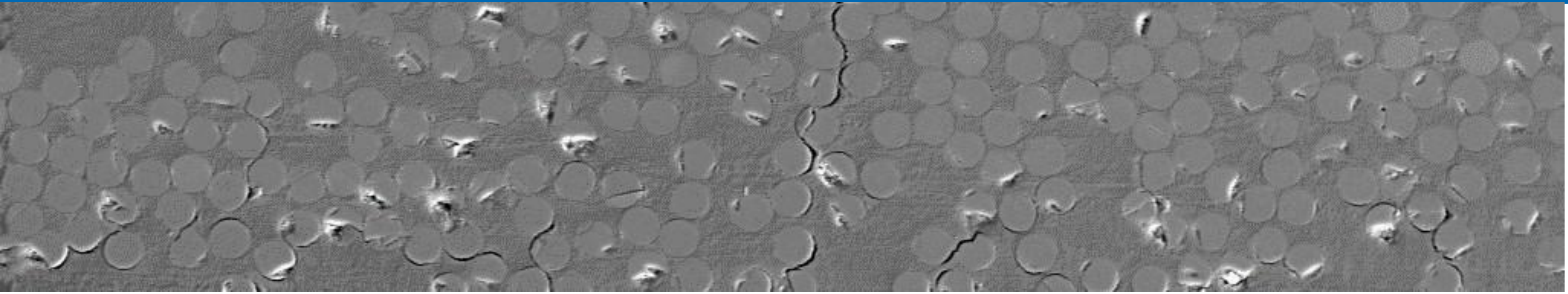


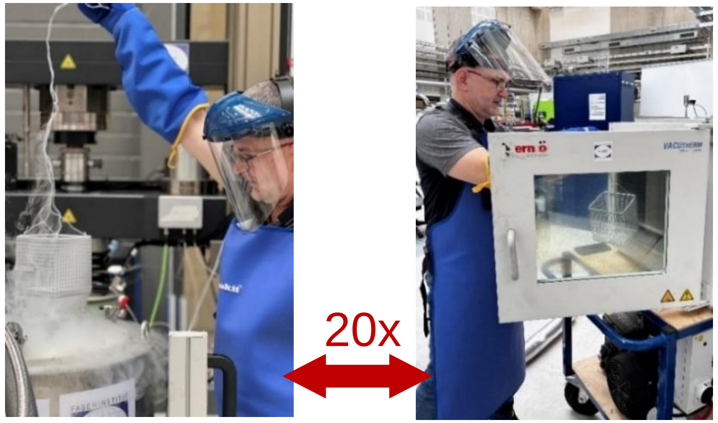
POLYAMIDE 12 COMPOSITES AS PERMEABILITY BARRIER FOR CRYOGENIC HYDROGEN STORAGE

Patrick Nowakowski, M. Barreto da Cunha, A. Rather, D. May

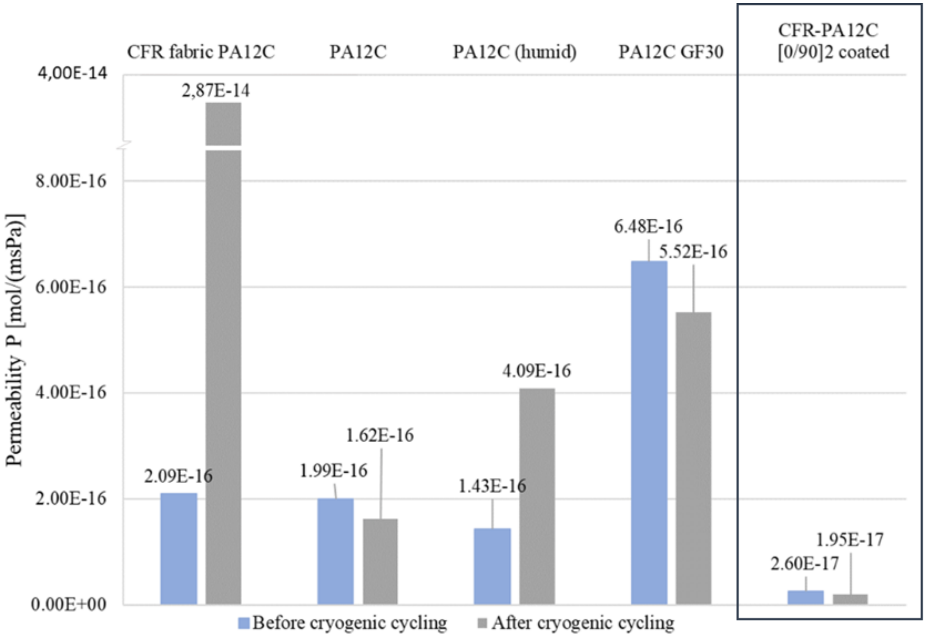
FPCM 17 – 17th International Conference on Flow Processes in Composites Materials
Sheffield, UK, 30th June - 2nd July 2026

Tailored Composites for Cryogenic Applications

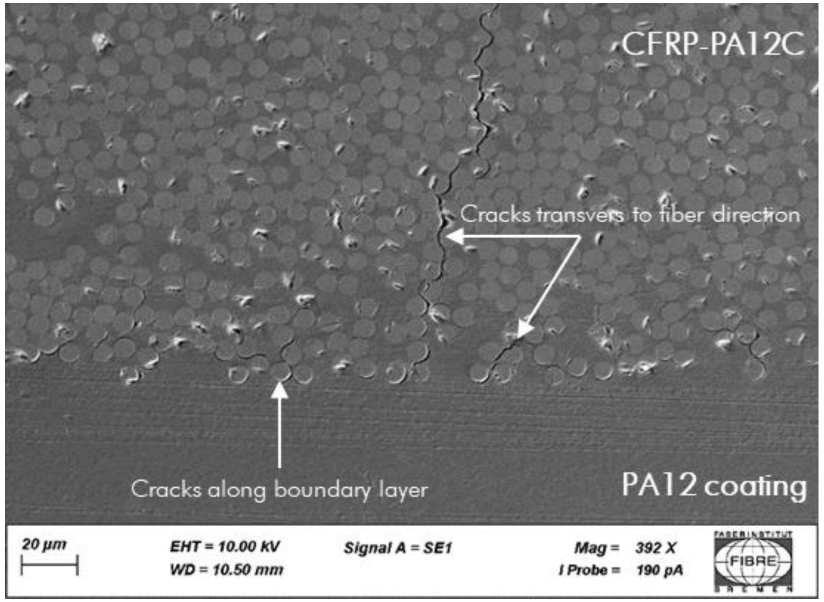
- Thermal induced cracks arise due to different CTE of fiber and matrix
- Gradient PA12 composites with neat PA12 layers potentially combine high crack resistance with strong interfaces between neat polymer and composite domain)



Permeability of before and after cryogenic cycling

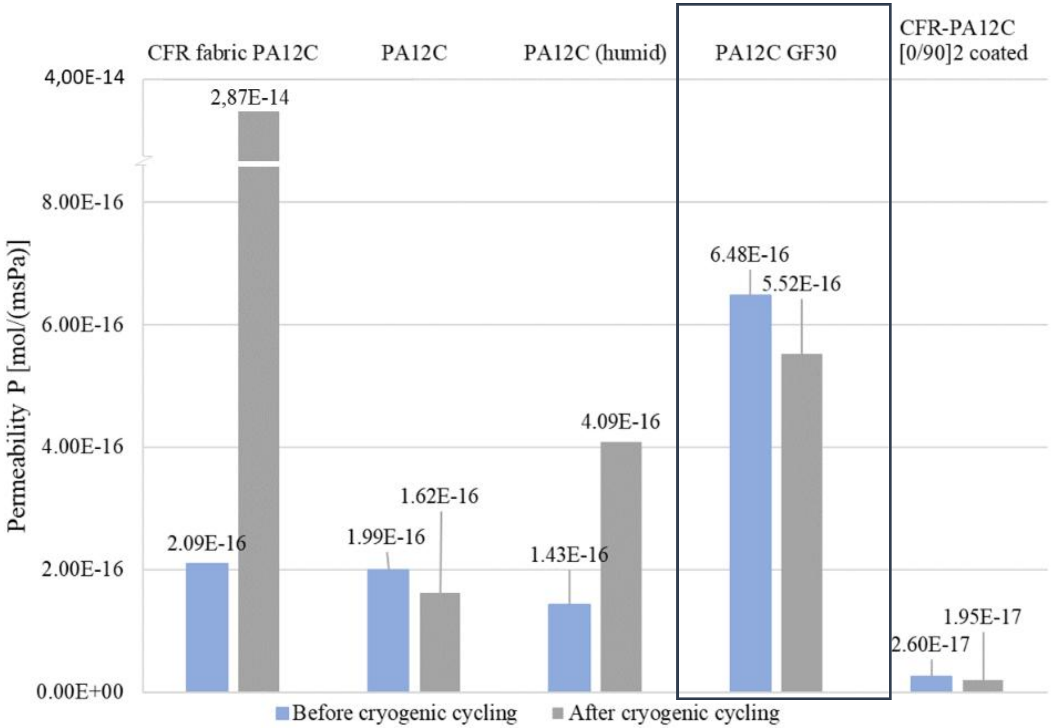


Cracks after 20 x Cryogenic Thermal Cycling

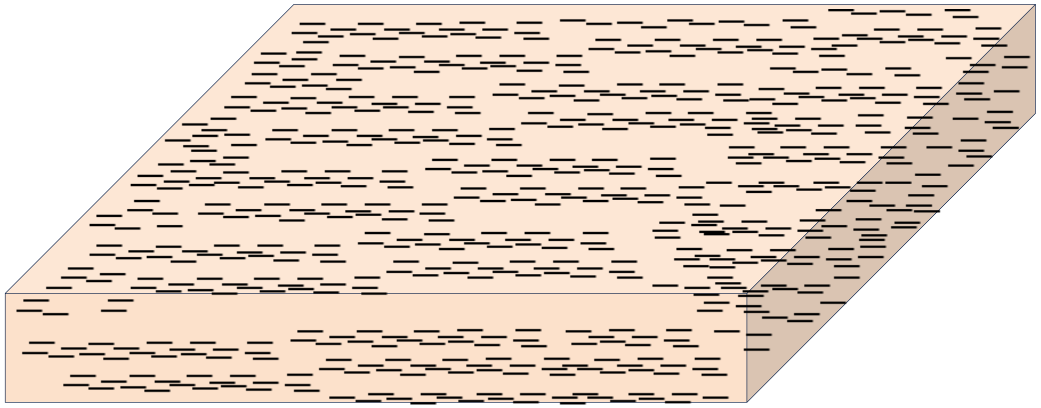


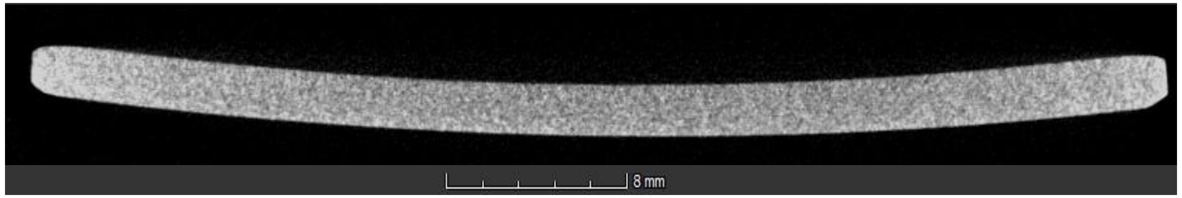
Recap - Influence of short glass fibers on permeabilty

