ComCarbon® technology
Melt spinning of a new class of PAN copolymers for carbon fibers

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Fraunhofer
IAP

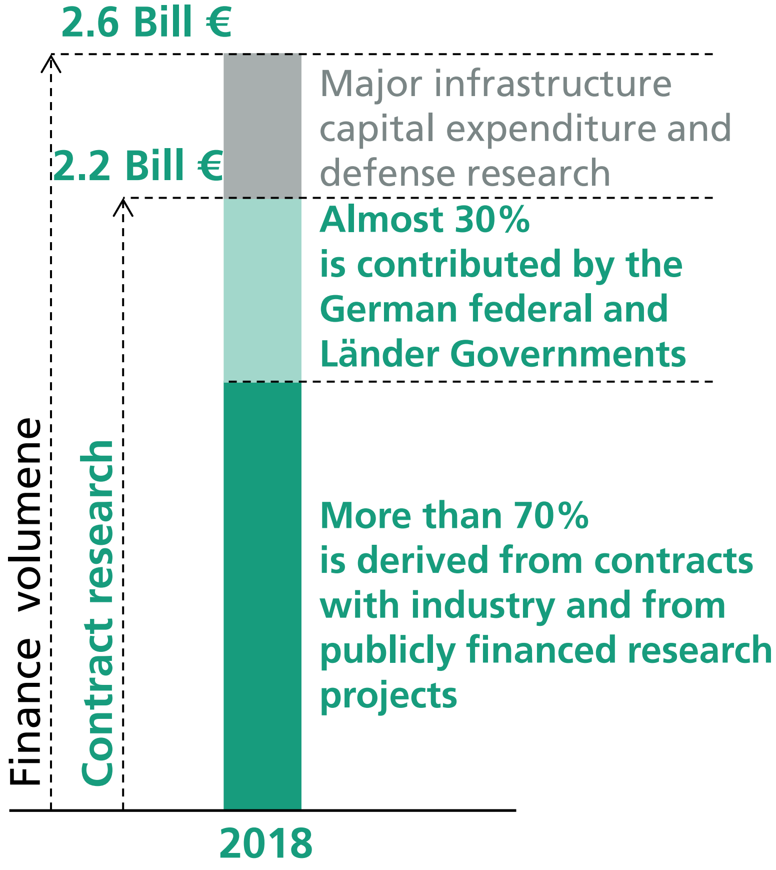
The Fraunhofer-Gesellschaft at a Glance

Largest applied research organization in Europe

The Fraunhofer-Gesellschaft undertakes applied research of direct utility to private and public enterprise and of wide benefit to society

26,600 staff

72 instituts and research units



Fraunhofer IAP

Fraunhofer Institute for Applied Polymer Research – IAP

Potsdam

Biopolymers

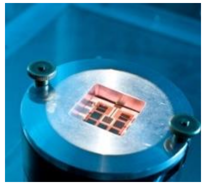
Prof. Dr. Johannes Ganster

biopolymers (cellulose, starch, lignin), biobased plastic, blends, composites, fibers, films, nonwovens, injection molded parts

Life Science and Bioprocesses

Prof. Dr. Alexander Böker

keratin fibers, protein conjugates, biotechnological processes, self-assembly techniques, “smart“ materials for medical applications



Center for Applied Nanotechnology CAN

Prof. Dr. Horst Weller

quantum materials, nano-medical applications, nanoscale energy and structure elements

Functional Polymer Systems

Dr. Armin Wedel

materials with specific optical and electronic properties, polymeric OLEDs, polymer electronic components, organic solar cells, chromogenic materials

Pilot Plant Center PAZ

Prof. Dr.-Ing. Michael Bartke

polymer synthesis and processing, scale-up to ton scale

- 248 employees (Status 12 | 2018)
- 2018: € 22.5 million institute‘s budget
  € 15.9 million external revenues
- research sites: **Potsdam**
  Hamburg
  Schkopau
  Schwarzheide
  Teltow
  Wildau

Synthesis and Polymer Technology

Dr. Thorsten Pretsch

polymer synthesis and process development, microencapsulation, membranes and functional films, shape-memory polymers

Polymeric Materials and Composites PYCO

Prof. Dr. Christian Dreyer

thermoset resins for applications in lightweight construction and micro- and optoelectronics

Carbon Fiber Competencies at Fraunhofer IAP

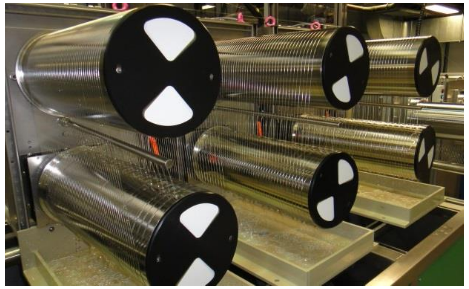
Raw materials → Spinning → Stabilization → Carbonization

