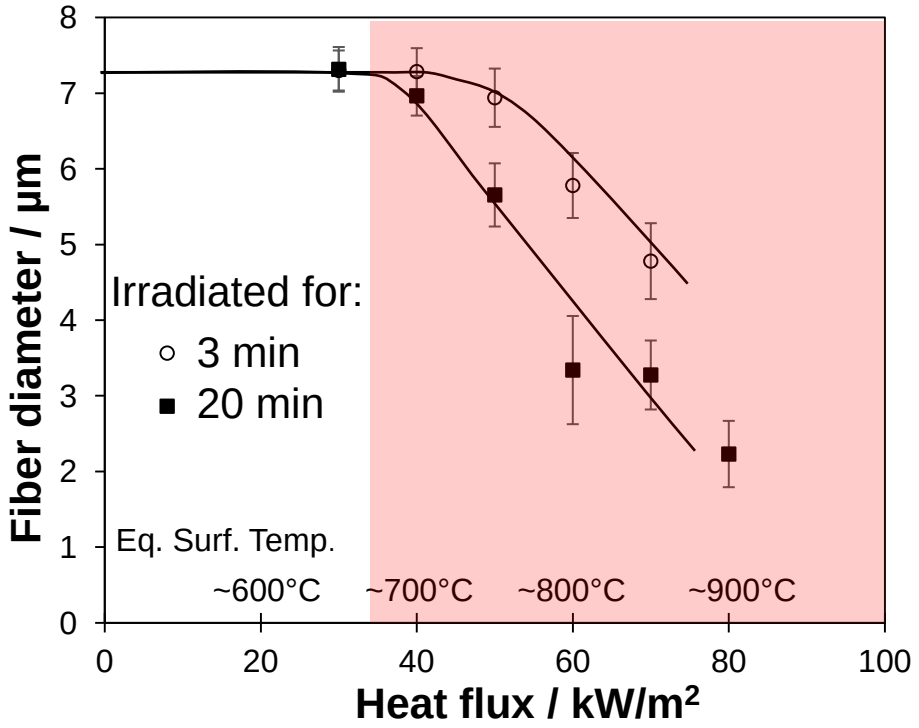


Fiber degradation: < 650°C

# Influence of heat flux and time

- Fiber diameter (original fiber diameter: ~7.2 µm)



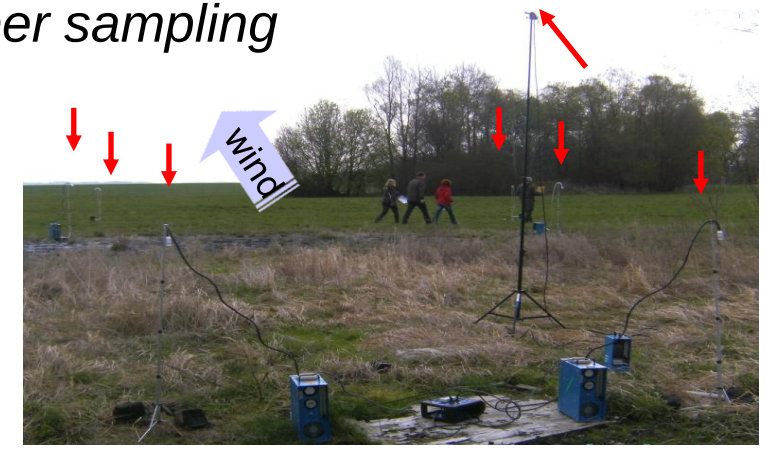

Minimum temperature necessary for fiber degradation
Prolonged heat load increases fiber degradation
External heat source is critical during mishaps