- Unchanged permeation rate after thermal cycling
- Effect of crack resitstance of short fiber reinforced polyamide needs to be researched more in detail



Permeability of unreinforced PA12C and CFR-PA12C before and after cryogenic cycling





µCT of short fiber reinforced PA12C with 30% short glass fiber content

Approach

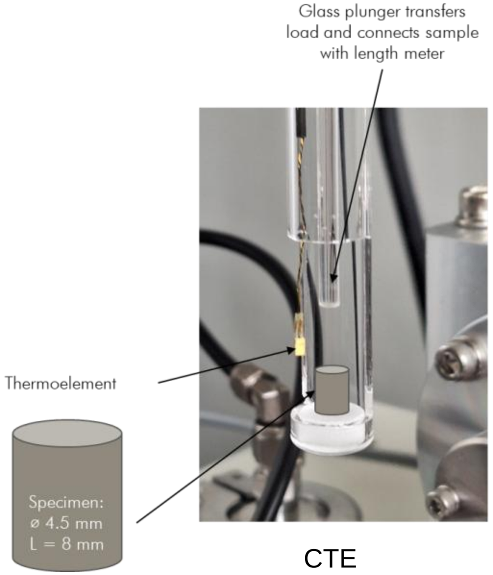
- **Parameter**
  - Short fiber
    - Carbon Fiber
    - Glass Fiber
  - Fiber volume fraction
- **Influence on**
  - Crack resistance of cryogenic thermal induced stresses
  - CTE (4K – Tg)
  - Cryo mechanical behaviour
  - Helium gas permeability

Objective

Material with

- high crack resistance
- reduced gas permeability
- Reduced CTE

ECOMAT CRYOLAB



CTE

CRYOGENIC THERMAL CYCLING

QUASISTATIC TENISLE TESTING

ECOMAT CRYOLAB

- Testing in **liquid nitrogen** bath (-196 °C, 100 kN)
  - **Quasistatic** and **dynamic** testing
- **Dynamic** testing in gaseous **helium** (-263 °C, 100 kN)
- **Permeability** testing of pipes/plates with Helium (-263 to 30 °C)
- Coming soon: stat & dyn. testing in **liquid hydrogen** bath (-253 °C, 100 kN)
- **CTE** measurement with (cryogenic) Helium (-269 to 200 °C)
- Helium Gas Permeability Test stand
- **X-ray** development platform (4x2,5 m²)

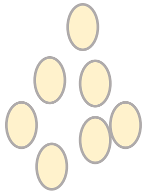
Research Topics

- Composite behavior under cryogenic conditions
- Crack formation & permeation
- Development of test methods
- Tailored materials

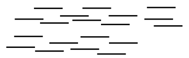
Universität Bremen
ECOMAT Bremen Center for Eco-efficient Materials and Technologies
BAB Die Förderbank
BREMEN BREMERHAVEN ZWEI STÄDTE. EIN LAND.
Europäische Union
Investition in Bremens Zukunft
Europäischer Fonds für regionale Entwicklung

Specimen preperation

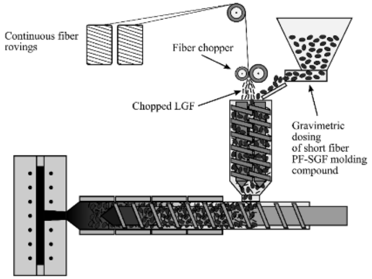
PA12 Granulate



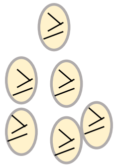
Short fibers



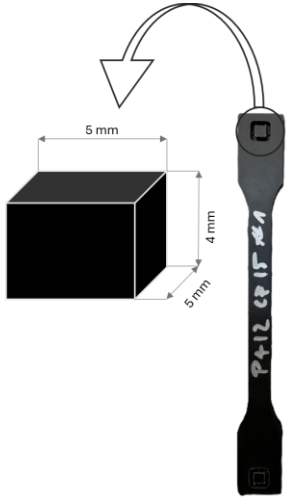
Compounding



Short fiber reinforced granulate



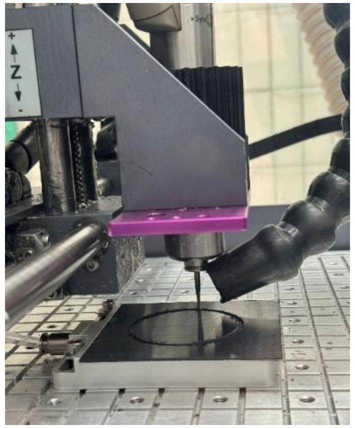
Injection molding



CTE
ISO 11359-2:2021(E)

Tensile strength
DIN EN ISO 527-5

Permeability



Milling

Helium Gas Permeability

Helium Gas Permeability Test Stand

FASERINSTITUT
FIBRE
BREMEN

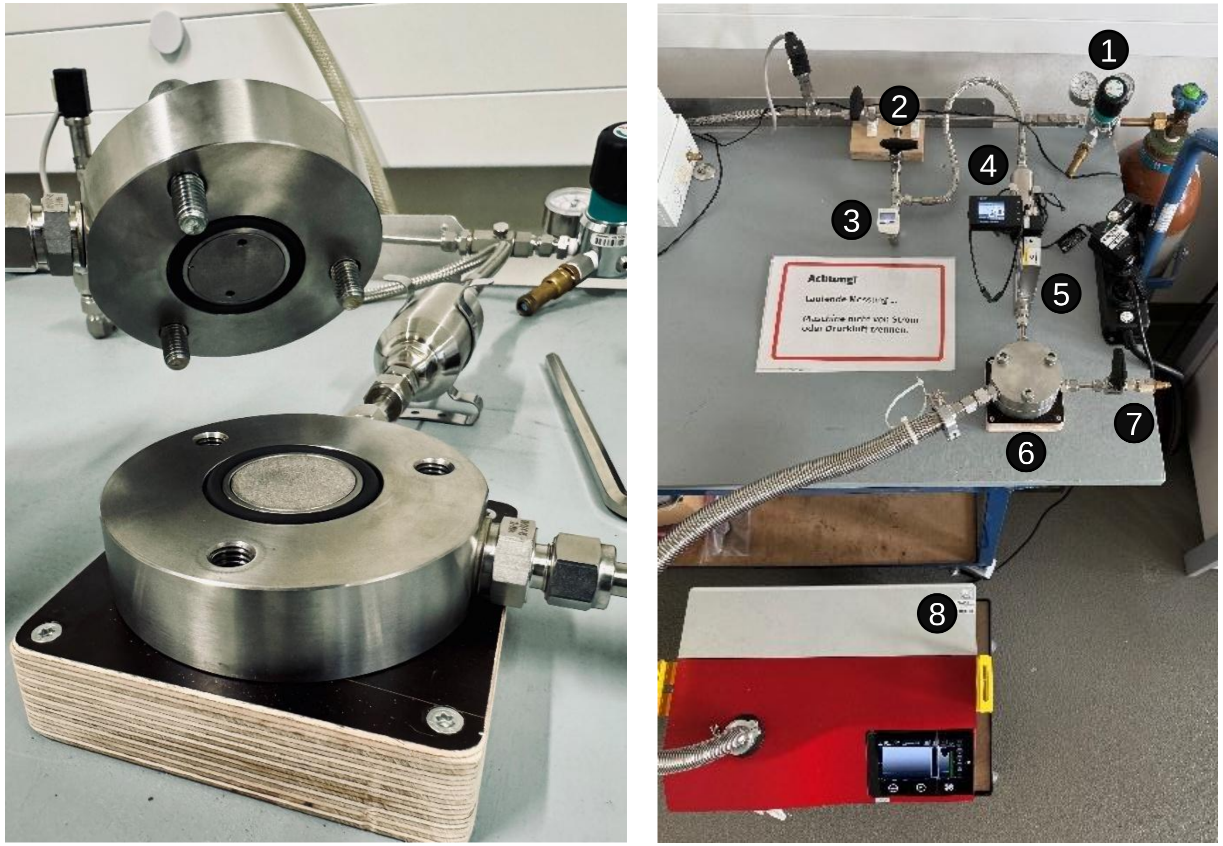


Figure 1: Helium Gas Permeability Test Stand

- Measurement He - Leakrate
- Inlet Pressure: 5 bar
- Outlet Pressure: 10^{-3} mbar
- Specimen size: ⌀ 55 mm, 2 mm Thickness
- Temperature: 293 K

Helium Leakrate: $Q_L \left[\frac{\text{mbar}}{\text{L s}}\right]$ – Output of leakage detector

Permeability: $P = \frac{Q_L}{A} \cdot \frac{d}{\Delta p} \cdot \frac{1}{R_m T} \left[\frac{\text{mol}}{\text{m s Pa}}\right]$

1. Pressure regulator
2. Shut of valve
3. Pressure sensor (inlet)
4. Gas reserve tank
5. Flow meter
6. Test cell
7. Shut off valve
8. Leackage detector

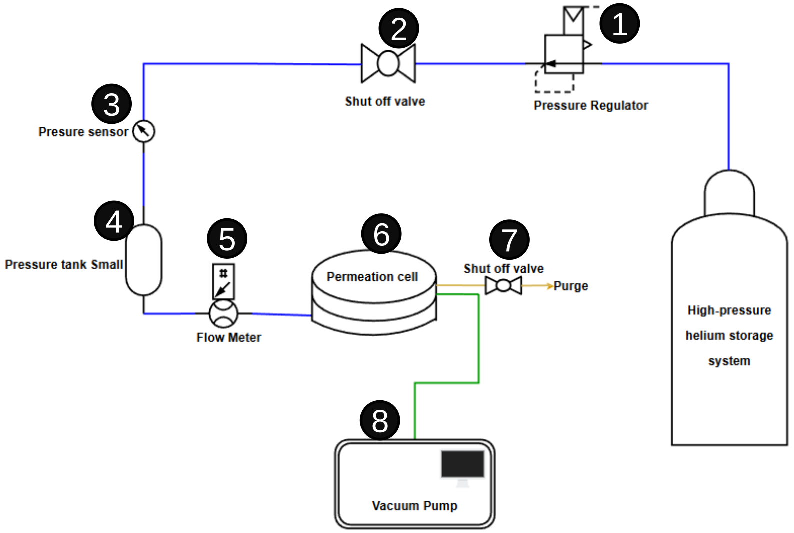


Figure 2: Scheme

Universität
Bremen

Cryogenic thermal cycling

Figure 1: Specimen holder & cryogenic cycling system

- Cryogenic cycling system from Cryovac
- Tracer gas: Helium 4.5
- Cooling rates up to 10 K/ min
- 2 stage cooling with intermediate precooling at 100 K
- In total: 100 cryogenic thermal cycles from 298 K to 20 K (-253 °C)