Raw materials
- PAN-Co-polymers, synthesis, Analyzes
- Cellulose, Cell.-derivatives
- Lignin, Lignin derivatives

Spinning
- Dry
- Wet
- Air-gap
- Melt

Stabilization
- Fiber tension controlled
- Structural change
- Regime development
- Optimization

Carbonization
- Contineous filament transportation
- Fiber tension controlled
- Oven up tp 2900 °C



Structure-Property-Relations

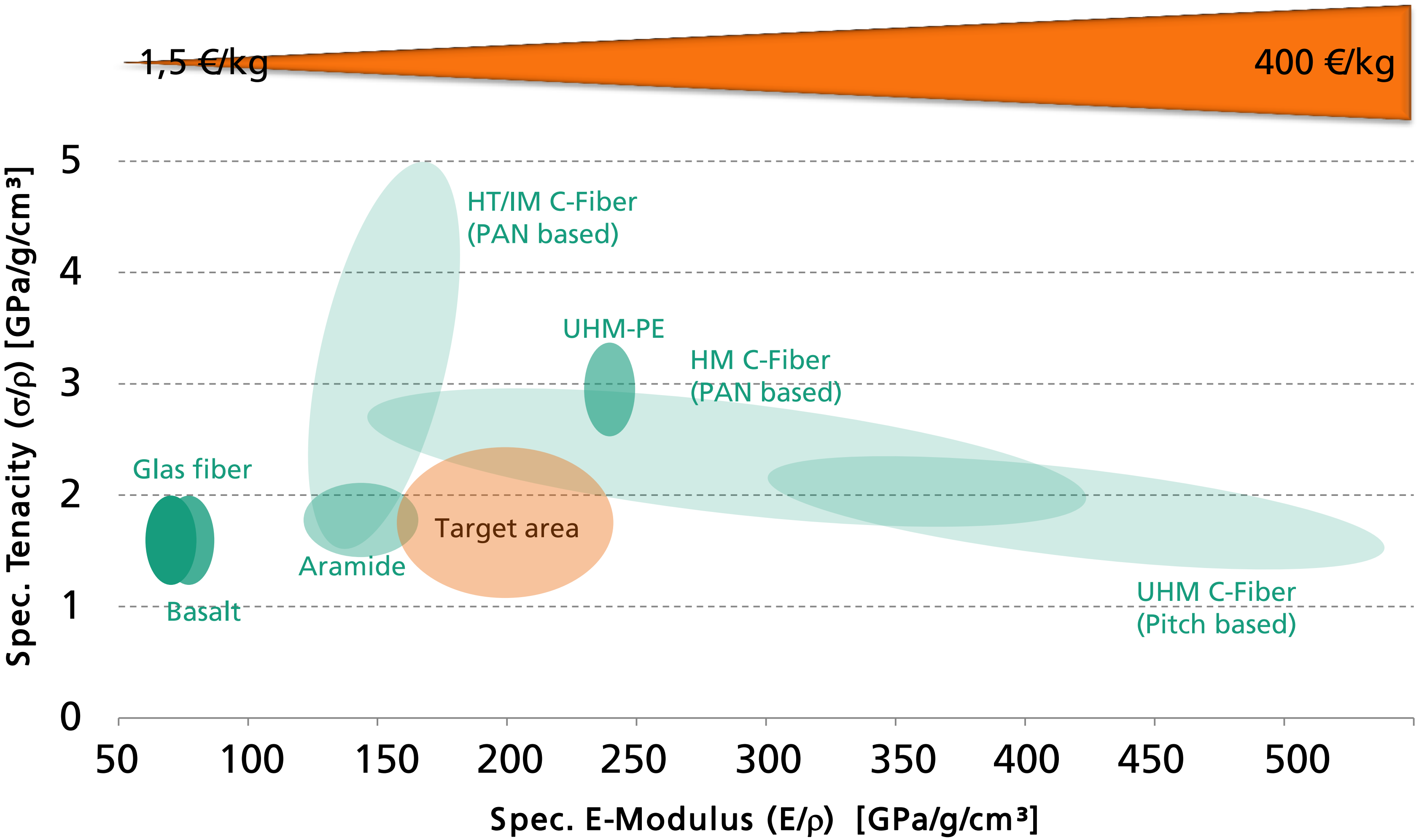
- Moleculare structure
- Spinning solution properties
- Melt behavior
- Solid state structure (NMR, EM, X-ray)

- Mechanical fiber properties
- Testing of model composites

ComCarbon – Commodity Carbon fibers
Project info

- Acronym: ComCarbon – Commodity Carbon fibers (mid tech – mid price) for mass markets
- Funding by Fraunhofer 3.6 Million Euros
- Departments involved:
  »Polymer synthesis«, »Fiber technology« and »Materials development and structure characterization« of Fraunhofer IAP
- IP owner: Fraunhofer Society

Fibers for composites



pictures: Uni Stuttgart ILEK, www.pegasus.com, www.auto-medienportal.net

Cost reduction potential by melt spinning

Melt spinning vs. solution spinning – PAN

	Wet spinning	Melt spinning
Dope	20 % PAN in DMAc	100 % PAN
Hole number	16x3k	16x3k
Spinning positions	16	16
Final titer single filament	1 dtex	1 dtex
Throughput spinning mass	6 m³/d	6.4 m³/d
Spinning speed	180 m/min	1000 m/min
Outcome fiber mass	1.2 t/d	7.5 t/d => Factor 6!