# Fiber concentration in real fire?
## Large scale fire test (2012)


*20 kg CFRP, 40 L kerosene*

*Max. temperature > 900°C (15 min)*

*Stationary and person related fiber sampling*

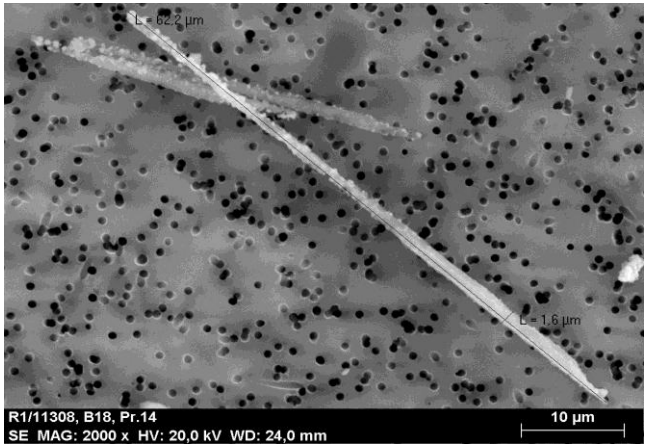


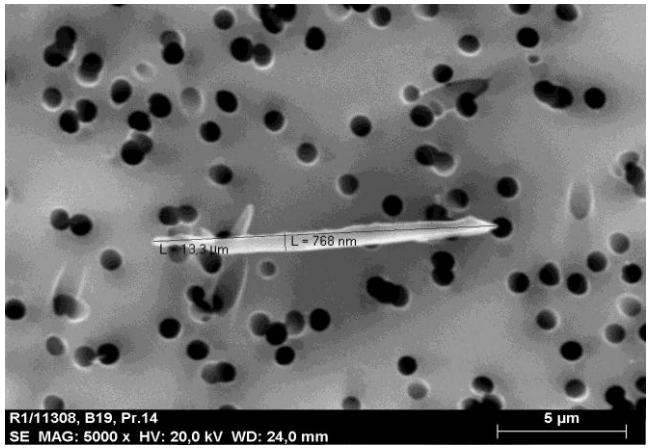
# Most important result

~90 000
WHO-Fibers/$m^3$

Handling of combusted CFRP material is critical

# Further fiber concentrations




*SEM: Critical C-fiber fragment on filter*

**Fire fighter:**

In smoke: no measurement possible

Downwind side:
0 F/m$^3$

**Stationary:**

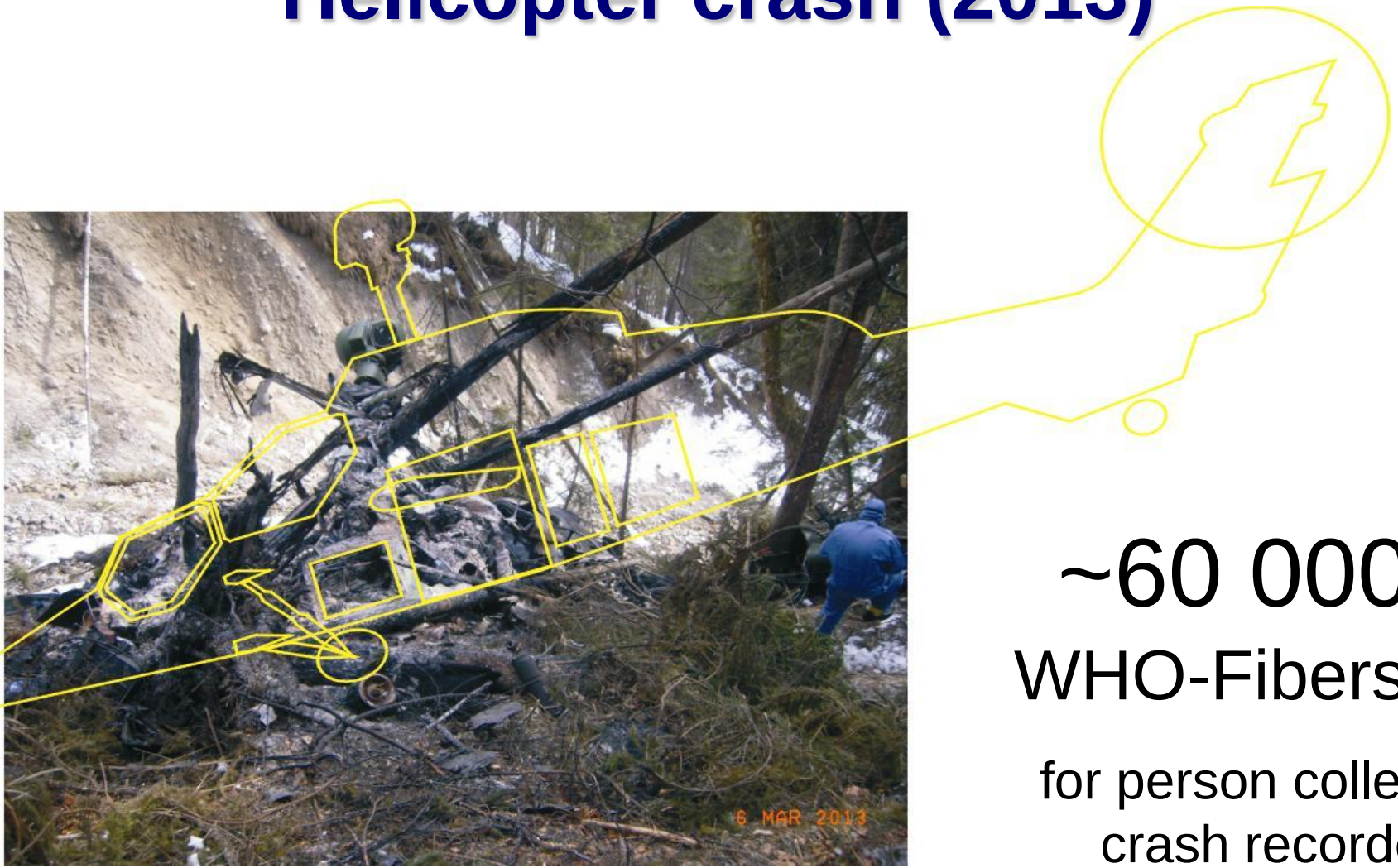
In smoke: no measurement possible
(at least 3000 F/m$^3$)

