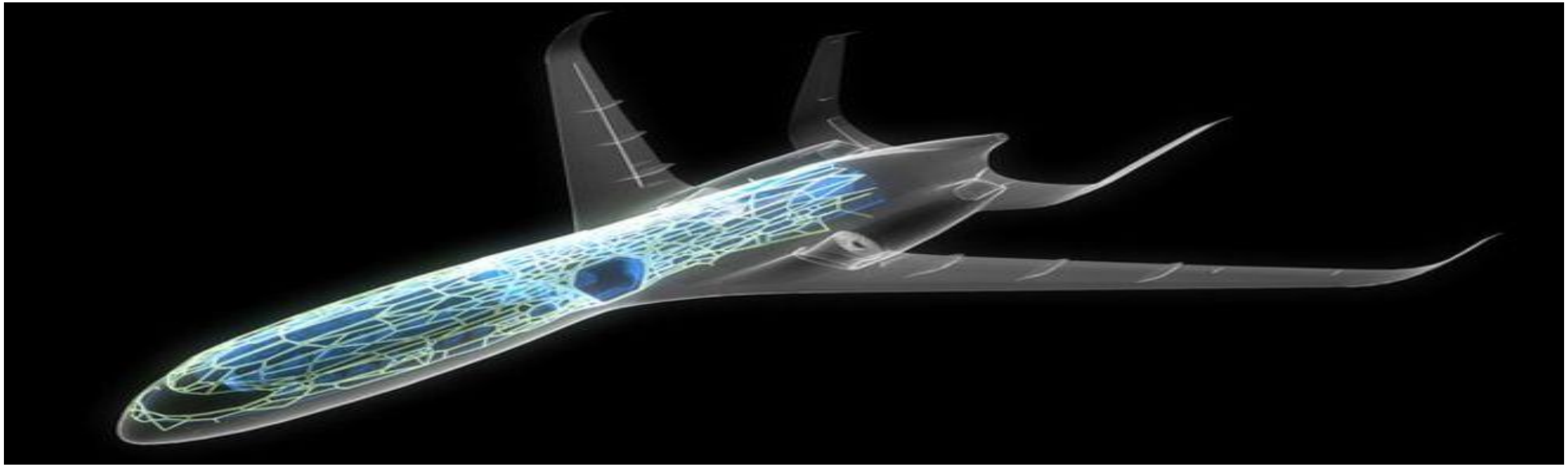
Carbon Fibre

Production methods, properties and composite applications

碳纤维

生产方法，性能和碳纤维复合材料应用



UK Carbon Fibre Industry 英国碳纤维工业

- UK has a strong carbon fibre sector which is a major exporter
- UK is strong in end-uses such as aerospace, Formula 1, automotive
- UK processes around 3000 tons of CF
  - 50% is used in the production of CF composite components
  - 50% is exported in the form of fabric or prepreg ("**Prepreg**" is the common term for a reinforcing fabric which has been pre-impregnated with a resin system)
- 英国拥有强大的碳纤维部门，是主要的出口国
- 英国在航空航天，一级方程式，汽车等最终用途方面表现强劲
- 英国加工约3000吨CF.
  - 50％用于CF复合材料部件的生产
  - 50％以织物或预浸料的形式出口（“预浸料”是增强织物的常用术语，已用树脂体系预浸渍）

Properties of Carbon Fibre
碳纤维的性质

- High strength, High stiffness
- Withstand temperatures to >2500°C
- High strength to weight ratio
- Tensile moduli range from $4x10^6$ psi to $100x10^6$ psi

- **高强度，高刚度**
- **耐受温度> 2500°C**
- **高强度重量比**
- **拉伸模量范围为4x106 psi至100x106 psi**

Methods of Producing Carbon Fibre
碳纤维的生产方法

- All commercial CF are made from one of the following
  - Polyacrylonitrile (PAN)
  - Rayon (cellulose)
  - Mesophase Petroleum Pitch

- New method for discontinuous CF
  - Vapor Growth (high performance application)

- **所有商业CF均由以下之一制成**
  - **聚丙烯腈（PAN）**
  - **人造丝（纤维素）**
  - **中间相石油沥青**

- **不连续CF的新方法**
  - **蒸汽生长（高性能应用）**

PAN Process PAN流程

- Accounts for 90% of commercial CF
- 93-95% acrylonitrile units
- PAN decomposes below its melt temperature
  - True Melt process not possible, extruded into filament form

- **占商业CF的90%**
- **93-95%丙烯腈单位**
- **PAN在其熔融温度以下分解**
  - **真正的熔融过程是不可能，挤压成长丝形式**