Precursor accounts for 50 % of the CF cost

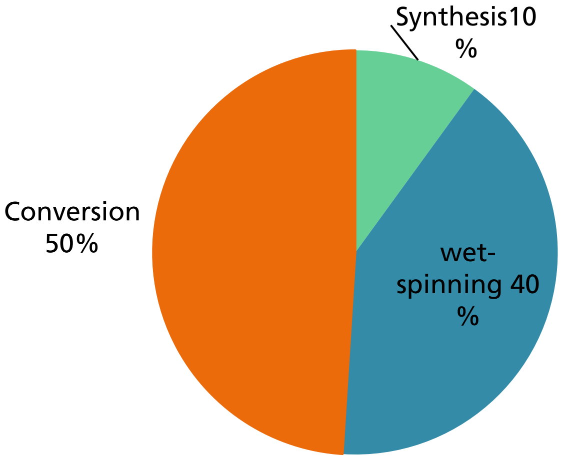
	Goss (1986)	Cohn (2001)	Kline (2004)	Harper (2011)	Trütz-schler (2012)	Das (2012)	This paper (2013)
Precursor	34%	47%	51%	31%	51%	54%	54%
Pretreatment	3%			69%	49%	6%	1%
Stabilization	20%	16%	16%			13%	12%
Carbonization	23%	26%	23%			8%	21%
Surface treatm.	4%	2%	4%			3%	4%
Sizing	7%	2%				4%	4%
Winding	5%	3%	6%			9%	4%
Other	4%	4%	0%			3%	0%

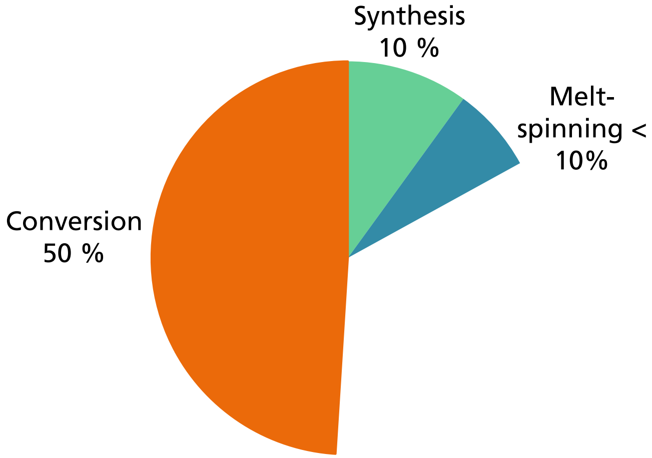
Source: T. Ellringmann, et al. Textile Research Journal. **86** (2015) ,178-190

Cost reduction potential by melt spinning

Melt spinning vs. solution spinning – PAN

Assuming melt spinning reduction factor of 4 (conversion the same)



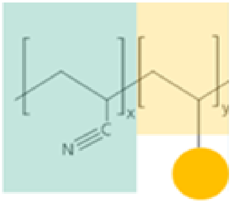


Final CF price reduction of **> 30 %** should be possible
(e.g. 15 to 10 €/kg)

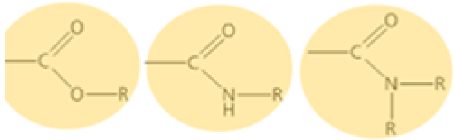
New approach by IAP: Melt spinnable PAN-Copolymers