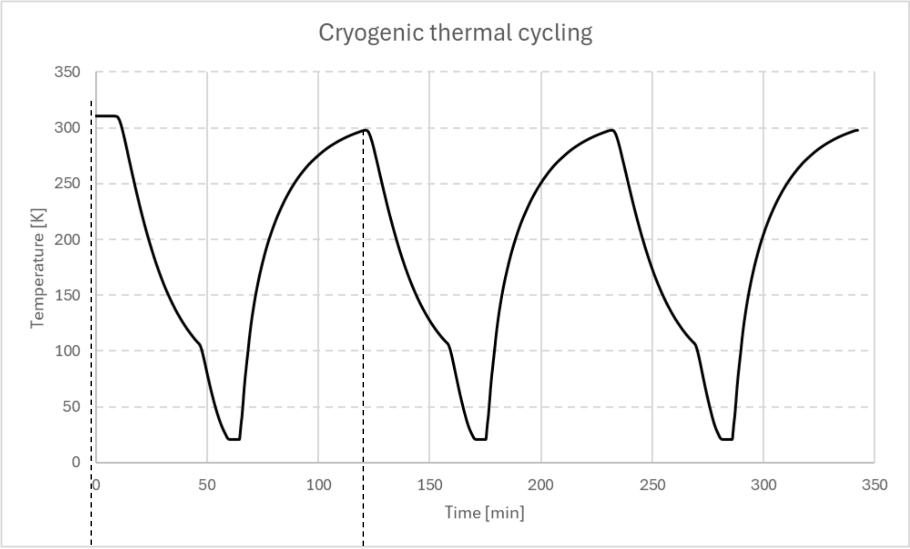
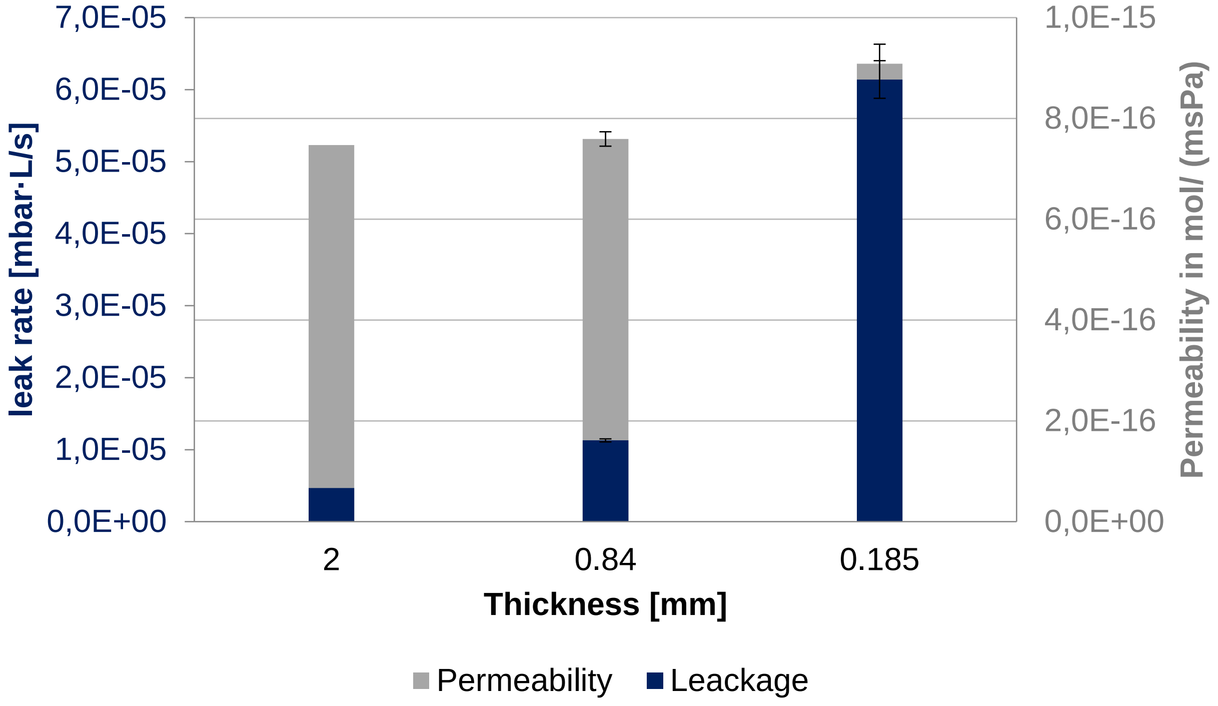


Figure 2: Thermal cycle

Influence of specimen thickness on permeability



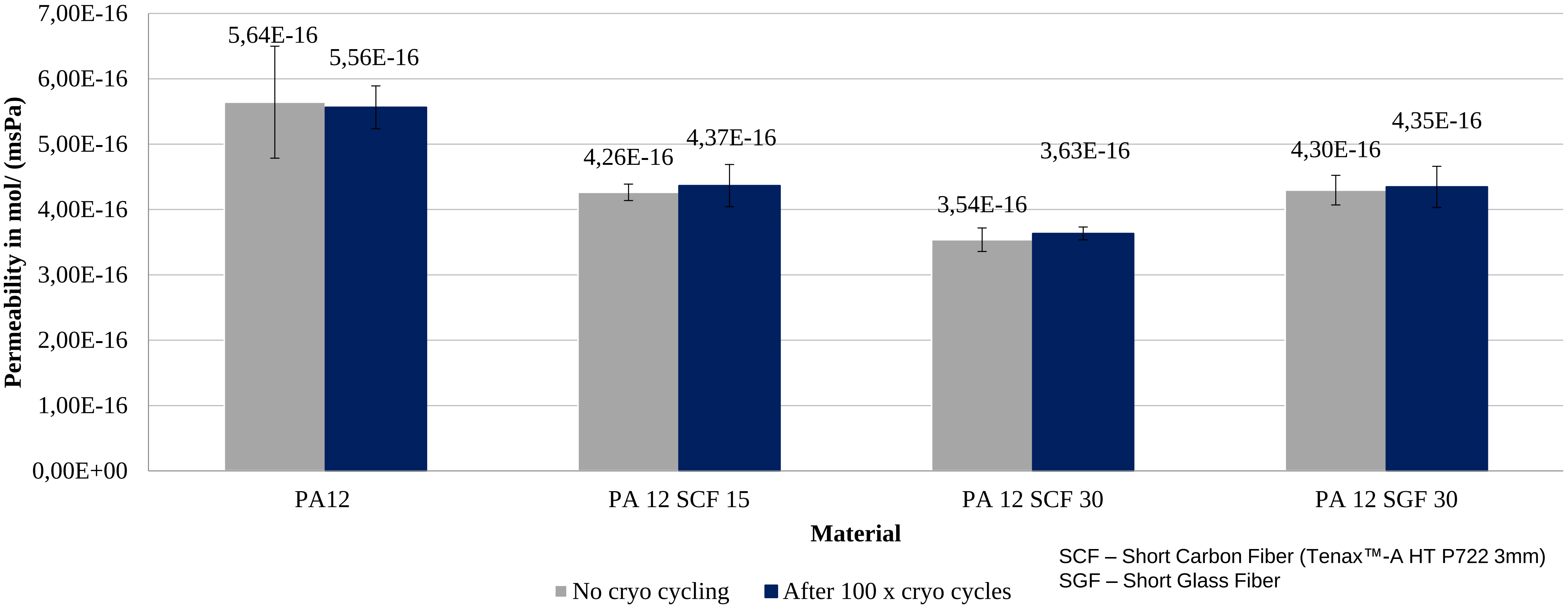
Helium Leckrate: $Q_L \left[\frac{\text{mbar}}{\text{L s}}\right]$ – Output Leckage detector (ASM 340)

Permeability: $P = \frac{Q_L}{A} \cdot \frac{d}{\Delta p} \cdot \frac{1}{R_m T} \left[\frac{\text{mol}}{\text{m s Pa}}\right]$

- As the sample thickness increases, the test time increases
- At the same time, the helium leakage rate decreases Permeability remains constant
- This is to be expected according to Fick's second law:
  - $J = -D \frac{\Delta c}{d}$ (Flux J, diffusivity D concentration difference Δc, thickness d)
  - Reason: With greater thickness, the helium molecules must travel a longer distance through the material
  - The pressure conditions otherwise remain the same
  - Therefore, helium transport per unit area and time decreases as thickness increases.
- In practice, this means:
  - Permeability can be measured on thin samples
  - These results can then be scaled up to estimate the helium flux in thicker tank walls during system design

Influence of fillerelements on permeabilty

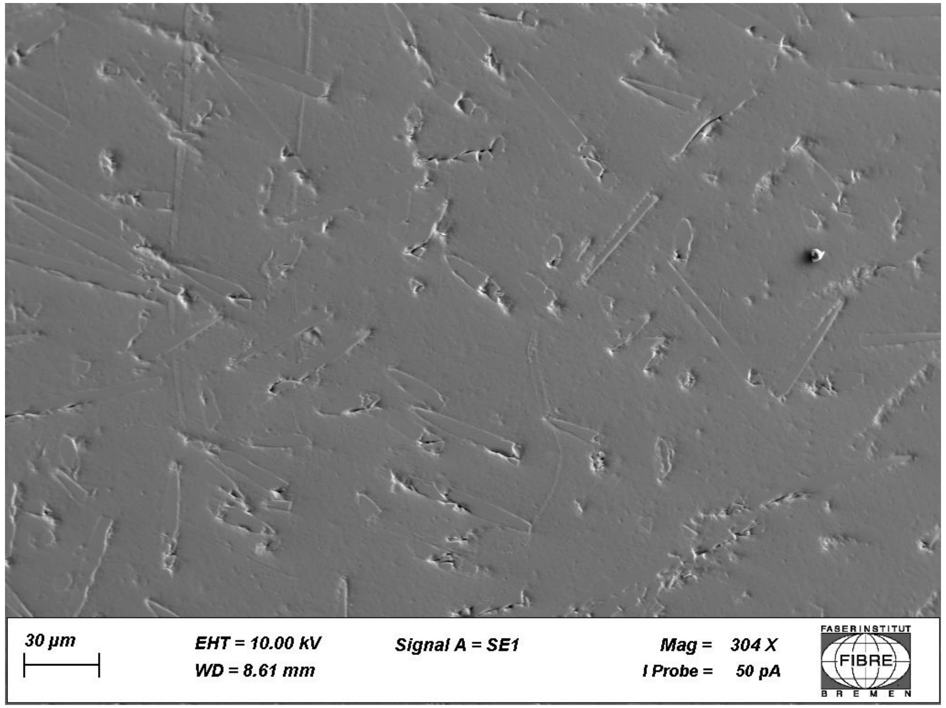
- Adding SCF and SGF improves helium gas tightness
- The V_f has a direct impact on the permeation rate
- After thermal cryogenic exposure (100 x at 20 K) permeability remains unchanged



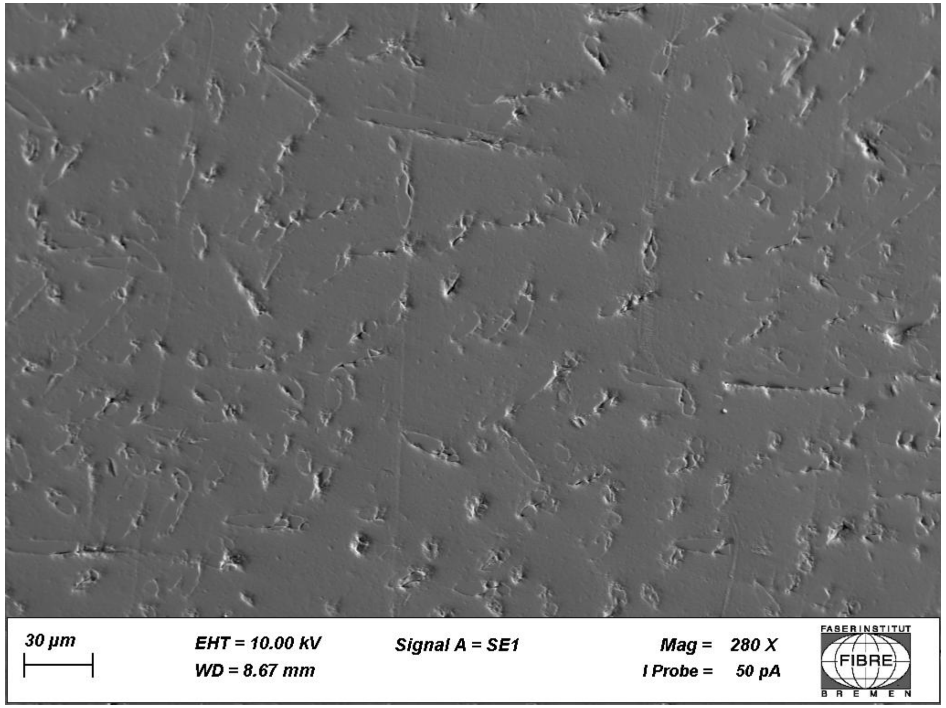
SCF – Short Carbon Fiber (Tenax™-A HT P722 3mm)
SGF – Short Glass Fiber

