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Carbon Fiber – From an Industrial Developer's Viewpoint

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Outline

- **Carbon material research**
- **How we think about carbon fiber**
- **What is the thinking of other material developers?**
- **Opportunities and areas for development**

Materials – carbon – research: who is doing what?

What is the primary focus?

- **R&D activities of the following:**
  - Academic research
    - New material forms
    - Property measurement
    - Explaining phenomena (both old and new) associated with materials or processes
  - Government research
    - Property measurement
    - Process/application development
  - Industrial research
    - Process development
    - Perturbations on known materials
    - Application development

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Carbon Research

- **Examples:**
  - Academic research
    - Examples of new material forms
      - Buckyball
      - CNT of all types
      - Graphene
    - Property measurement
      - CNT chirality correlating with electronic properties
    - Explaining phenomena
      - Extension of BCS to superconducting C_{60} compounds
      - Mechanistic understanding of formation of various carbon structures

Carbon Research

- **Examples:**
  - Government research
    - Property measurement
      - NIAR standard house for allowables
      - Specialized coherent light sources
    - Process development
      - Renewal and expansion of lignin-based low-cost carbon fiber research
      - Accelerated processing in carbon fiber
    - Application development for military platforms

Carbon Research

- **What is available?**
  - Bonding arrangements
    - sp^2 self-associated
      - Graphite
      - Nested kinked-graphite structures
      - MWCNT
        - Compact structures: SWNT & Buckyball (C_{60}, C_{70}, etc)
    - sp^2 stabilized via dispersive interactions
      - Graphene
      - Graphene oxide (chemically "stabilized")
    - sp^3 diamond [cubic and hexagonal diamond structures]
    - sp^3 network
      - Polycarbyne structures [Bianconi]
      - Diamond-like carbon (DLC)

Carbon Research

- **What is available?**
  - Elaborated forms
    - sp^2 Filamentous
      - Pitch fiber
      - PAN-based fiber
      - Yarns/webs
        - From CNT via spinning or electrospinning
    - sp^2 film
      - Graphene [Ruoff UT Austin]
    - sp^3 diamond/DLC film
      - Via CVD or thermal decomposition of polycarbyne
      - Plasma deposition
    - sp^3 diamond filamentous is known but in limited lengths (few hundred microns) by CVD

How we think about carbon fiber

Carbon Fiber Precursors

Carbon-rich materials (rearrangement approach)

Pitch

Cokes

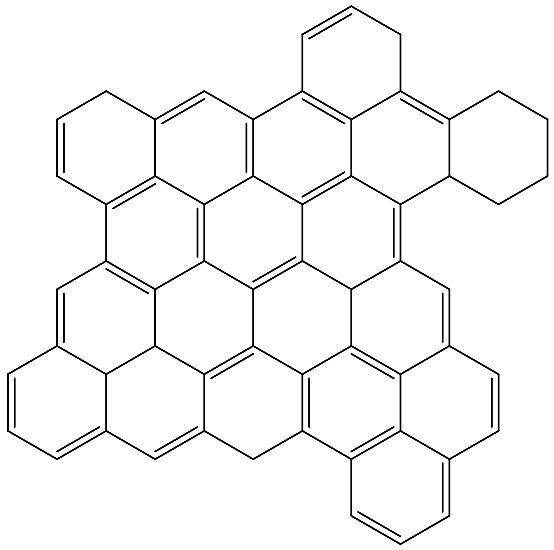
Coal-derived materials

Carbon-poor materials (Aufbau approach)