Challenge: Weakening the nitrile interaction

Internal plasticizing



Alkyl derivative of acrylic acid or acryl amide

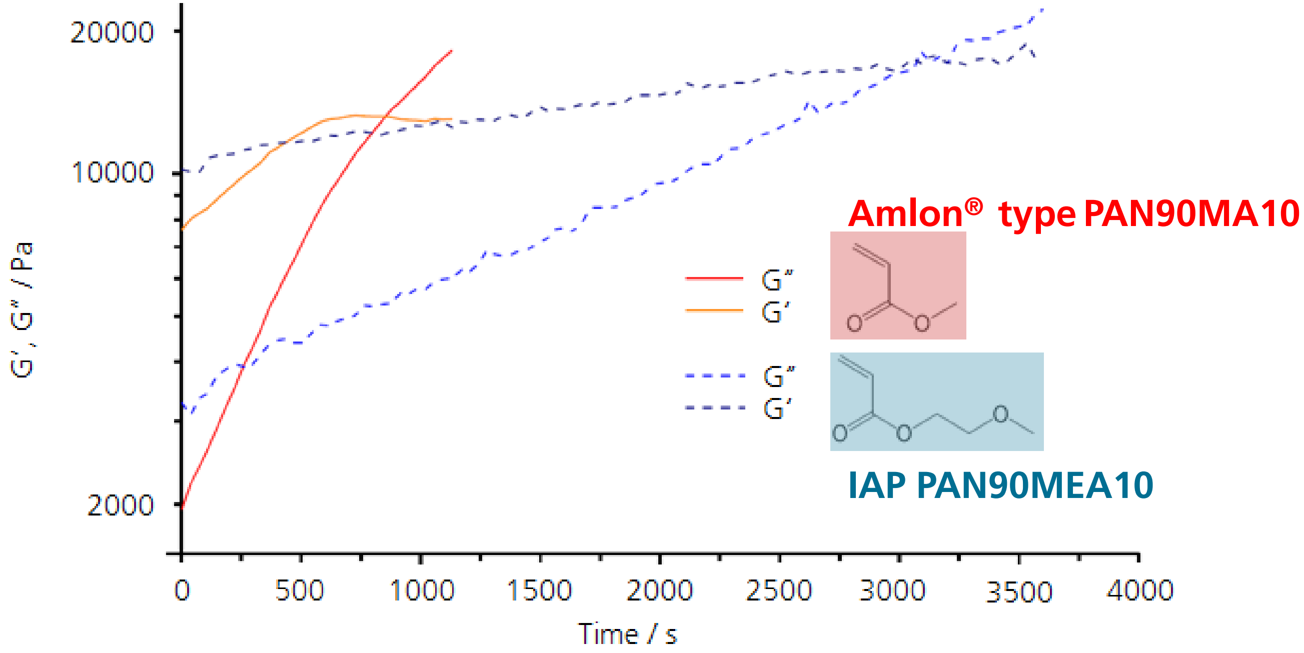


Target parameters

- meltable copolymer with comonomer of ≤ 10mol%
- sufficient thermal stability for melt spinning without thermal degradation

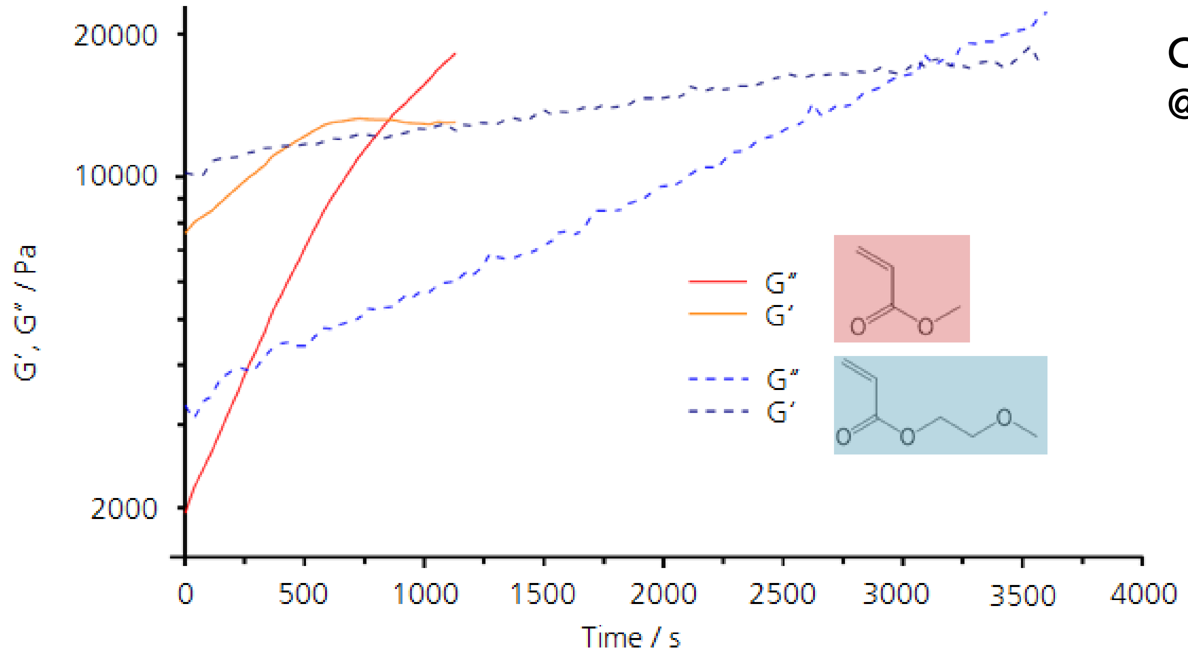
→ t_{cross} (G'=G") > 30min

- Systematic screening of comonomers with regard to the effect of polarity and different funtional groups
- Resulted in the identification of a suitable class of comonomers → alkoxy acrylates