Processing Method 途径

- Copolymer is first dissolved in suitable solvent
  - e.g.Dimethylacetamide
  - 15-30% polymer by weight
- Extruded through a spinneret
  - large # of approx.100μm capillary holes
- Enters coagulating bath (Wet spinning)
  - Also hot gas environments
- 1-2 Stages of further stretching
  - Aligns polymer molecules parallel to fiber axis
  - Molecular orientation must be locked into place
    - Effects final mechanical properties of CF

- 首先将共聚物溶解在合适的溶剂中, e.g.Dimethylacetamide, 15-30%聚合物重
- 通过喷丝头挤出
  - 大约100微米毛细孔
- 进入凝固浴（湿纺）
  - 也是热气体环境
- 1-2进一步拉伸的阶段
  - 使聚合物分子与纤维轴平行排列
  - 分子取向必须锁定到位
    - 影响CF的最终机械性能

PAN Precursor Fibre Process
PAN前体纤维工艺

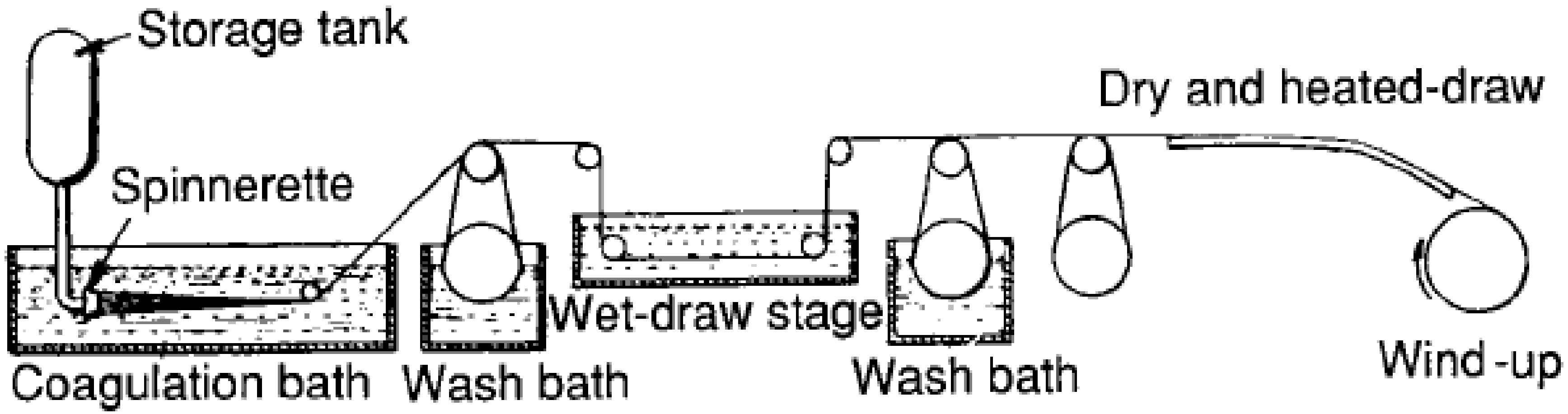


Figure 2. Schematic of process for wet-spinning PAN precursor fibers (ref. 2).

Aspects of PAN　　PAN的方面

- Wet spinning
  - Requires excessive solvent
    - Necessitates removal, solvent recovery cost
    - Trace impurities limit final CF properties
- BASF pseudo-melt alternative
  - Acrylonitrile copolymer polymerized in aqueous solution
  - Purified, dewatered and palletised
  - Homogenous melt below degradation temperature
  - Eliminates need for expensive solvent
  - Lower waste water requirements

- 湿纺
  - 需要多余的溶剂
    - 需要去除，溶剂回收成本 痕量杂质限制了最终的CF特性
    - 痕量杂质限制了最终的CF特性
- 巴斯夫伪熔替代品
  - 丙烯腈共聚物在水溶液中聚合
  - 纯化，脱水和托盘化
  - 均匀熔体低于降解温度
  - 无需昂贵的溶剂
  - 降低废水需求