PA12 SCF 30

Before cryogenic cycling



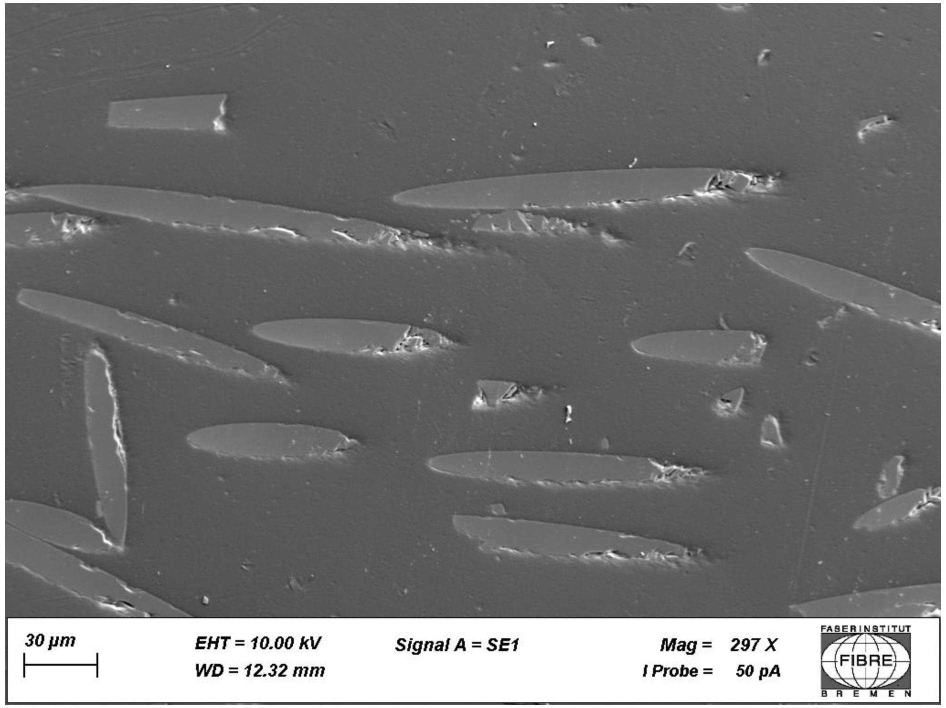
After 100 cryogenic cycles



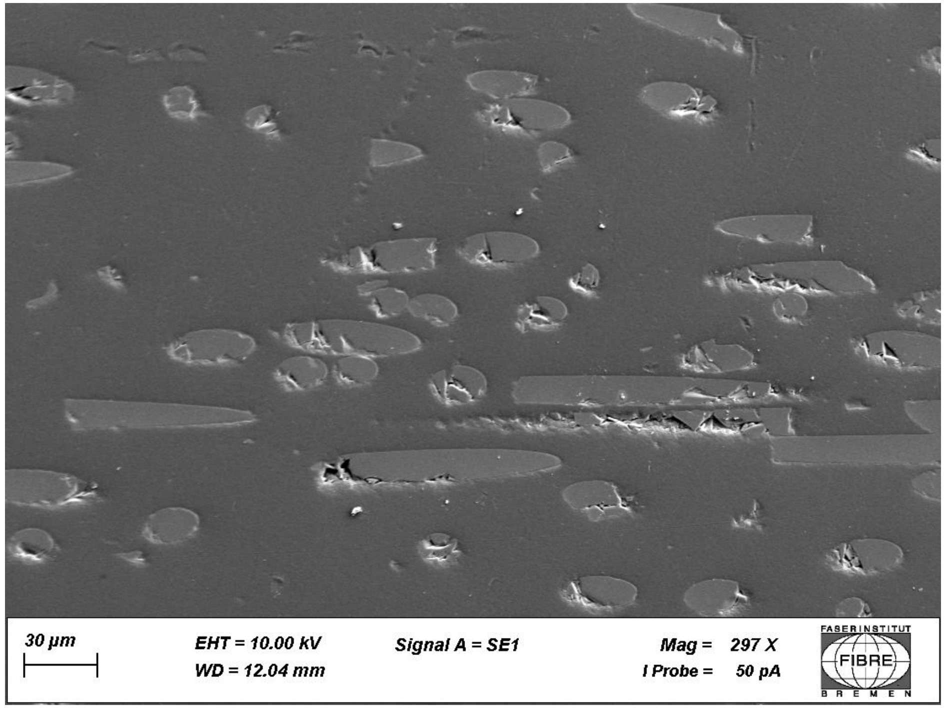
- After thermal cycling a slightly higher Fiber/ Matrix debonding is visible

PA12 SGF 30

Before cryogenic cycling



After 100 cryogenic cycles

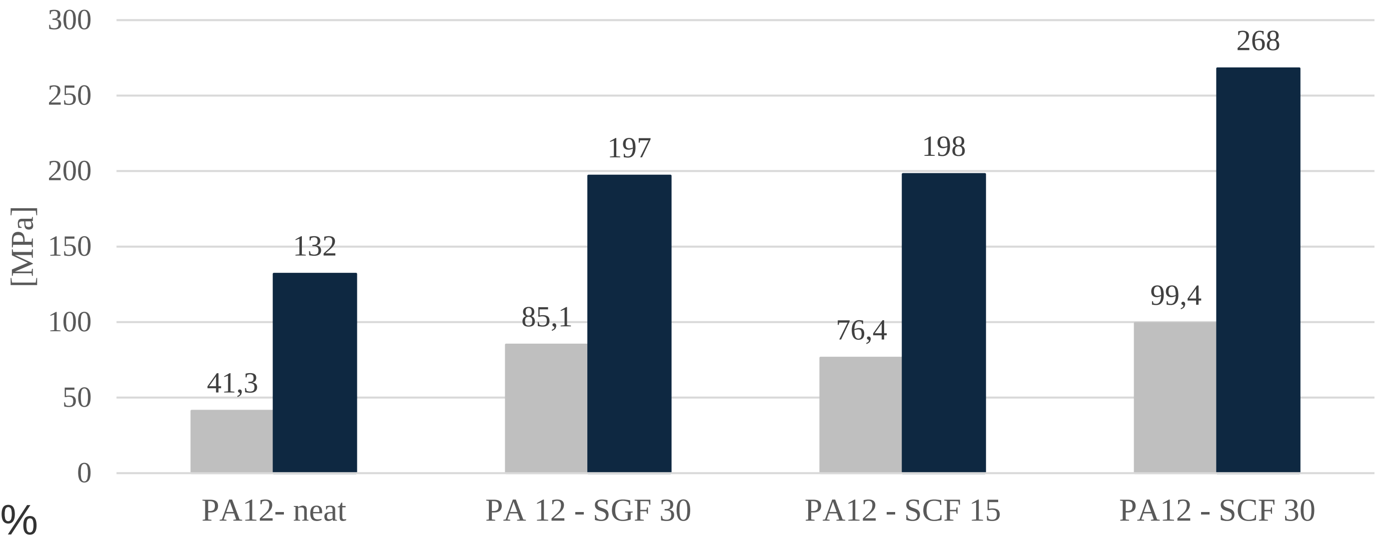


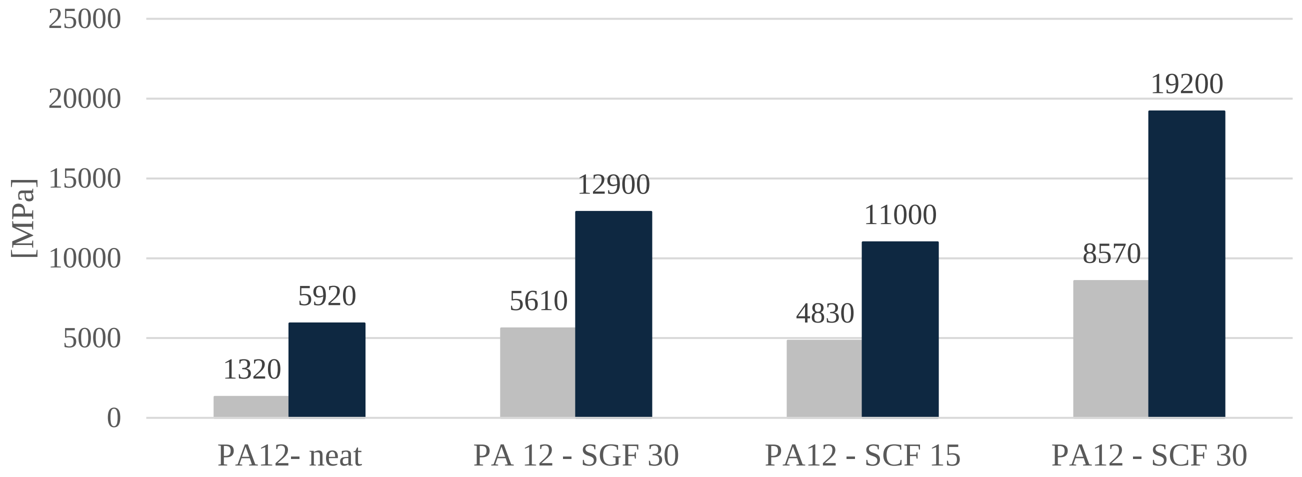
- After thermal cycling a slightly higher Fiber/ Matrix debonding is visible

Tensile Strength

Result tenisle strength test comaparison: 293 K vs. 77 K

- **Neat PA 12**
  - **Tenile strength** rise at 77 K by factor 3
  - **Youngs modulus** rise at 77 K by factor 4
- **Short carbon fiber reinforcement**
  - **Tenile strength** rise by factor 2,5
  - **Youngs modulus** rise factor 2 – 2,5
  - E-modulus rises by factor 2 from 15 to 30 wt%
- **Short glass fiber reinforcement**
  - **Tenile strength** rise factor 2,5
  - **Youngs modulus** rise factor 2,5