Challenge: Weakening the nitrile interaction

- Systematic screening of comonomers with regard to the effect of polarity and different funtional groups
- Resulted in the identification of a suitable class of comonomers → alkoxy acrylates
- largely improved thermal stability



Copolymers with 10% of comonomer, M_w ca. 35.000g/mol, @235°C

- Amlon® type PAN (PAN90MA10) vs. PAN90MEA10
- Time for Sol-gel transition increased by factor ~4

- PAN90MEA10 synthesized by emulsion polymerization developed by Fraunhofer IAP

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Precursor
Melt spinning

Melt-spinning of PAN90MEA10

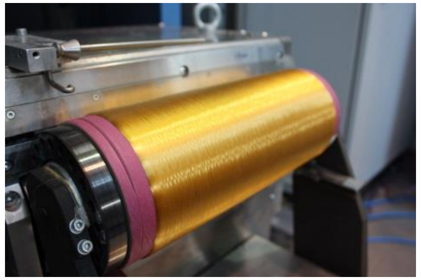
- Spinning speed: 200 – 1000 m/min
- $T_{Spinning}$: 215 °C – 230 °C

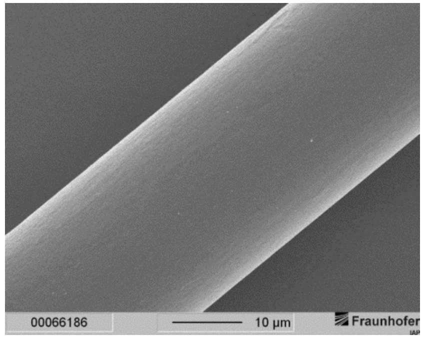
Textile-physical values

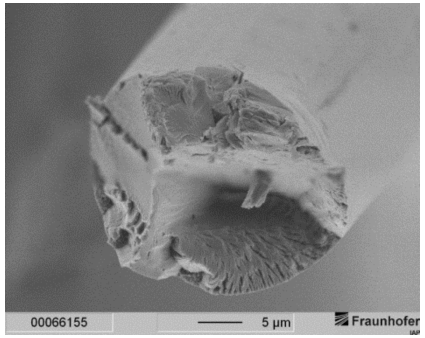
- Titer: 1.8 – 7.0 dtex
- Tenacity: 10 – 40 cN/tex
- E-Modulus: 350 – 900 cN/tex
- Elongation: 9 – 20 %

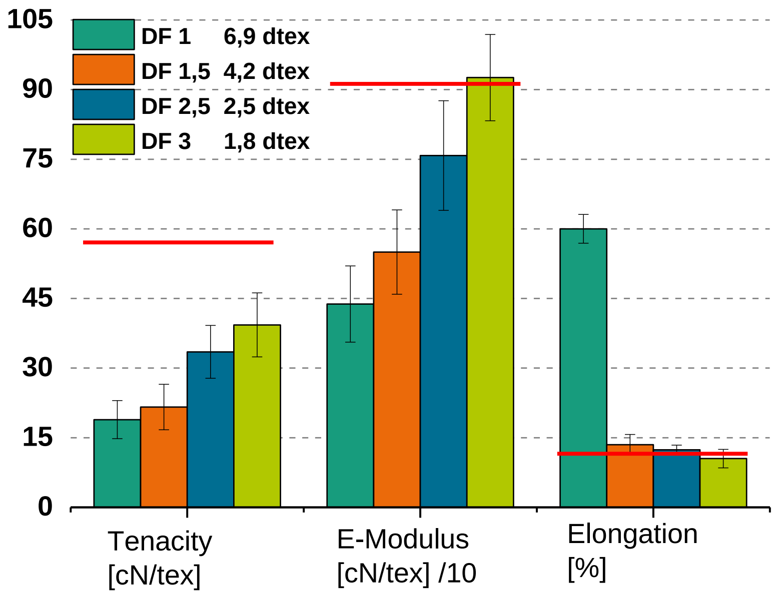
Structural parameters

- Round cross-section
- Compact structure
- Degree of orientation $OG_{(100)}$: 0.8 – 0.9









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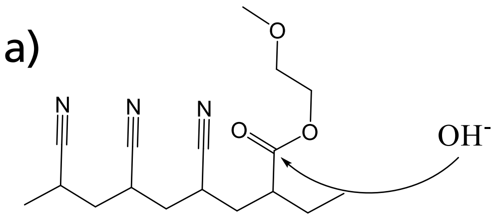
Precursor – Pre-stabilization