Rayon

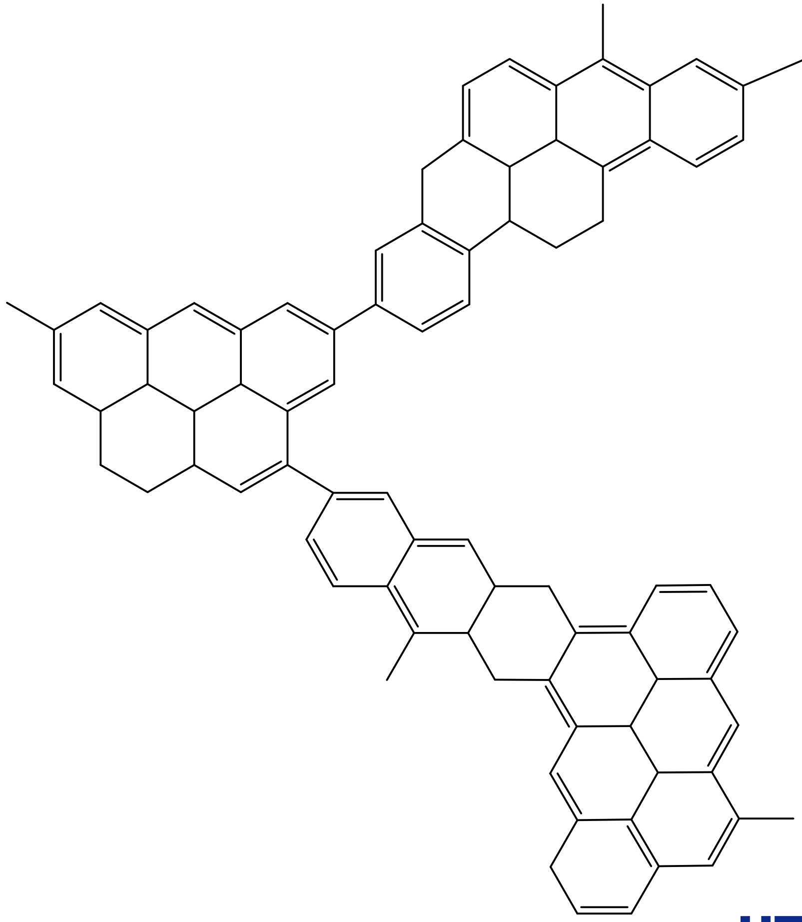
PAN

Carbon-Rich Materials



Model of Coal Pitch

Model of Petroleum Coke

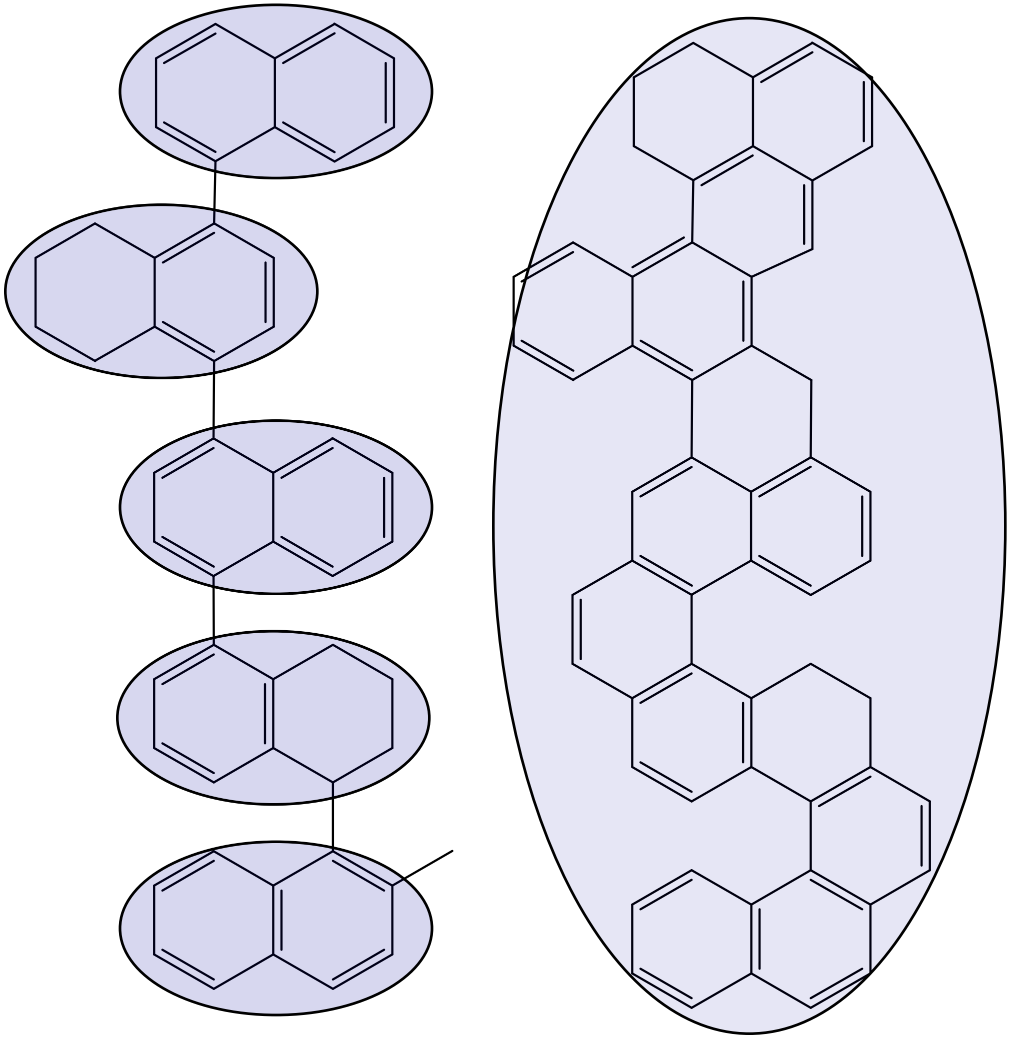


Mesophase Materials

Liquid Crystal Structures

Ordered discotic structures

- **Napthalene hydronapthalene**
- **Oxidation-prone moiety for intermolecular crosslinking**