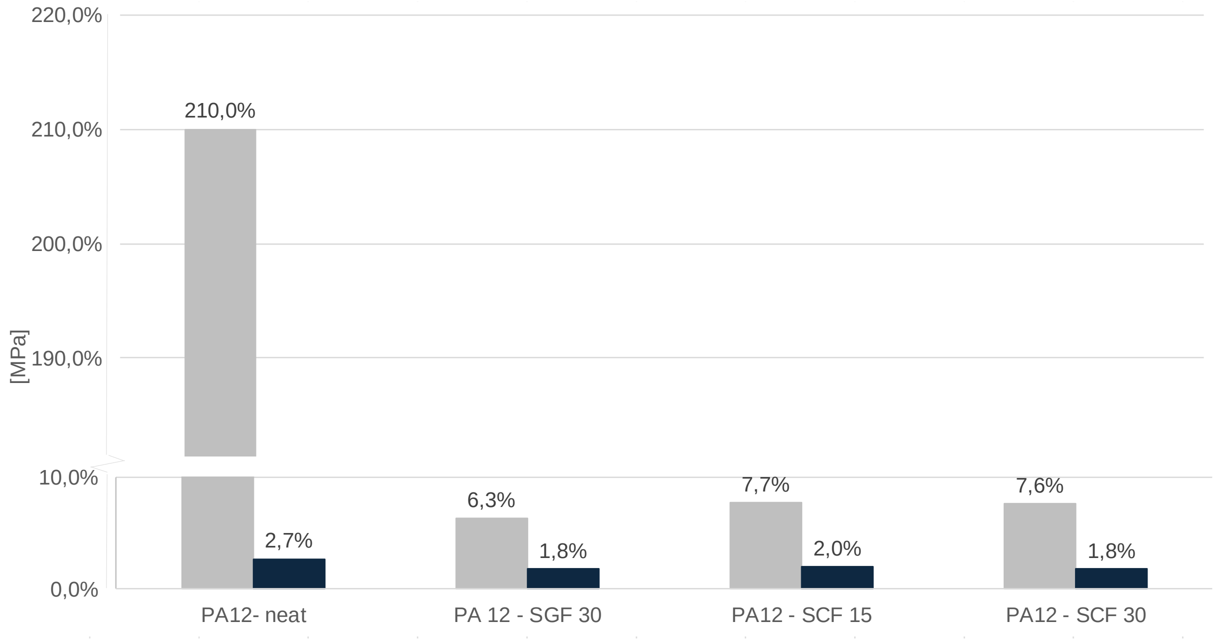




SCF – Short Carbon Fiber (Tenax™-A HT P722 3mm)
SGF – Short Glass Fiber

Tensile stregth test comparsion: 293 K vs. 77 K

- **Neat PA 12**
  - **Elongation at break** drops significantly at 77 K
- **Short fiber reinforcement**
  - **Elongation at break** decreases by 70 %



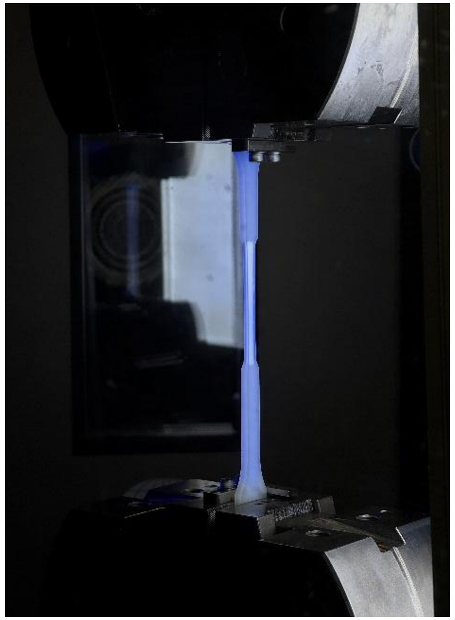
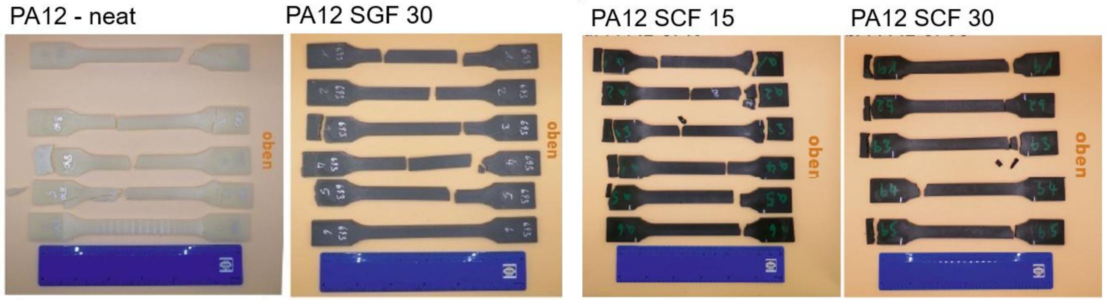


Figure 1: Tensile strength test at 293 K

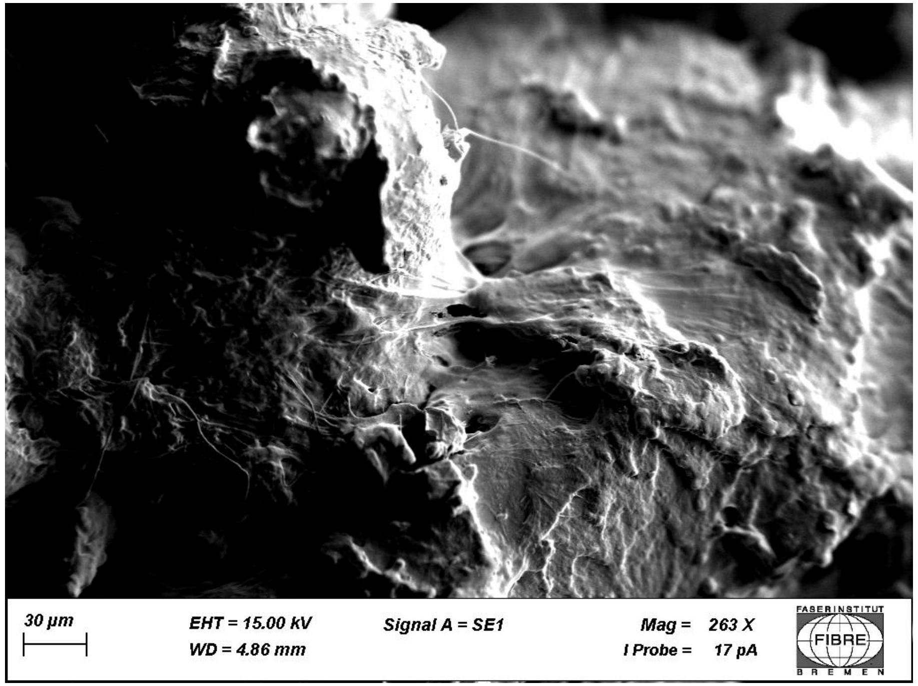
Figure 2: Tensile strength test at 77 K in LN2



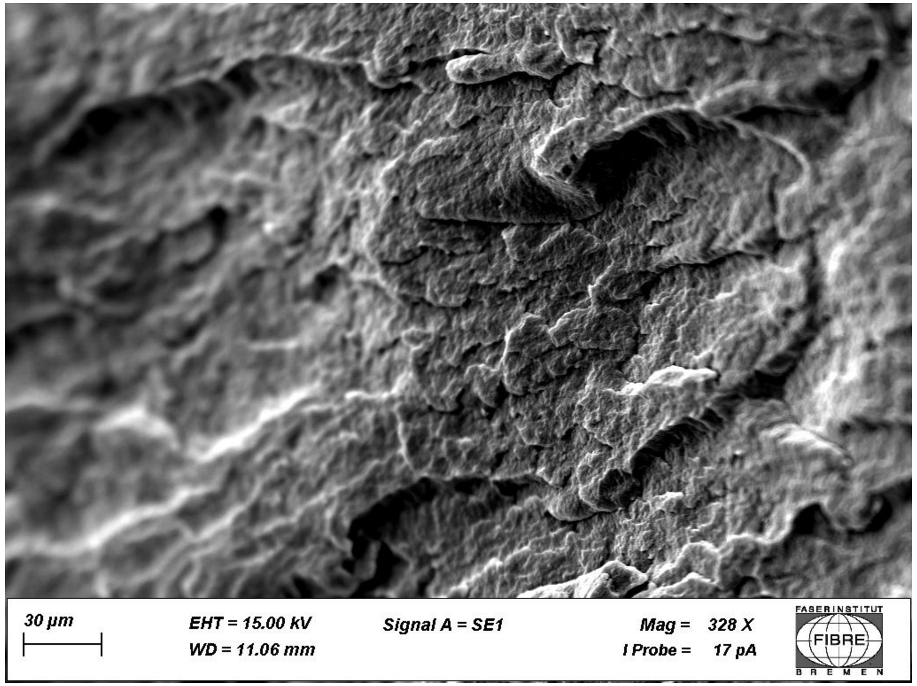
Fracture surface – PA12 neat

- Plastic deformation of the material at room temperature
- Brittle fracture in a cryogenic environment

293 K



77 K

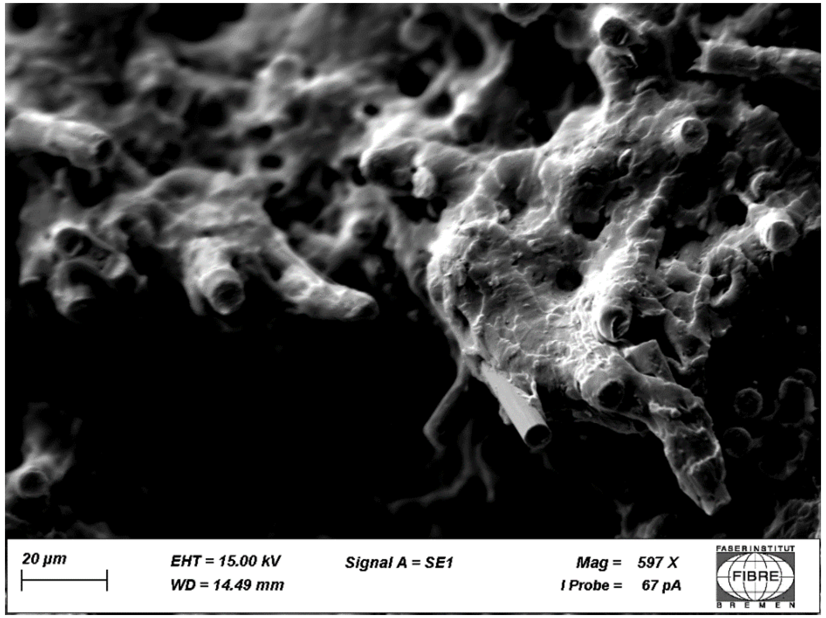


Fracture surface – PA12 SCF 30

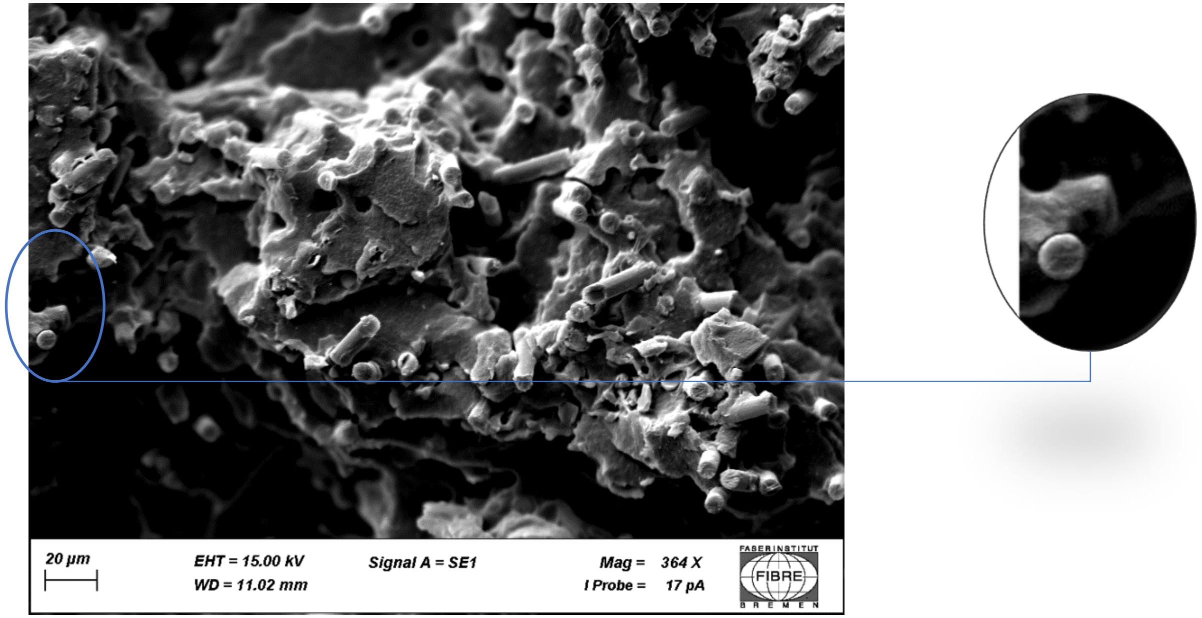
- **Room Temperature**
  - The matrix undergoes plastic deformation
  - Fiber-matrix adhesion is still largely intact