BASF PAN Pseudo-Melt
巴斯夫PAN Pseudo-Melt

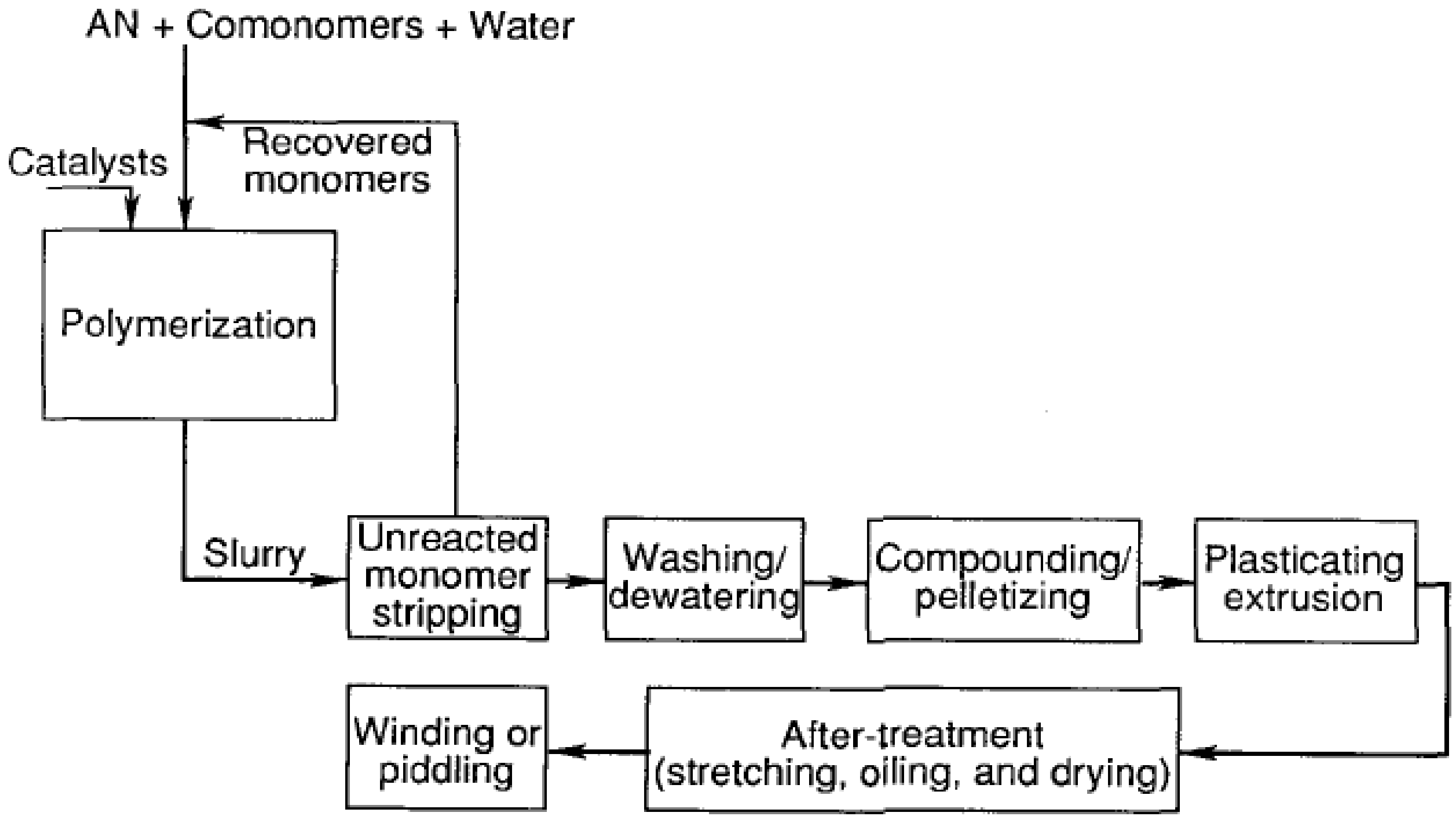


Figure 3. Flow diagram for BASF melt-assisted spinning process (ref. 3).