This type of arrangement is designed into synthetic pitch

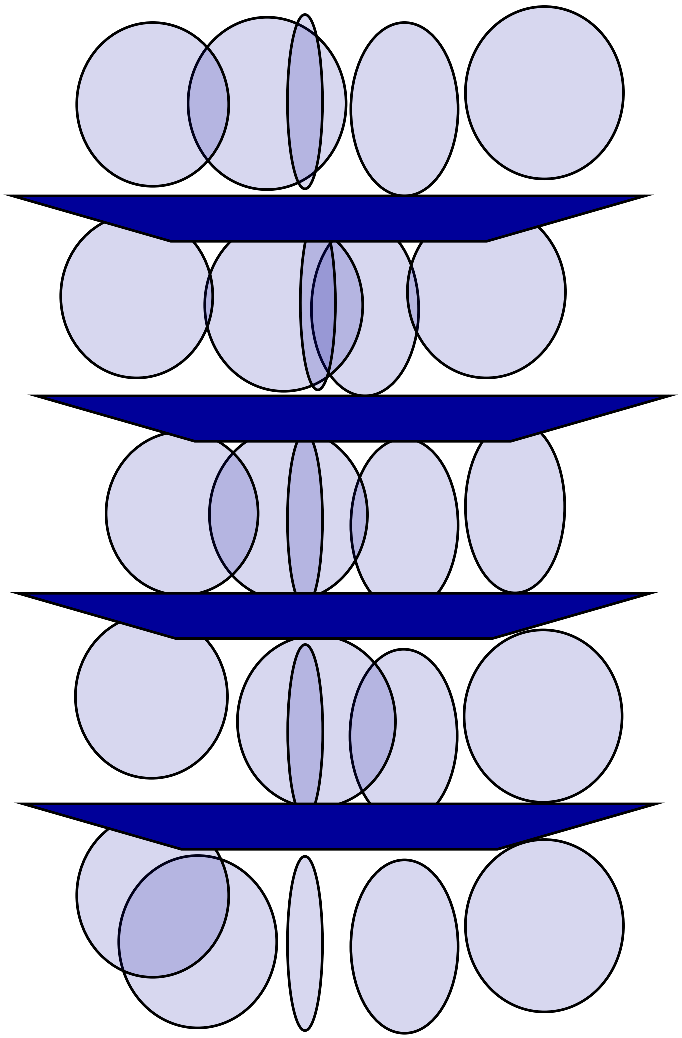
Mesophase Materials

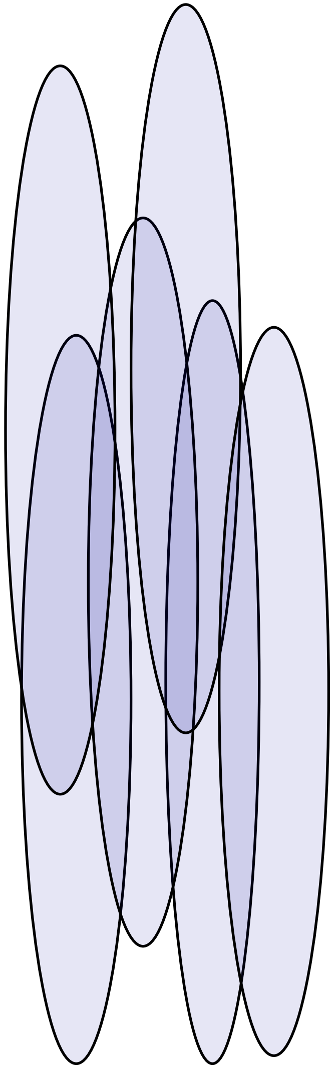
Liquid Crystal Structures

Ordered discotic structures

- **Preamble to graphitic crystallites**

- **Smectic-type structure is shown on left; however, simple nematic interaction (right) is more likely**





Carbon-Poor Materials: PAN

Fiber spinning is less of issue than in carbon-rich materials

Reaction Control Approach

Catalysis

- **Addition of external catalytic species (Rayon)**
- **Intrinsic to polymer: copolymer design (PAN)**

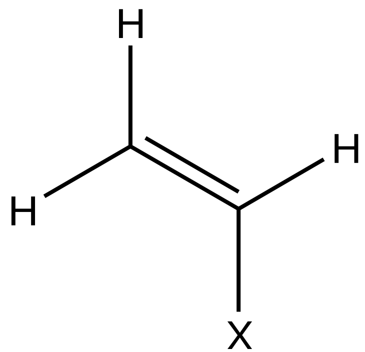
Process conditions

- **Access reaction manifold at the “appropriate” time**

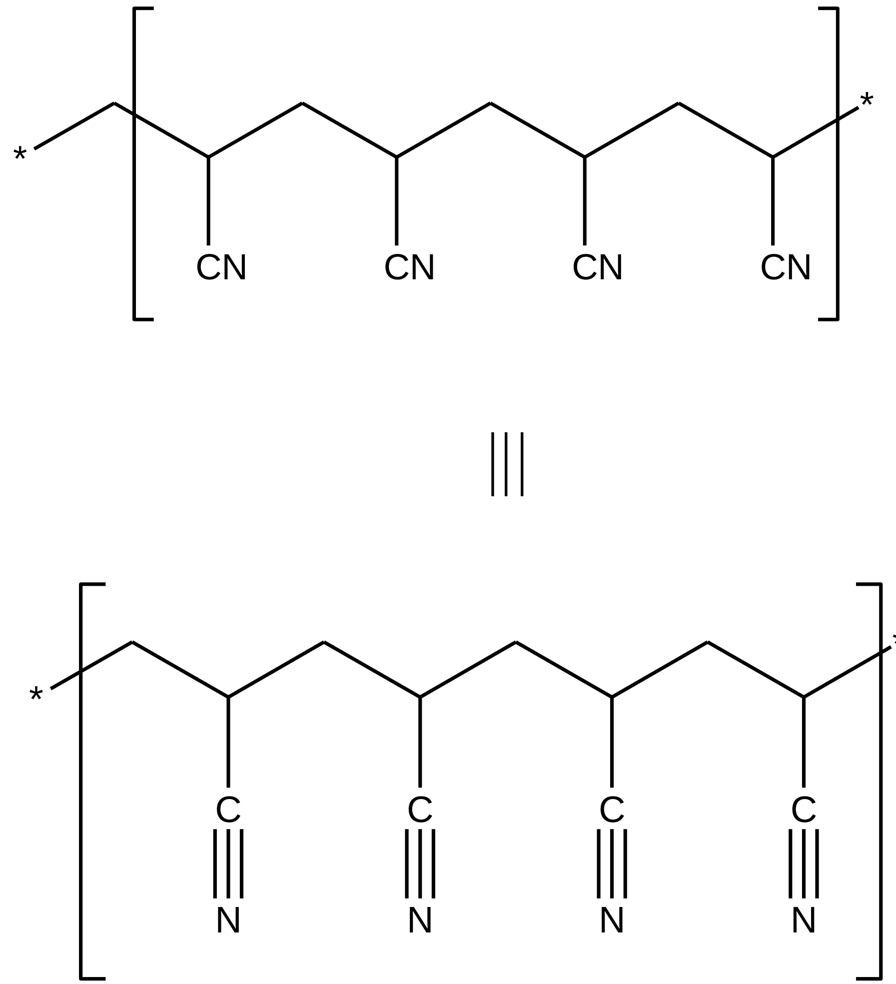
Objective:

Drive total yield while building desired structures

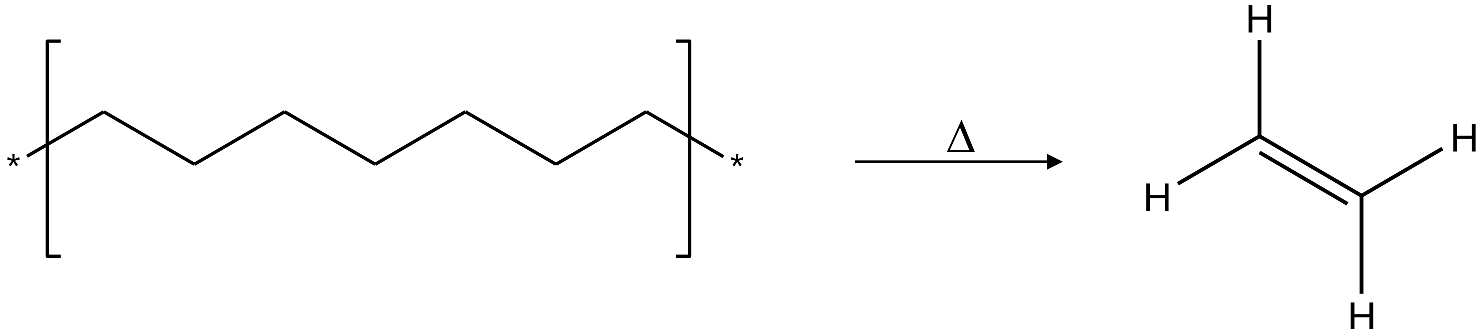
Acrylonitrile Homopolymer



X = CN

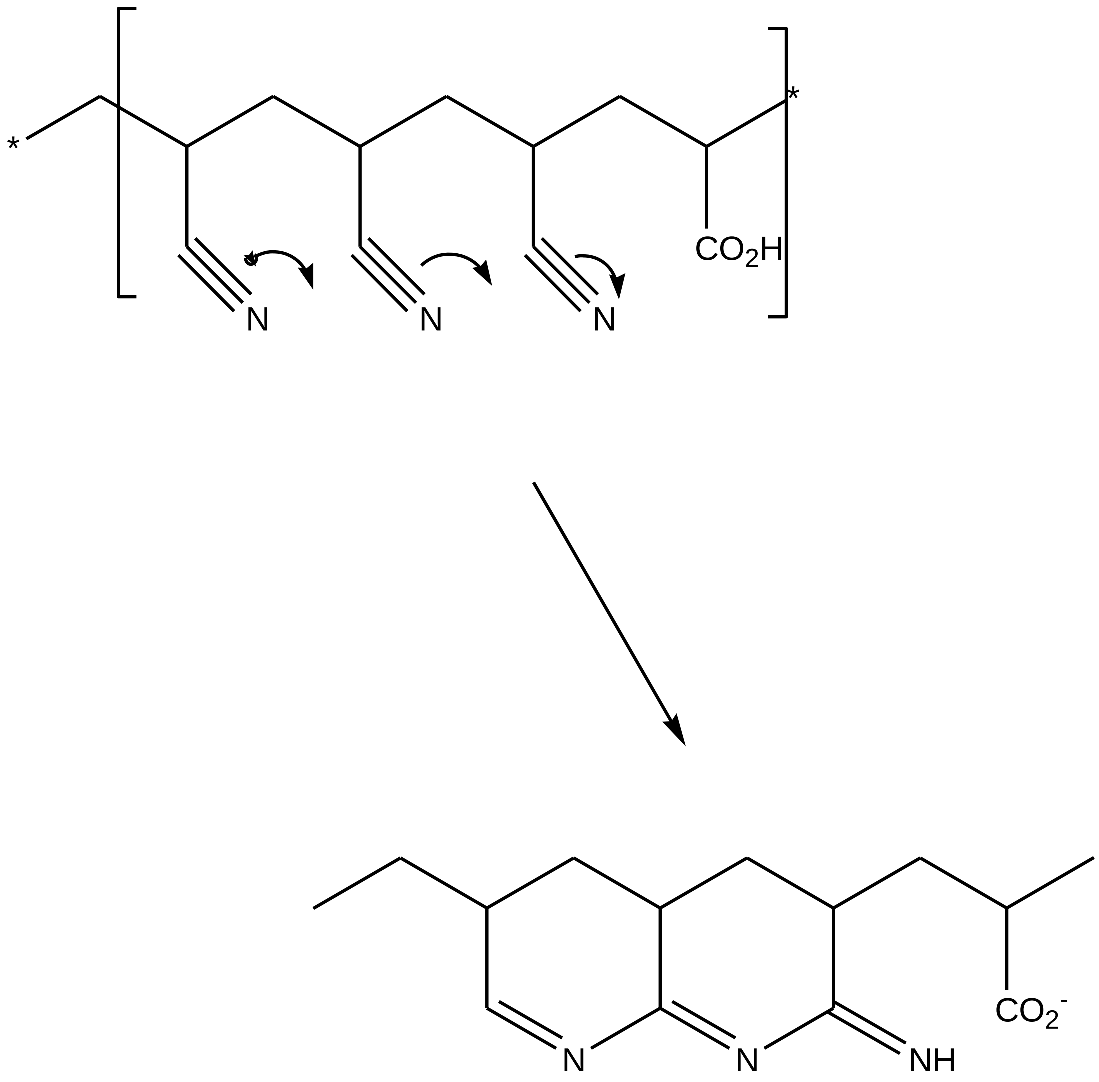


Polyethylene Thermolysis

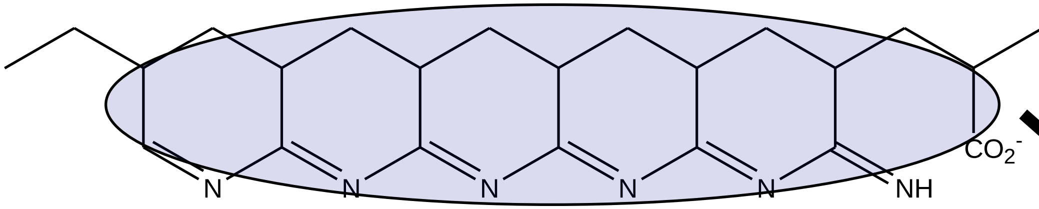


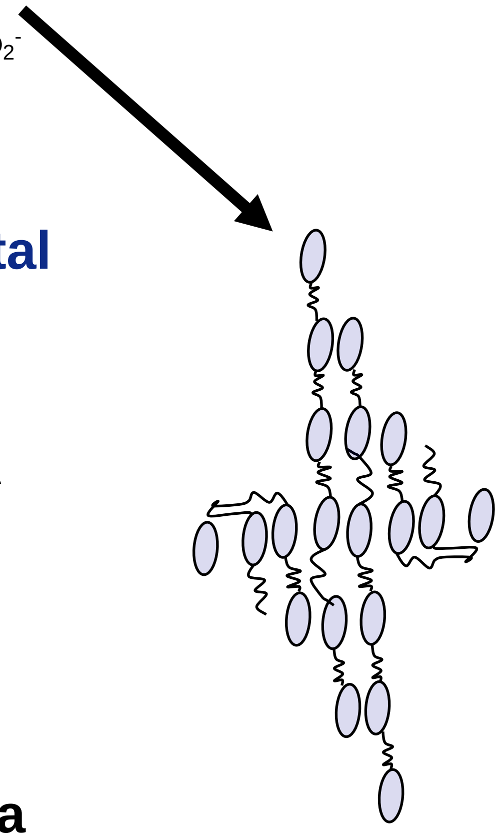
Polyethylene undergoes depolymerization

Polyacrylonitrile Thermolysis



Polyacrylonitrile Thermolysis