- **Cryogenic temperature (77 K)**
  - Brittle fracture
  - Debonding between the fiber and matrix
  - Fibers are partially pulled cleanly out of the matrix (low fiber-matrix adhesion)

293 K



77 K

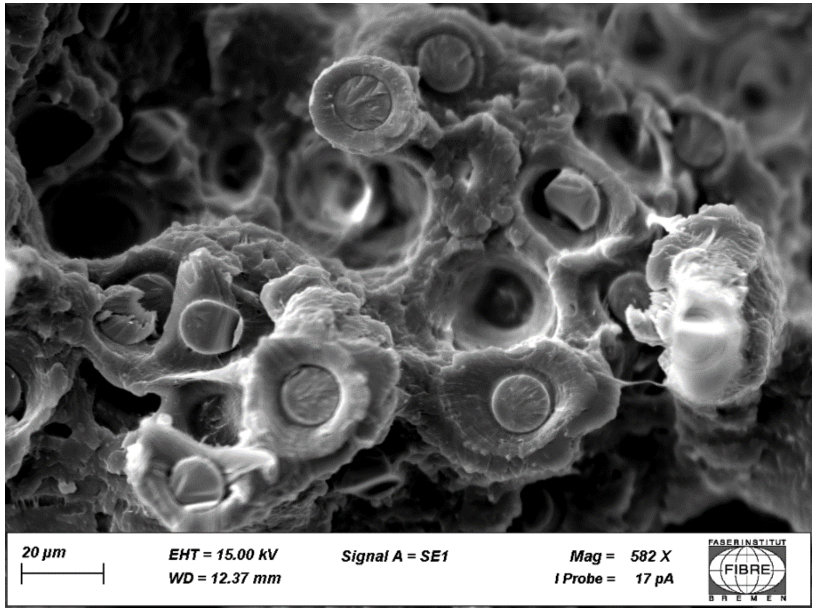


Universität
Bremen

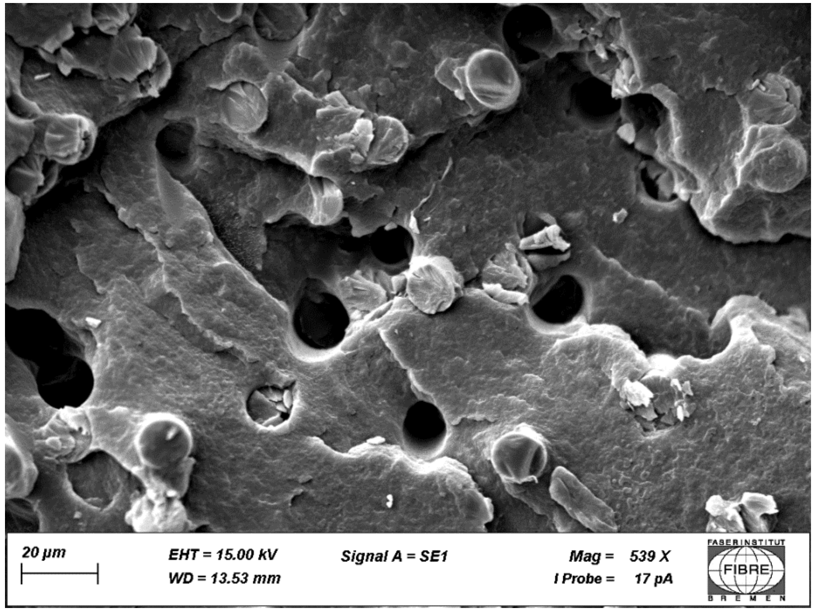
Fracture surface – PA12 SGF 30

- **Room Temperature**
  - The matrix undergoes plastic deformation
  - Fiber-matrix adhesion is still largely intact
- **Cryogenic temperature (77 K)**
  - Brittle fracture
  - Debonding between the fiber and matrix
  - Fibers are partially pulled cleanly out of the matrix (low fiber-matrix adhesion)

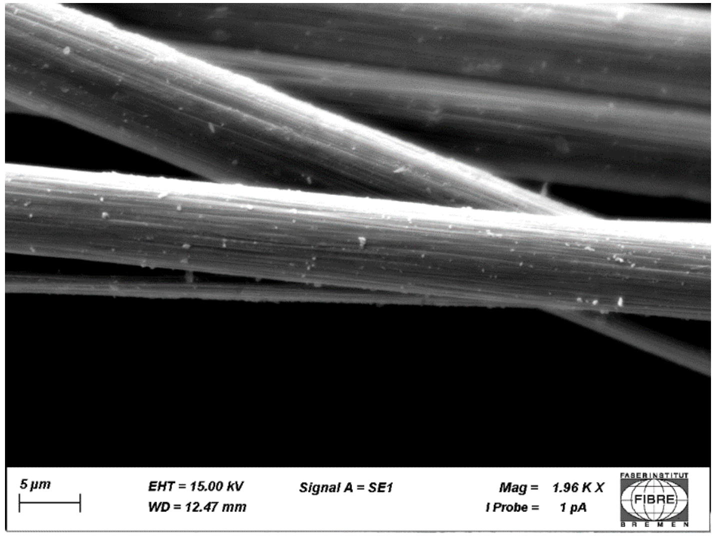
293 K



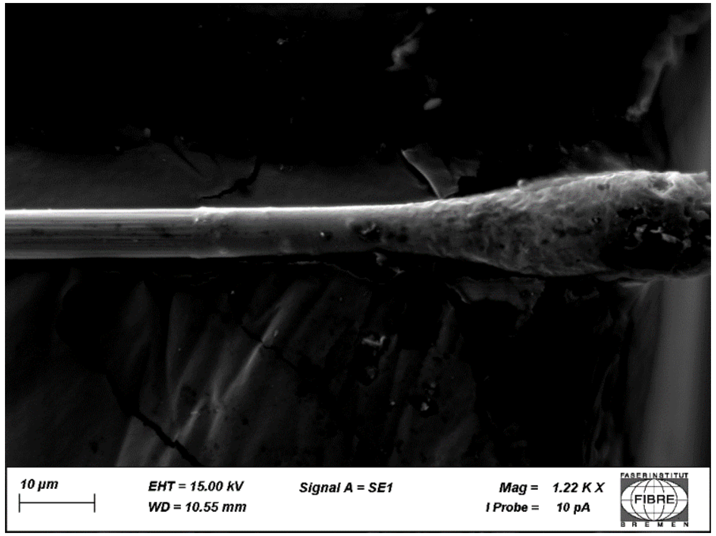
77 K



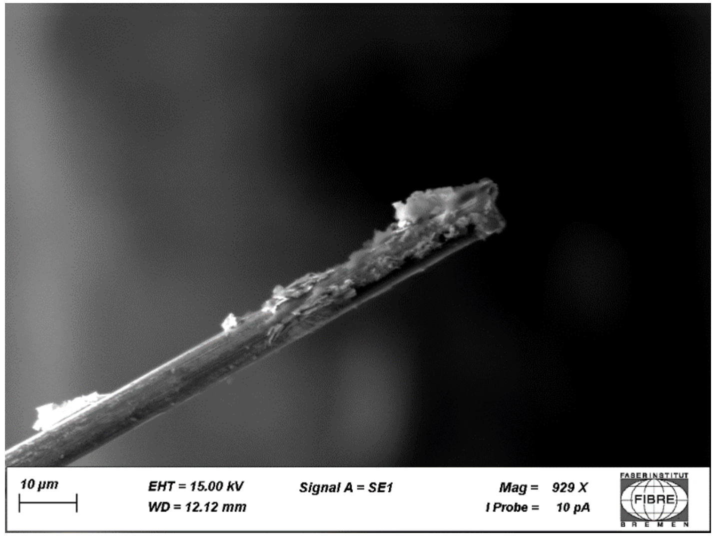
Influence of cryogenic temperature on single fiber pull-out



Teijin HTS 45 P12 vor Einbettung

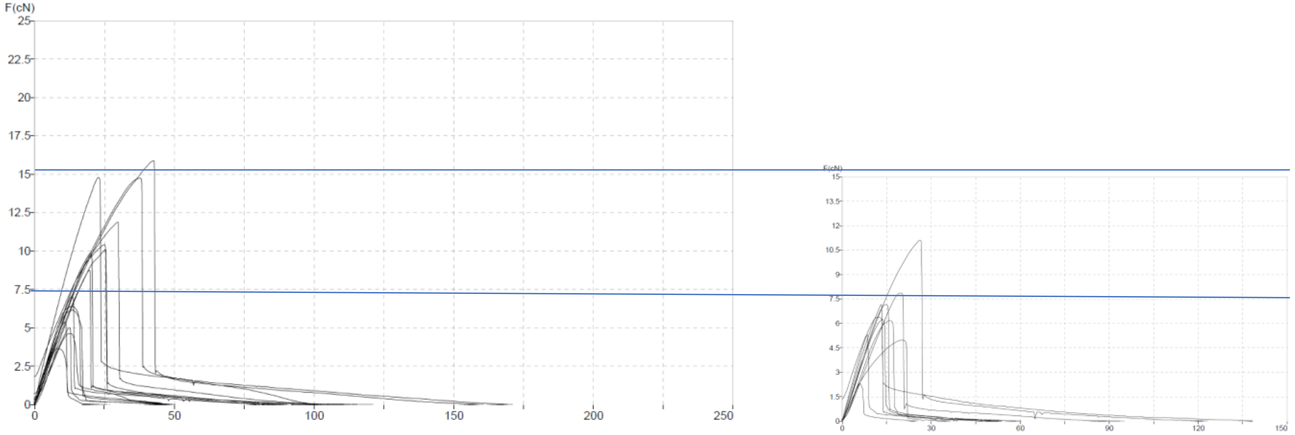


Teijin HTS 45 P12 nach Pull Out Test



Teijin HTS 45 P12 nach Pull Out Test
(10 x kryogene thermische Belastung auf 20 K)