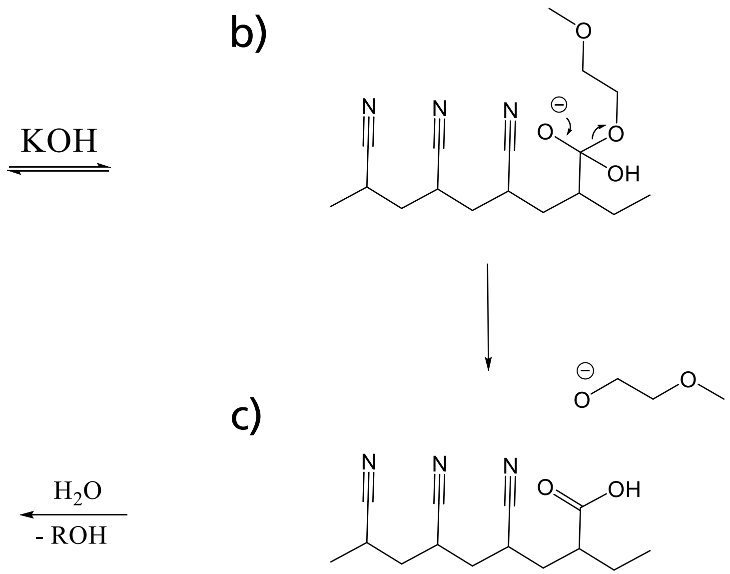
Splitting-off the internal plasticizer by wet chemistry

a)



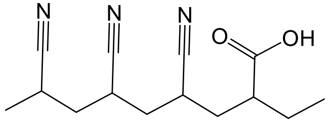
PAN with internal plasticizer (MEA)

b)

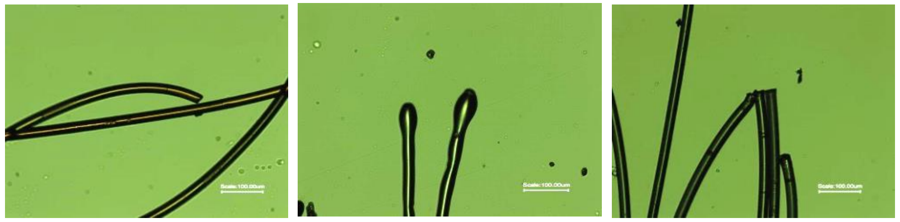


c)

d)



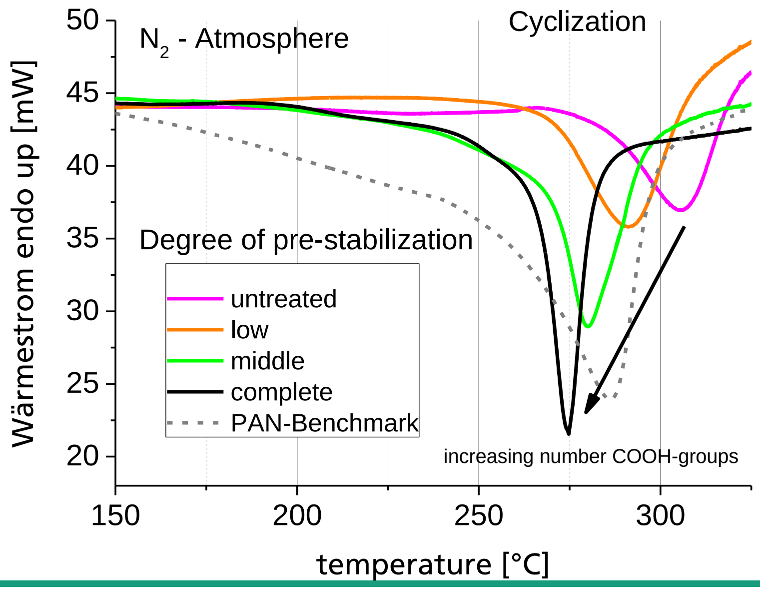
PAN without internal plasticizer



MEA G3 180 °C

MEA G3 250 °C

MEA G3 250 °C, 40s pre-stabilized



Treatment of melt-spun filament yarn with solution made of H_2O/DMSO (for accessibility) + KOH (for splitt-off)