Lamellar Mesophase (analogous to Liquid Crystal Structures)

Cyclization reaction with domain size of 13 nm

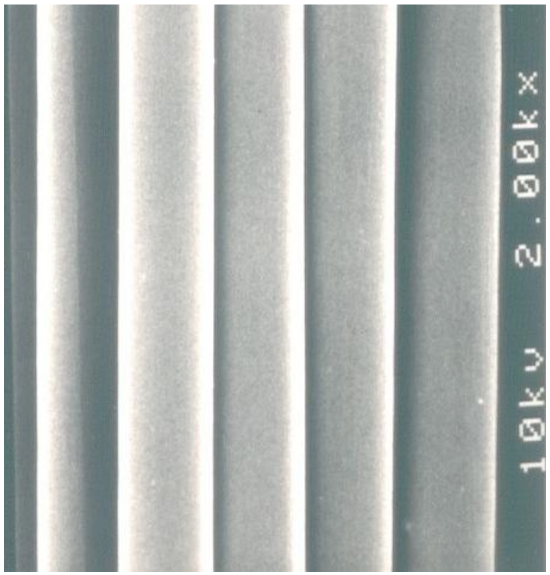
(SAXS data Thuenemann, Ruland *Macromolecules* **2000,** *33*, 2626**)**

Hexcel estimate for above structure is 1.23 nm

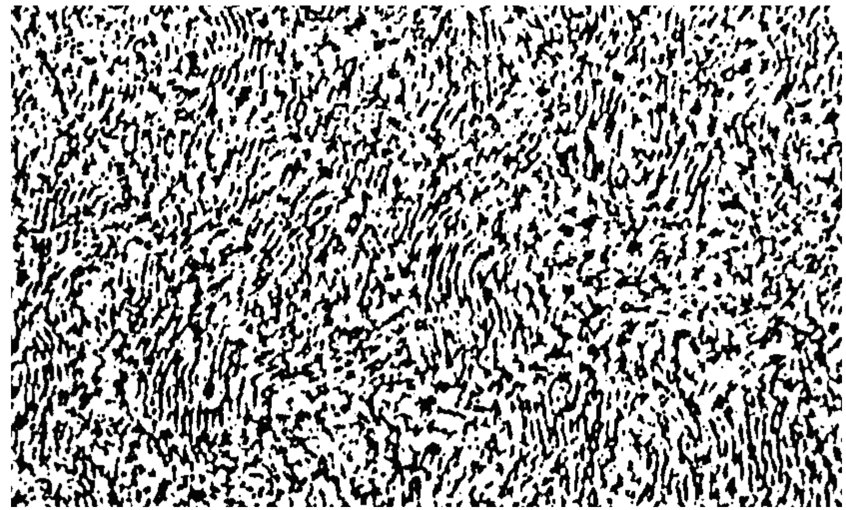
- **Much larger disordered phase between lamella for PAN**