Single Fiber Pull Out Specimen

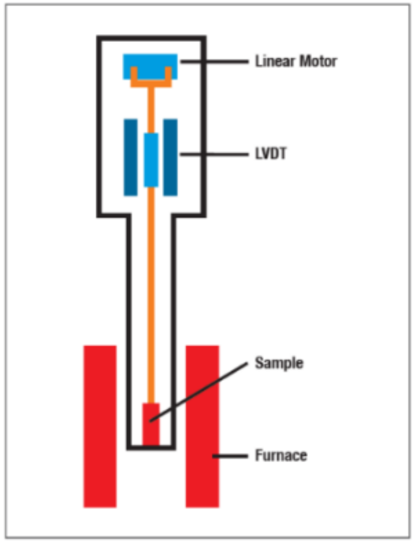


Thermo mechanical Testing

Cryo TMA testing following ISO 11359-2:2021(E)

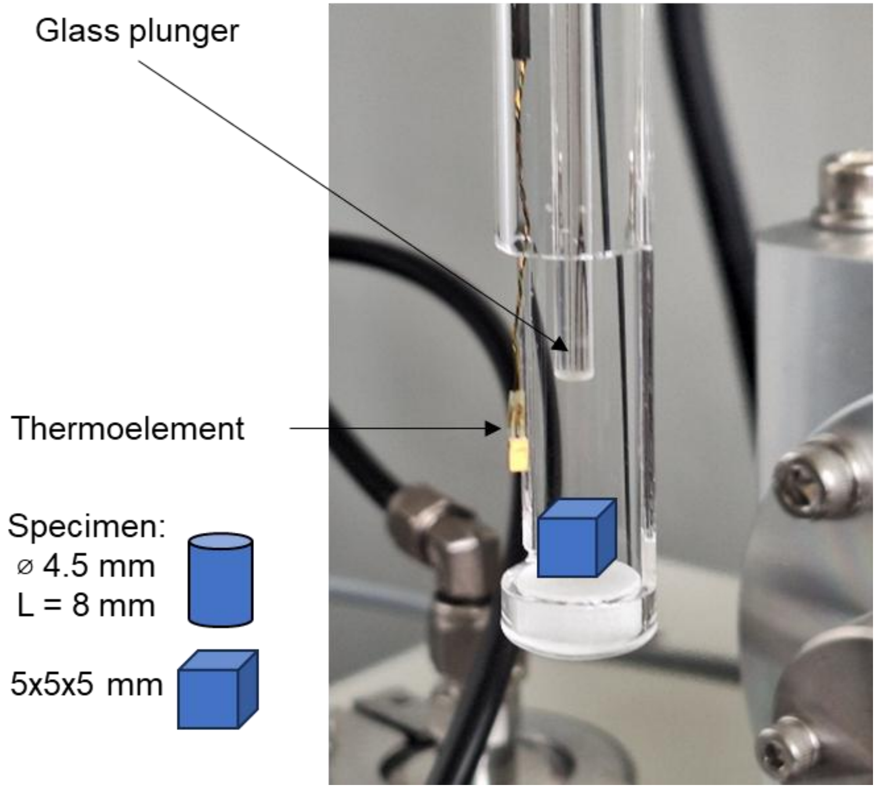
Setup & method

- 500 mN (Standard: max. 25 mN) is necessary to ensure contact with the sample
- Preconditioning with gaseous helium: -50 °C to +70 °C, held for approx. 5 min
- cryo-TMA measurement procedure: Cooling to approx. -269 °C,
- followed by heating run (measurement) up to Tg at 1 K/min



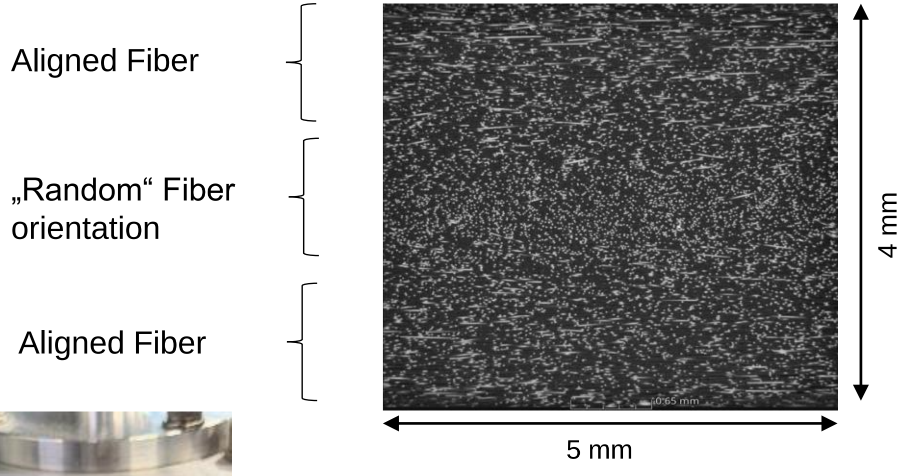
Source: linseis.com

Source: linseis.com

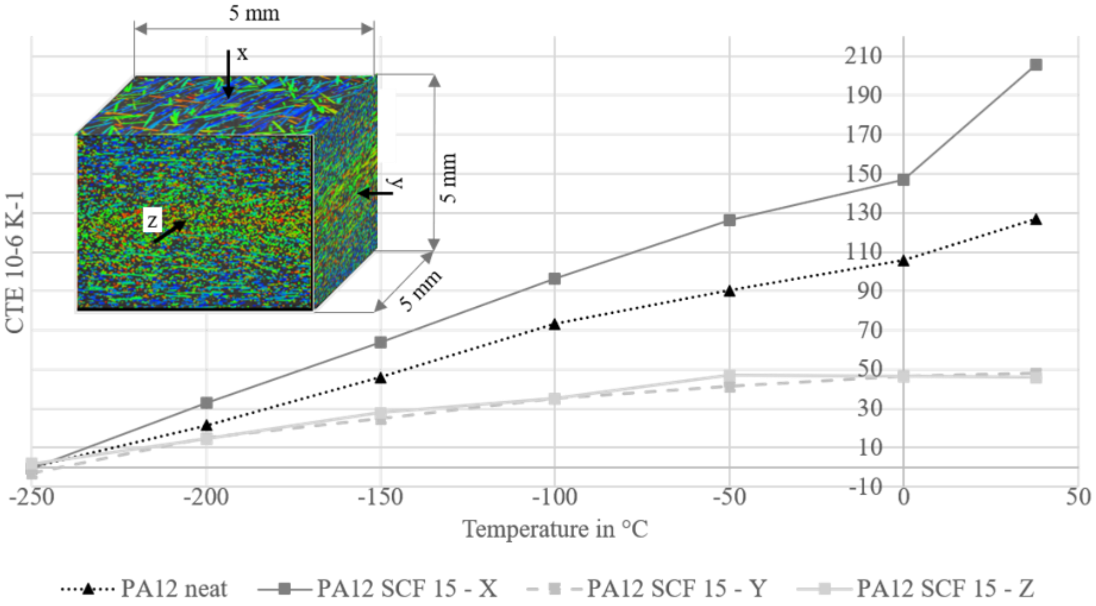


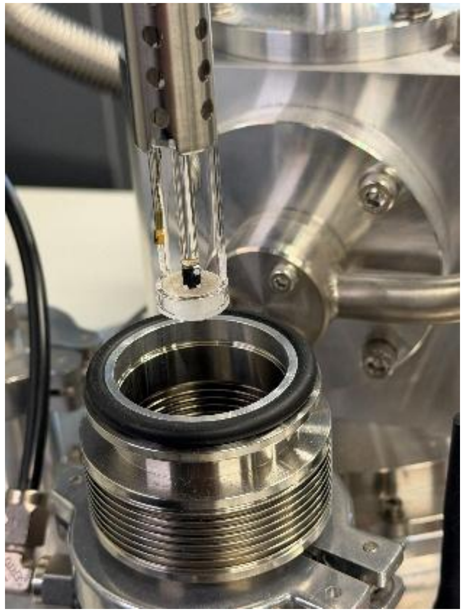
CTE - Influence of short carbon fiber

- The CTE of neat PA12 decreases almost linearly with decreasing temperature
- Short-fiber reinforcement leads to pronounced anisotropic thermal expansion behavior rather than a uniform CTE reduction
- In the fiber-dominated Y/Z directions, the CTE is strongly reduced, indicating constrained matrix expansion
- In the transverse X-direction, higher CTE values are attributed to strain redistribution and possible relaxation of processing-induced residual stresses.