Upwind side without smoke:
~2000 F/m$^3$

Downwind side:
0 F/m$^3$

Measurement of total fibre emission not possible

# Helicopter crash (2013)




*Helicopter wreck*

~60 000

WHO-Fibers/m³

for person collecting crash recorder

# Other examples

*before*

*B2, Guam (USA) 2008*

*after*

Other examples: From: Harrier (1990) to A400M Spain (2015)

# Legislation

…Final assessment of hazardous potential of carbon fiber fragments is still missing

…German substitute: Regulations by TRGS 521 *„(…) Sanierungs-(…)arbeiten mit (..) Mineralwolle“:*

Expositon categories for activities with:

1: no or very little fiber exposition: < 50 000 fibers/m³
2: little or medium fiber exposition: 50 000 - 250 000 fibers/m³
3: high: 250 000 fibers/m³

Inter alia: Personal protection equipment is necessary

# Personal protection

- Personal protective equipment:
  - breathing mask (FFP3)
  - protective garment
  - robust gloves
- Occupational health monitoring
- Avoid dust, do not throw CFRP parts
- Minimize exposed personell
- Transport/disposal packed in foil
- Instruct exposed people

TIGER crash

# Binder for fibers

*Application of fiber binder on helicopter wreck*

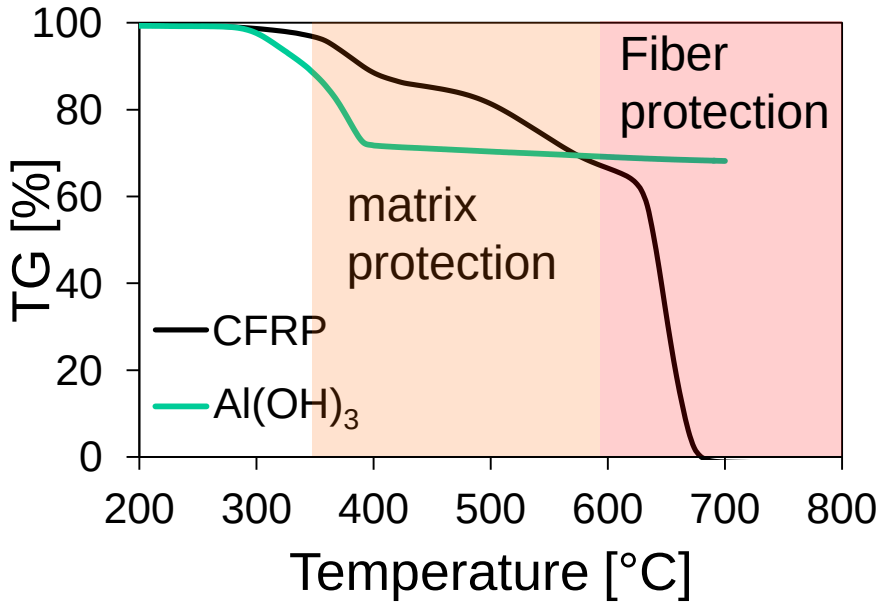
Patent:
Faserbindelack bei CFK-Brandschäden (biodegradable)
DE 102014010465 A1