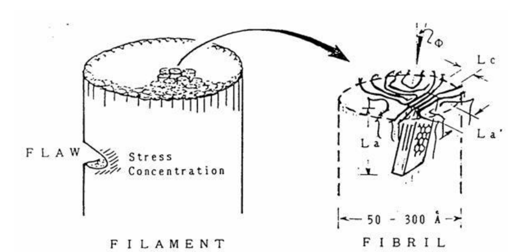
Creation of Carbon Fiber Structures

PAN



“Composite” structure of CF



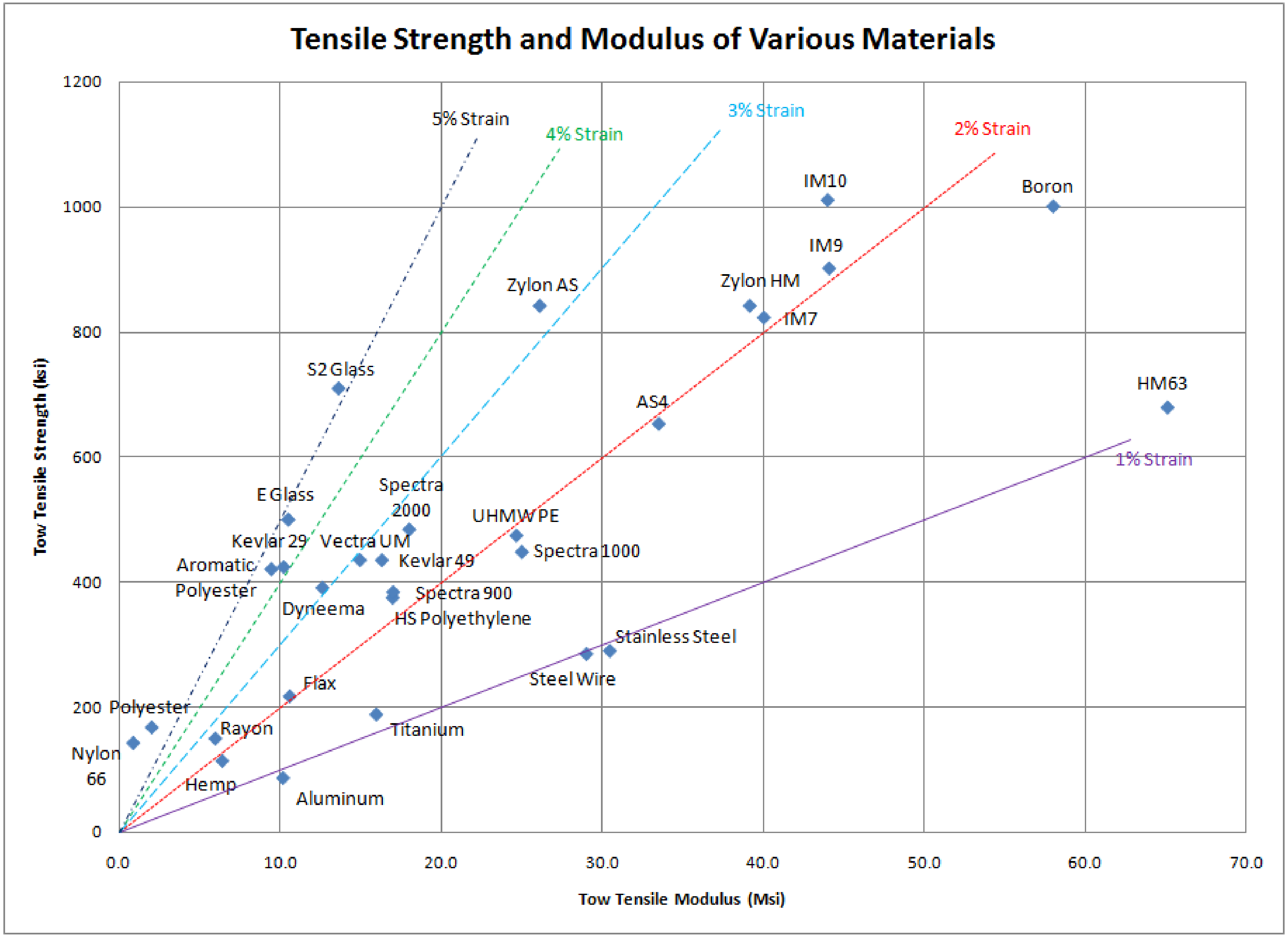


Oxidation Stabilization

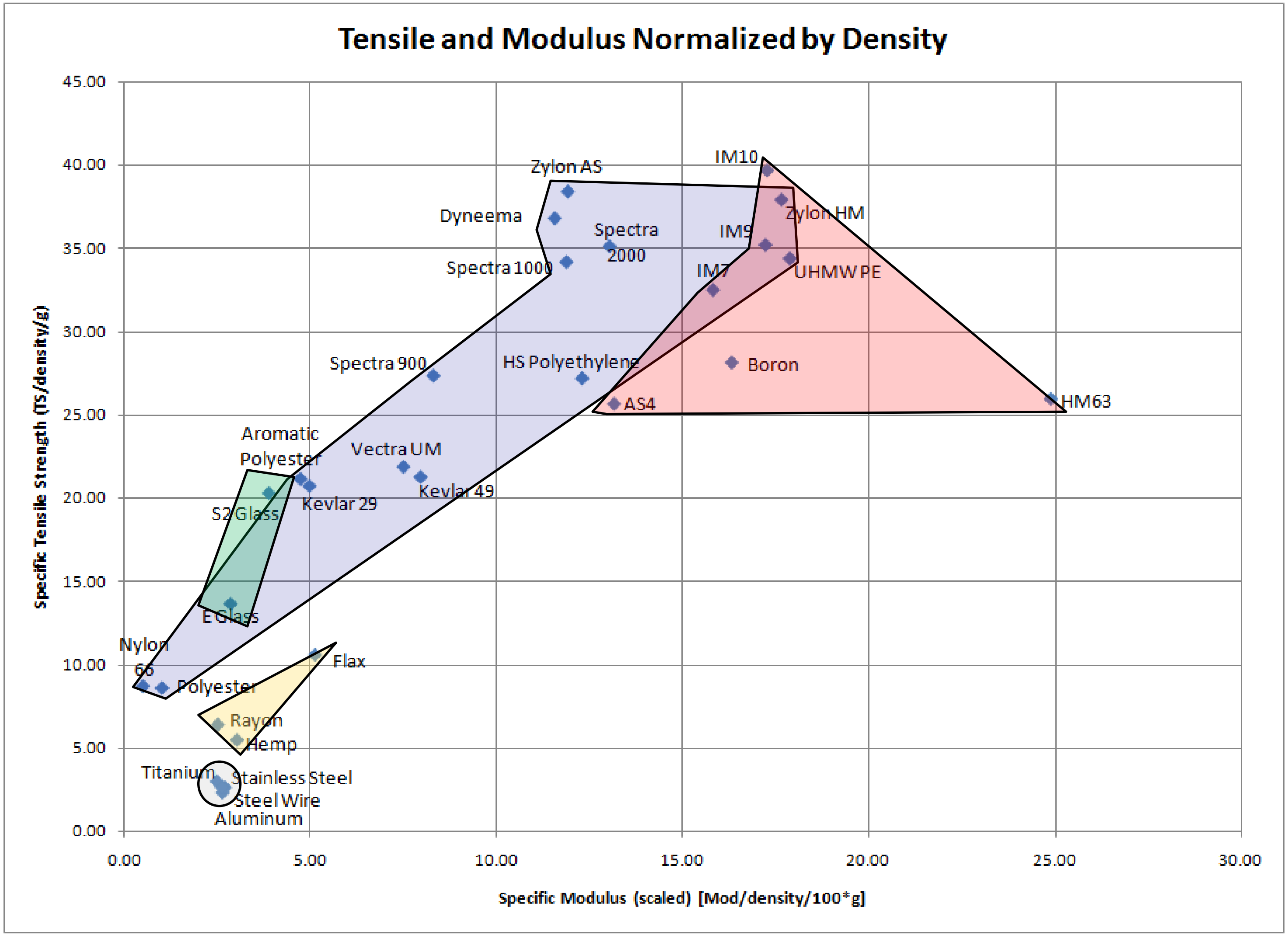
Carbonization

What’s the thinking of other materials developers?

Fibers: Strength versus Modulus



Fibers: Specific Strength versus Specific Modulus



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What are the non-composites developers doing?

- **Metal alloy R&T**
  - Aluminum continues focus:
    - Strength
    - Toughness
    - Fatigue crack growth rate
    - Exfoliation and stress corrosion resistance
    - Weight
  - Titanium (temperature and density properties distinguish this material) however work continues on:
    - Lessened distortion in cooled parts
    - Higher strength with equivalent ductility and fracture toughness
    - Lower machining costs

What are the non-composites developers doing?

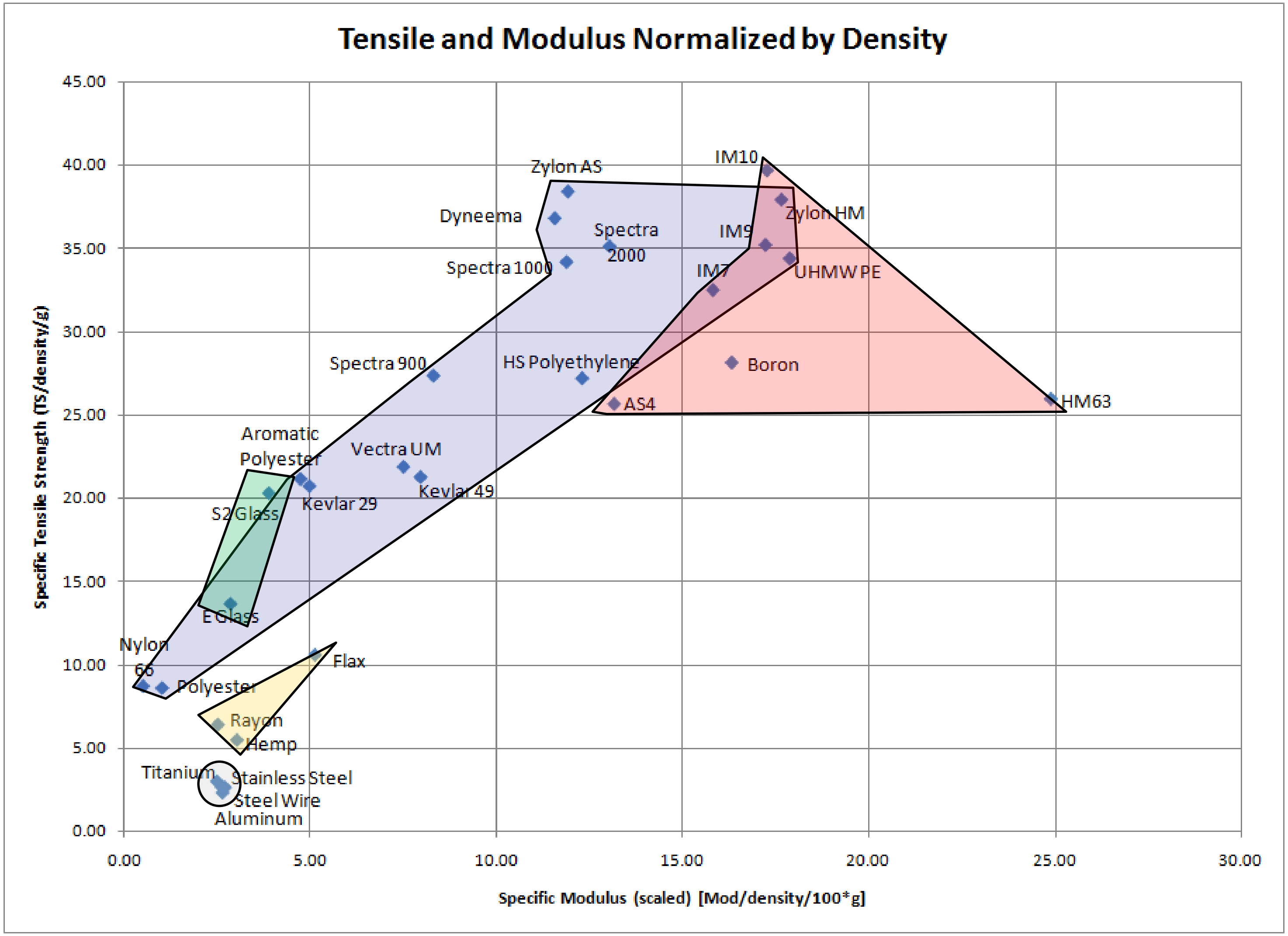
- **Metal Alloy Systems with History**
  - Al-Zn-Mg-Cu (7000 series)
  - Al-Cu-Mg (2000 series)
  - While there is some interest in the Al-Mg-Li system, no serious use
    - Lithium addition has found use as anti-oxidant
  - Recent introduction of Airware (Al-Cu-Li-Mg-Ag): adopted by Bombardier
- **The efforts to improve performance continue; however what was a "simple" material is becoming much more complex**

What are the non-composites developers doing?