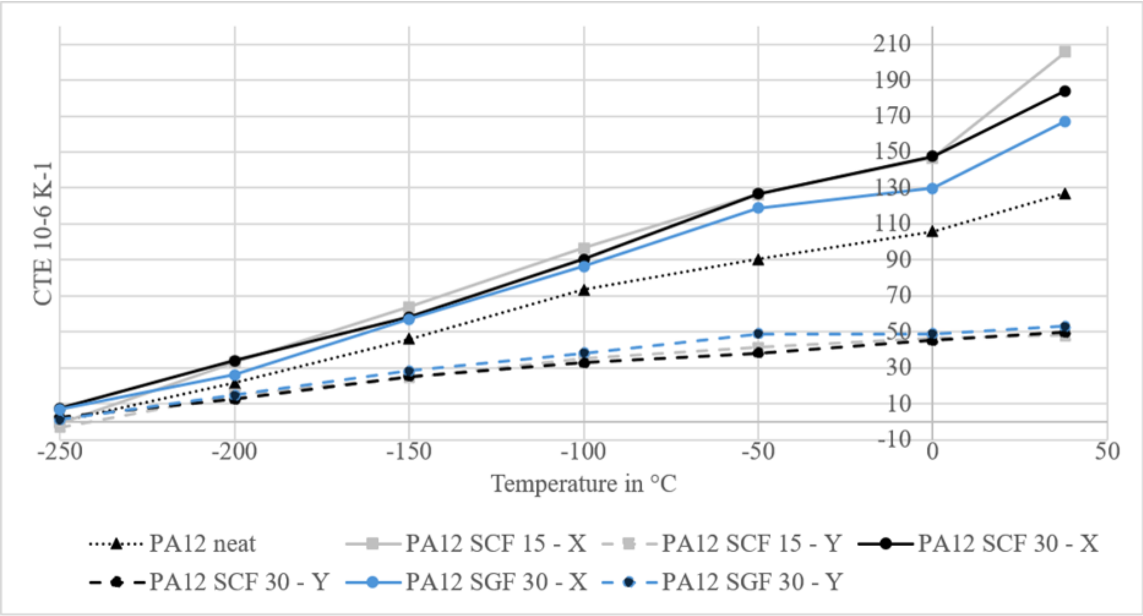
µCT Querschnitt PA12 SCF 20

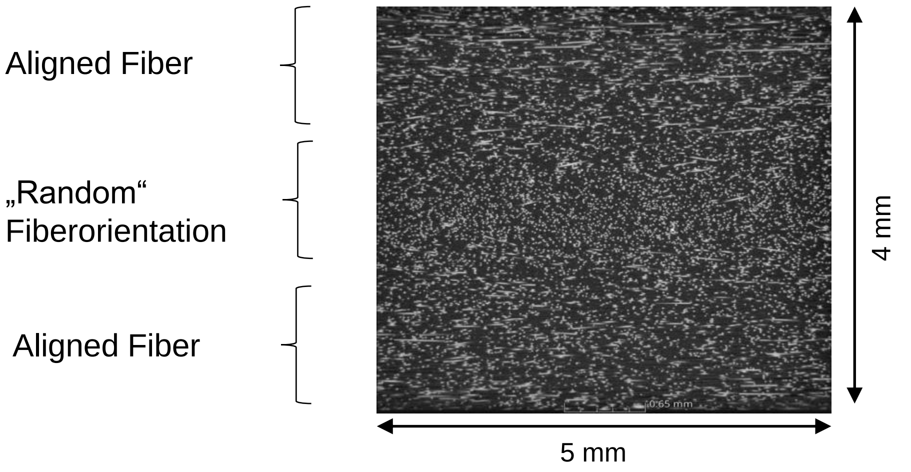




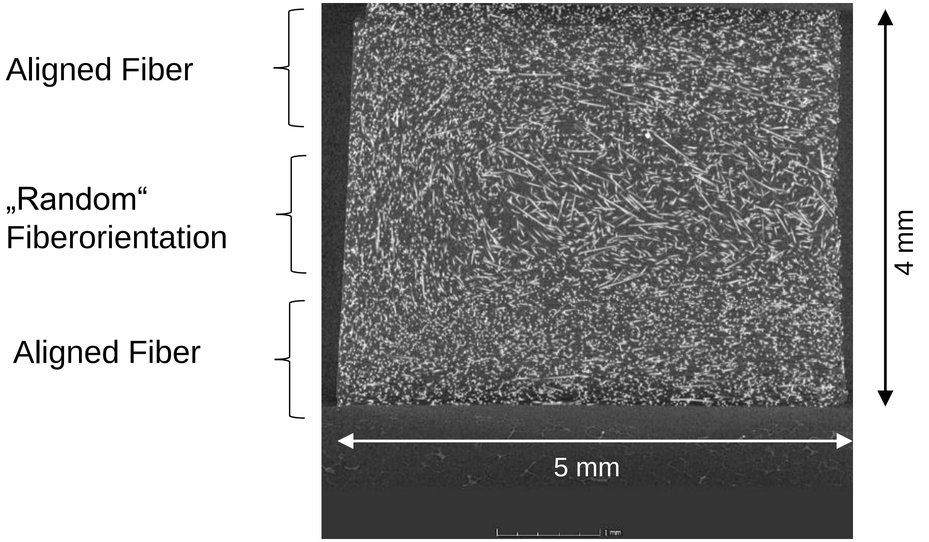
CTE - Influence of short glass fiber

- SGF 30 shows the same anisotropic CTE trend as SCF compounds
- CTE decreases with decreasing temperature in both directions
- Lower X-directional CTE for SGF 30 is attributed to lower fiber stiffness compared with SCF
- Directional CTE behavior is mainly controlled by fiber orientation, stiffness, and matrix constraint





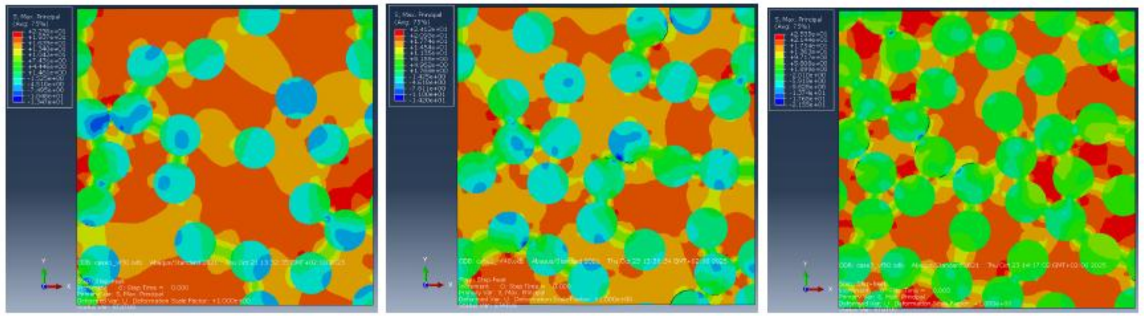
µCT PA12 SCF 30



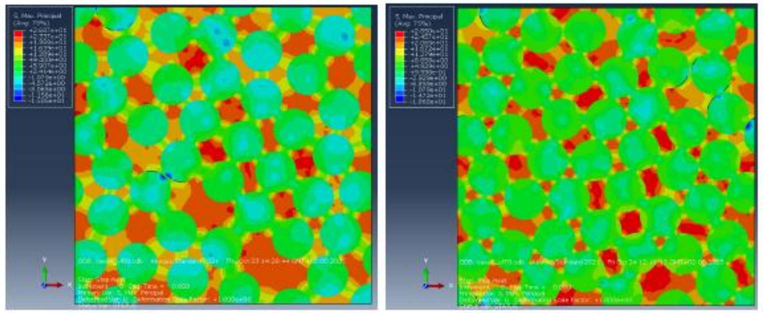
µCT PA12 SGF30

Simulation

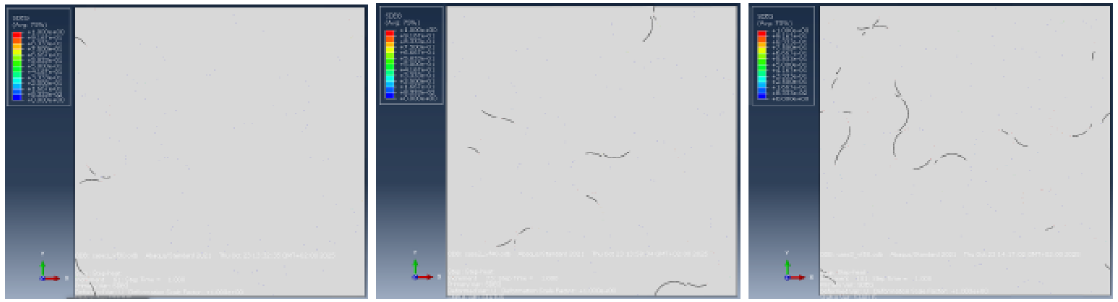
Influence of Fiber Volume Content



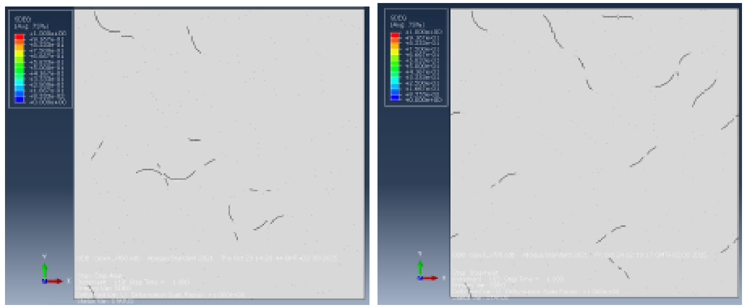
(a) fvf30% (b) fvf40% (c) fvf50%



(d) fvf60% (e) fvf70%



(a) fvf30% (b) fvf40% (c) fvf50%



(d) fvf60% (e) fvf70%

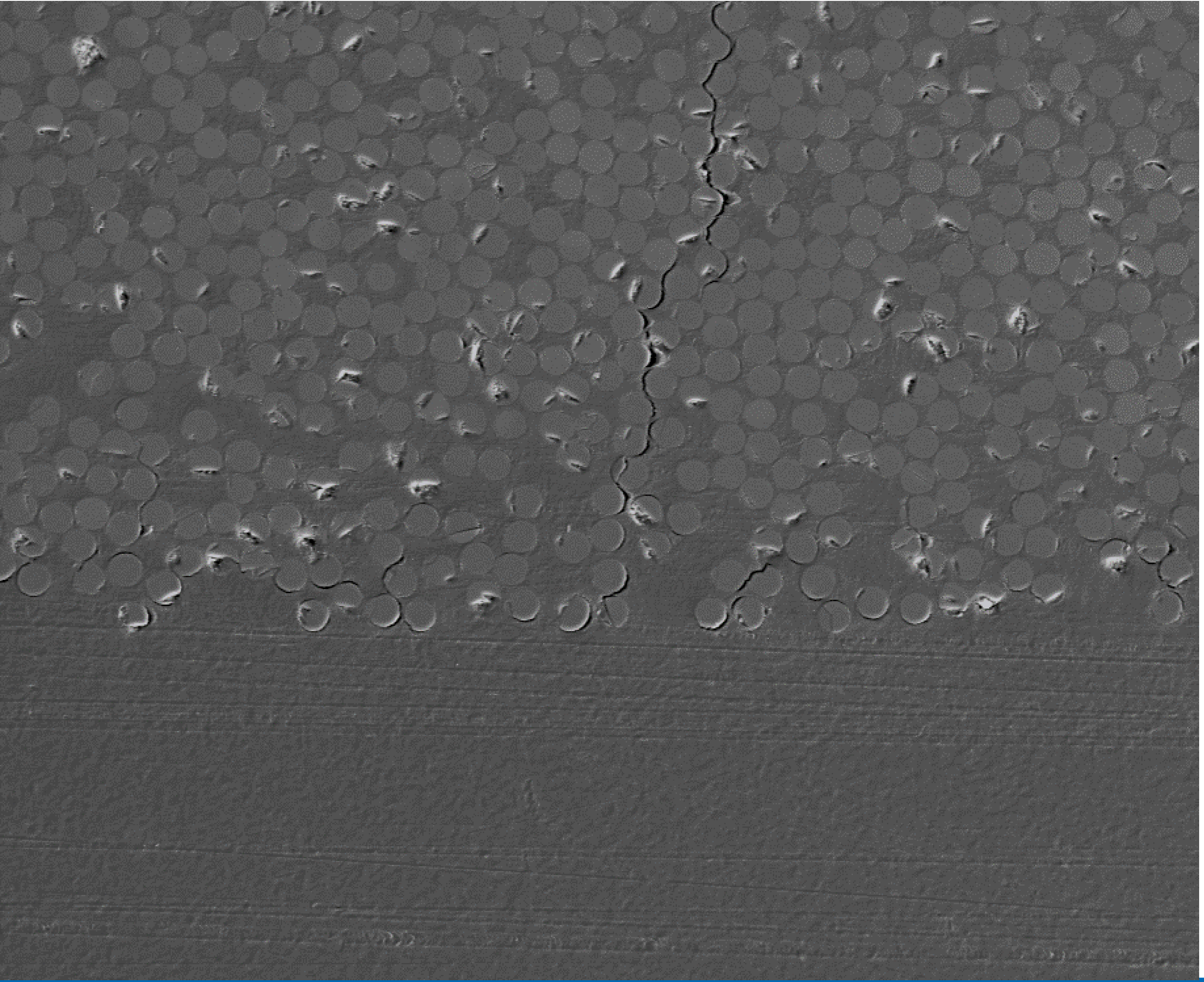
- Fiber volume fraction (Vf) influences the magnitude of stresses in the matrix
- This results in more debonding between fiber and matrix

➡ Transfer/application to short-fiber-reinforced material

Conclusion and next steps

- Short Fiber reinforced PA12 has high potential as permeability barrier for hydrogen storage
- Fiber-Matrix Interface is a key parameter to be investigated more deeply for cryogenic application
- Effective CTE decreases by adding SCF
  - Could be benefitial in a PA12 cfrp laminate to increase crack resistance

- **Next steps**
  - Further investigation of scf and gsf in a crossply CFRP Laminate regarding
    - Permeability behaviour
    - As barrier in a PA12 interlayer
    - Crack resistance
    - Cryo mechanical performance
  - Improve and replicate permeabilty test cells for parallel measurement



Patrick Nowakowski, MSc.

Faserinstitut Bremen e.V.
nowakowski@faserinstitut.de
www.faserinstitut.de

Thank you!