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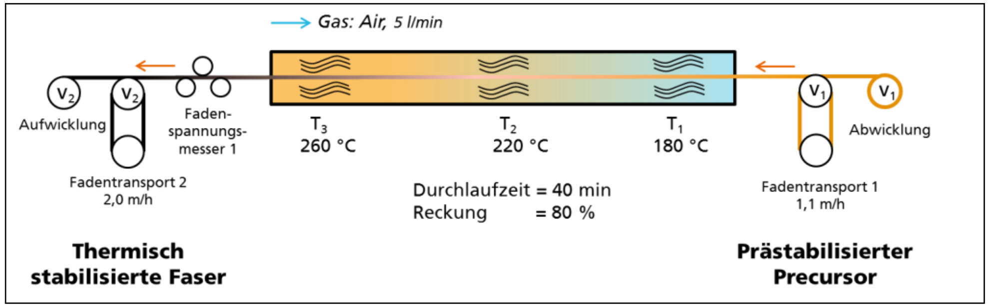
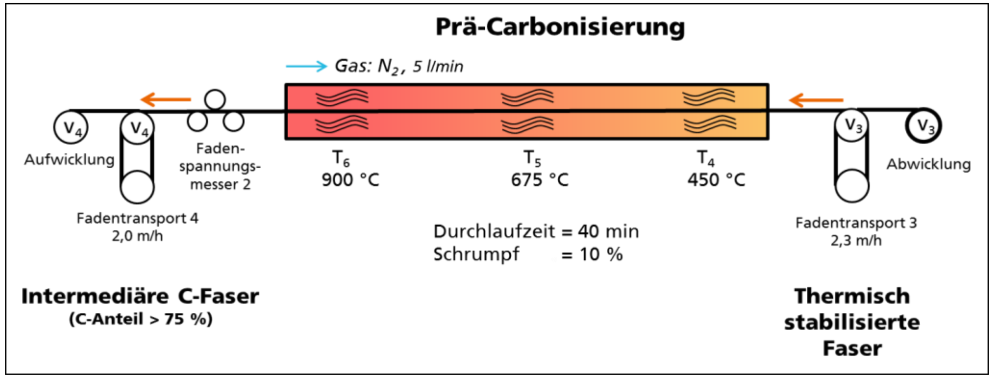
Conversion



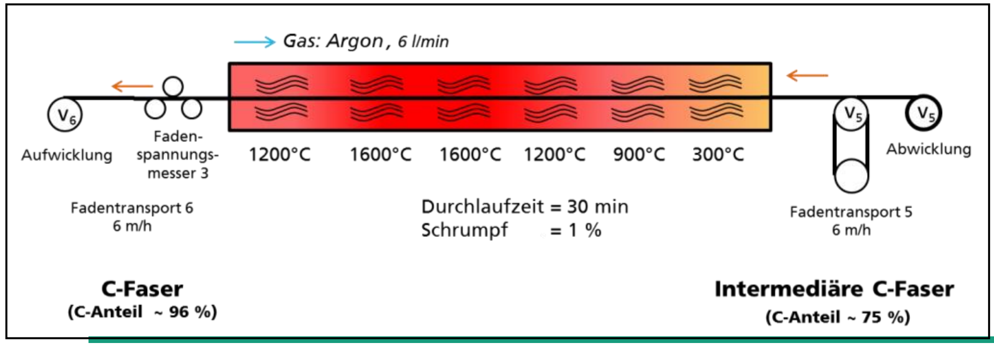
Stabilization

- Temperature: 180, 200, 210, 220, 230, 240, 250, 260, 280 °C
- Residence time: 15, 20, 30, 35, 40, 45, 60 min
- Drawing: 0, 30, 50, 80, 100 %
- Gas flow: 2, 5, 10 l/min, (Air, N_2 , Air/N_2)



Pre-Carbonization

- Carbon content ~76 mass-%
- Mass loss ~ 40 % (H_2, N_2, CH_4, CO, HCN, CO_2, H_2O, NH_3)
- Heating rate ≤ 15 K/min
- Shrinkage ~ 10 %