- **Issues for Metal Alloy**
  - Process capability
    - Fundamental understanding of grain structure and formation is being developed
    - Process speeds tend to be markedly lower for alloy
    - Secondary process actions including calendaring can have significant effects on physical properties
  - Database for performance in real-world situations
  - Drive to higher purity (reduced Fe, Si) to control nucleation phenomena
  - Quench and temper is an art form of sorts
  - Control has gone to a new level
- **Initial impressions of aluminum as "known" material are being re-examined**

Opportunities and areas for development

Fibers: Specific Strength versus Specific Modulus



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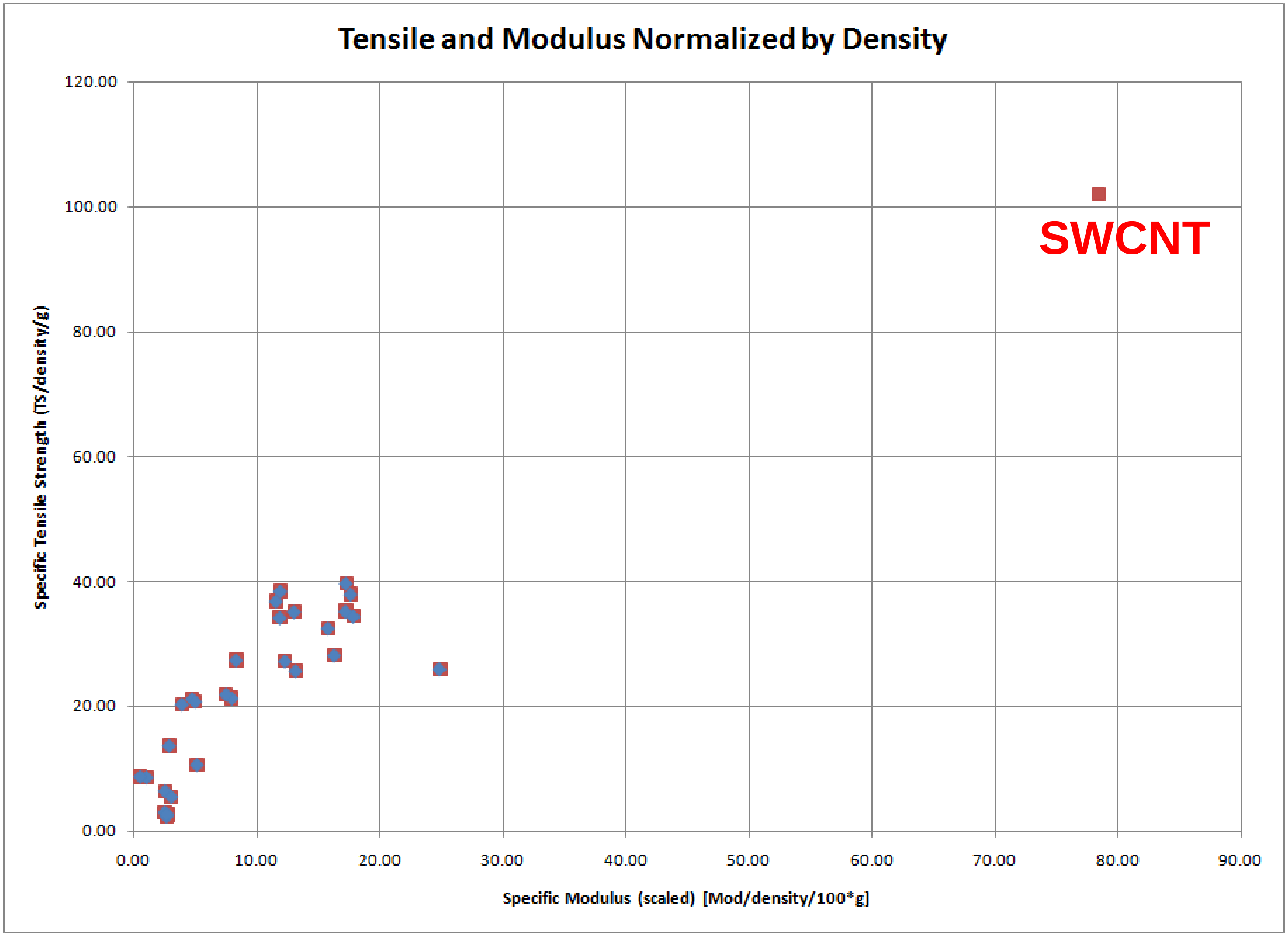
Fibers: Specific Strength versus Specific Modulus



Production Capacity and Scale-up

There is a premium to pay for order and entropy changes

- **Process speeds reflect the amount of chemical change or complexity of structures produced**
  - Steel sheet (hot roll): 2000 m/min (>1000C/sec quench) [200,000 to 400,000 tonnes/yr]
  - More recent metal alloys have a penalty versus simpler versions: line rates reduced to ~1.5 m/min (1000 – 1050 kg/hr/meter of width)
  - Simple melt and stretch of polyester (no chemistry; no change in structure beyond rotational states of polymer chains): 10000 m/min (60 g/hr)
  - Carbon fiber: standard production line producing ~1000 tonnes/yr
  - CNT yarns: (Windle, Cambridge Press release) 1g/day: ~29,000 meters of yarn; 1200 m/hr [gas phase condensation to elaborated MWCNT]
- **Large scale redundancy in process streams or specialized high speed processes may need to be developed**
- **Other properties (conductivity; shielding; surface area) of CNT may near term hold more interest than large-scale physical property**

Conclusion

- **Breakthrough in understanding of elaborated structures over past two decades**
  - is beginning to affect material design
  - cuts across wide range of materials

- **Scale-up to significant quantities can be an issue for those applications having significant order and chemical change**

- **Demands greater control than previous technologies**