# Additive flame retardants

Flame retardant has to:

- primarily protect carbon fiber from oxidation in a high temperature range
- instead of typically retarding resin combustion at lower temperature
- act close to the fiber (not in the matrix)
- not affect fiber to matrix adhesion

- Thermogravimetric analysis




„New type of high temperature **in situ** fiber protection“ as „flame retardant“ forming stable layers is under current research

# Summary

- Critical concentration of respirable fibers in contact with combusted CFRP material
- But only after high heat loads (temperature > 600°C)
- Parameters influencing formation of critical fiber fragments are: temperature, time, heat flux, initial diameter, flame retardant
- Flame retardants forming protection layers seem to be efficient at rather high temperature

Hazard is limited to personell, frequently in contact with combusted material
Risk can be kept under controll

# Outlook

- **Norm test** to determine the potential for fiber formation of different CFRP under **thermal and mechanical** load has to be established (comparison of materials)
- **CFRP** should be **optimized** with flame retardants providing fiber protection
- Methods to **detect** critical fibers must be improved for fast and mobile use
- Further **toxicologic investigation** of carbon fiber fragments is necessary

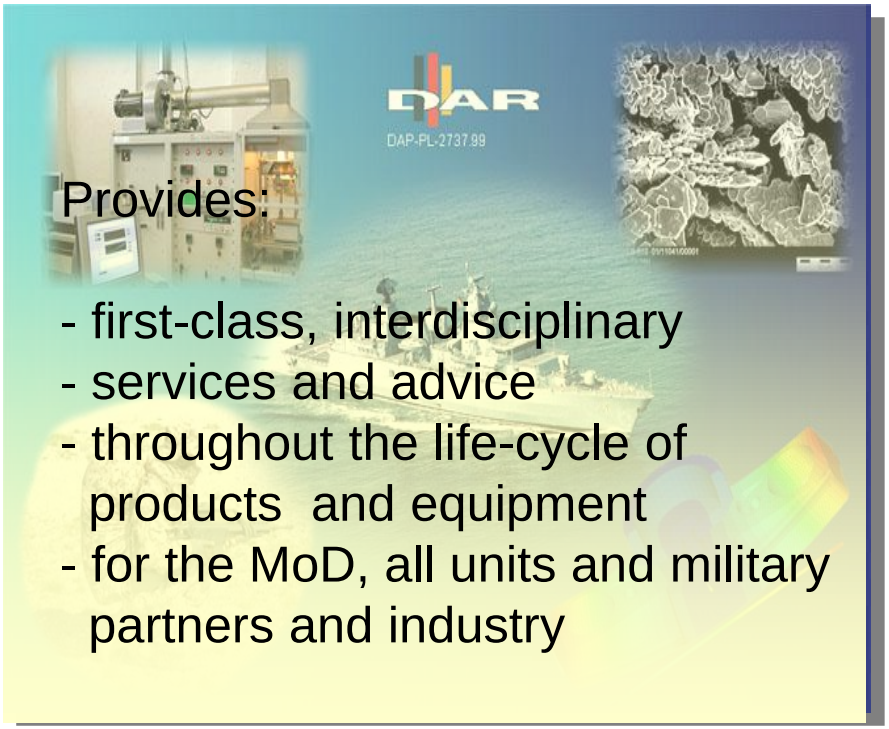
*Wind generator blades*


*Lamborghini Gallardo*

Eibl S., N. Scholz: „Besondere Gefährdung beim Abbrand von Carbon verstärkten Kunststoffen“, BrandSchutz Deutsche Feuerwehr-Zeitung, Ausgabe 6/2014, Verlag W. Kohlhammer, ISSN 0006-9094 / E 1889, 423-427
Eibl S. Potential for the formation of respirable fibers in carbon fiber reinforced plastic materials after combustion, Fire and Materials DOI 10.1002/fam.2423 (2017)

# Wehrwissenschaftliches Institut für Werk- und Betriebsstoffe

(Bundeswehr research institute for materials, fuels and lubricants)





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