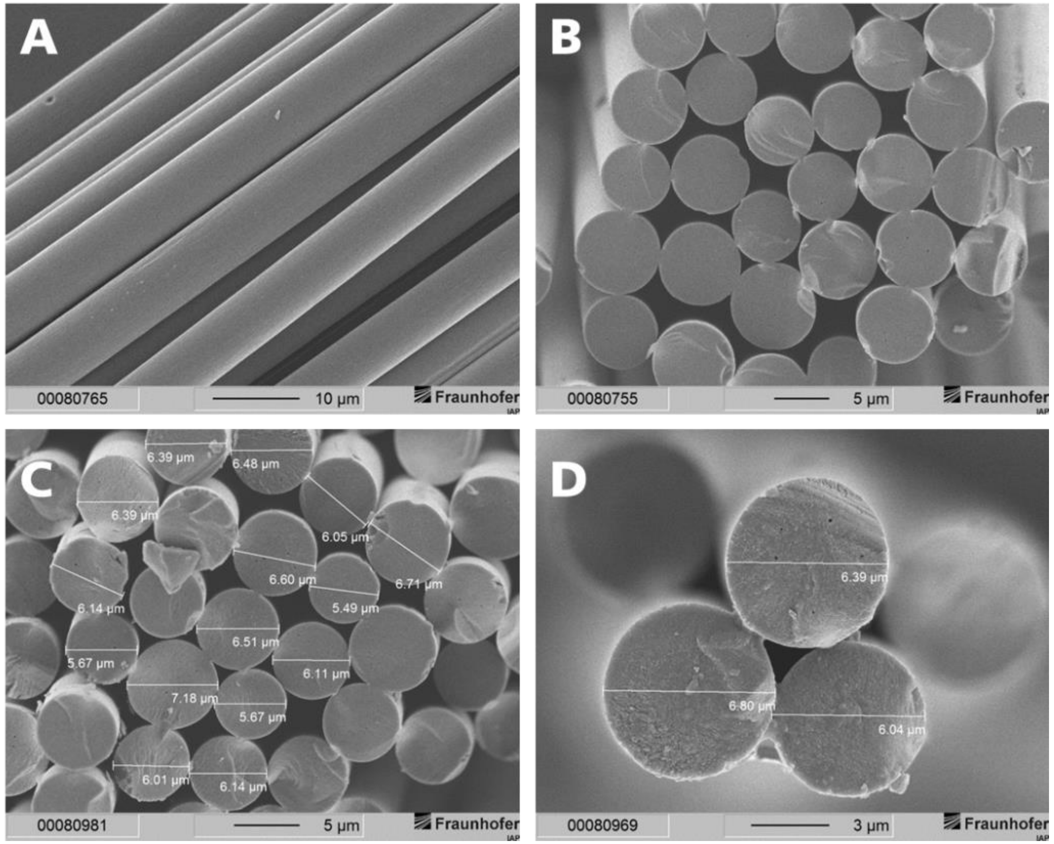
Carbonization

- Carbon content ~ 96 mass-%
- Heating rate up to 100 K/min tested

Structure and properties of carbonized fibers

Morphological characterization

- Fiber cross section
  → ideal round
  → no voids
  → smooth cross section area
- Surface
  → in general smooth
  → fibers partially stick together
- Average single filament diameter
  → 6.4 +/- 0.4 µm



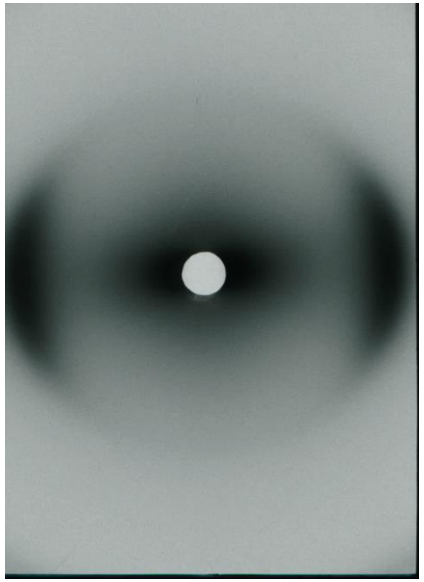
Structure and properties of carbonized fibers

Morphological characterization

- Graphitic structure
- High graphitic content
- Highly oriented structure $OG_{(002)} = 0.7$

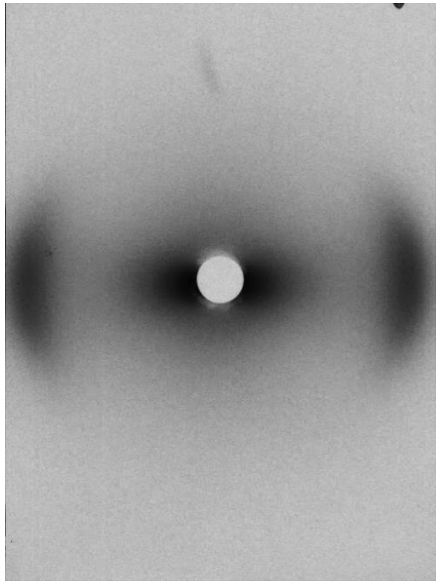
Precursor	E-Modulus [GPa]	Tenacity [MPa]	Elongation [%]
MEA G3.2	170 ± 10	1400 ± 100	0.7 ± 0.1
MEA G9	143 ± 16	1630 ± 185	1.1 ± 0.2
PAN (Tenax E, HTA 5131)	220 ± 12	3600 ± 700	1.5 ± 0.3

MEA G3.2



$OG_{(002)} = 0.70$

PAN benchmark



$OG_{(002)} = 0.77$

Degree of orientation

What has been achieved

- Evaluation and synthesis of new PAN-copolymer class
  - Synthesis by emulsion polymerization in kg-scale
  - Max. 10 mol% comonomer
  - Enables thermoplastic behavior with high melt stability and finally good carbon fiber properties
- Contineous melt spinning
  - Reaching 1000 m/min spinning speed
  - High degree of orientation accessable
  - Fineness and textile-physical properties similar to wet-spun precursor
- Continuous Conversion
  - Pre-stabilization to reach unmeltable stage
  - Stabilization and carbonization regime similar to wet-spun precursor

What needs to be improved/solved

- Pre-stabilization by wet-chemistry no economic way to reach unmeltable state
  - Combination of external and internal plasticizer?
- Achieved carbon fiber properties need further improvement
  - Increasing degree of orientation in precursors
  - Spinning oil
  - Optimizing molecular weight

Thank you for your kind attention

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