Production of Carbon Fiber from PAN
PAN生产碳纤维

- Heating/Stretching
- Pre-carbonization
- Carbonization
- Surface Treatment

- **加热/拉伸**
- **预碳化**
- **碳化**
- **表面处理**

Chemistry of Carbon Fibre Production
碳纤维生产化学

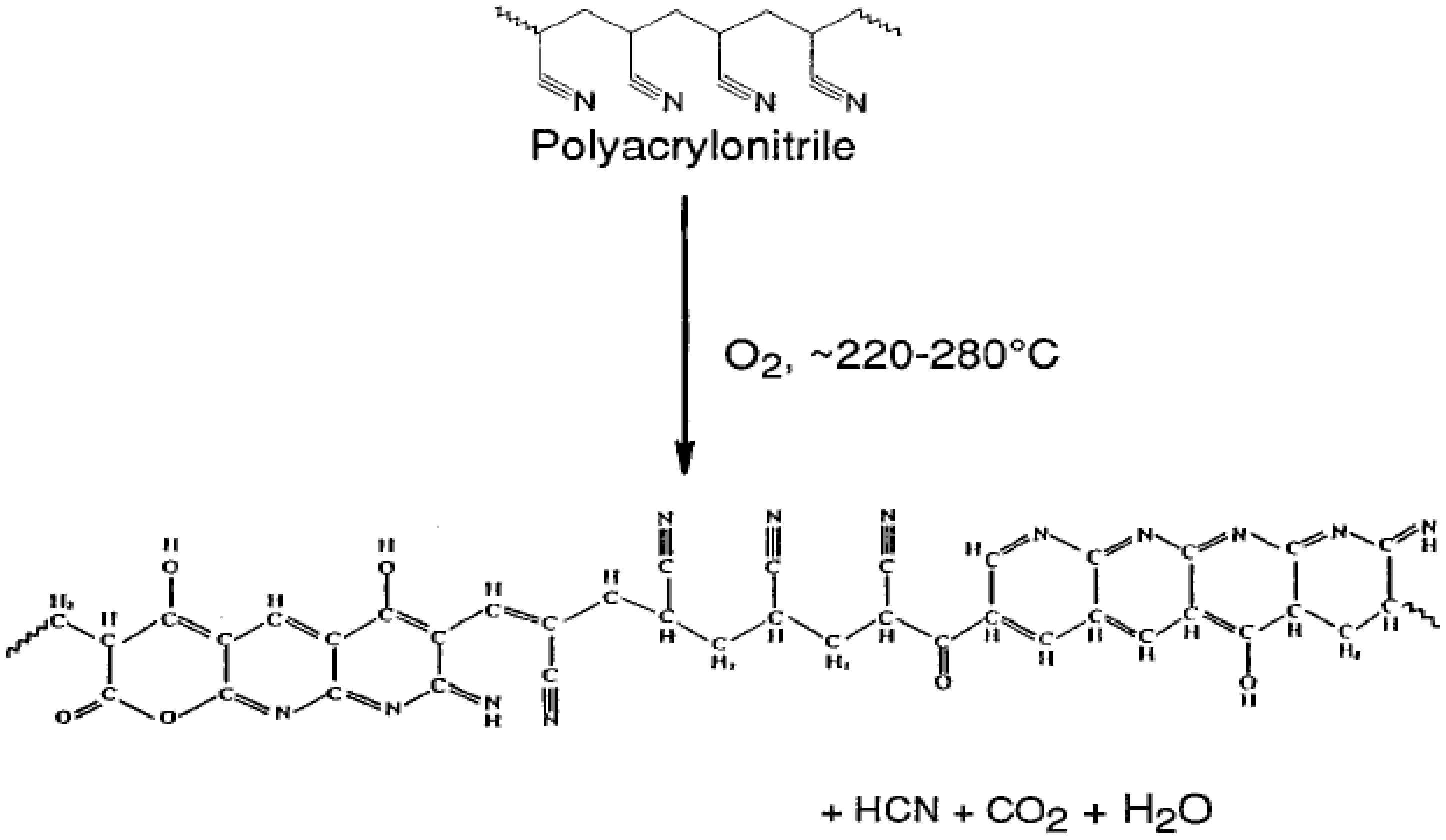


Figure 4. Stabilization PAN precursor summarizing the most frequently observed functional groups (ref. 5).

Heating / Stretching 加热 / 拉伸

- Stretching (500-1300%) **拉伸（500-1300%）**
  - 220-270 ^{o}C for 30min to 7hrs **220-270 oC 30分钟至7小时**
    - Temperature/Time dependent on composition and diameter of precursor
    - **温度/时间取决于前体的组成和直径**
  - Chemical changes **化学变化**
    - Cyclization of nitrile groups, dehydration of saturated C-C bonds, oxidation
    - **腈基环化，饱和C-C键脱水，氧化**
    - Generates carbon dioxide and hydrogen cyanide
    - **产生二氧化碳和氰化氢**
  - Large furnace + Drive rollers **大炉+驱动辊**
    - Controlled tension essential for alignment **控制张力对齐是必不可少的**
  - PAN carbon content: 54%
  - **PAN 碳含量：54%**

Pre-carbonization 预碳化

- Heating up to 1100°C
- Non-Carbon elements driven off
  - Initially larger molecules
    - CH_4, H_2O, NH_3, N_2, HCN, CO_2, CO
- Slower heating rate

- 加热至1100oC
- 驱动非碳
- 元素 最初是较大的分子 CH4,H2O, NH3,N2, HCN CO2, CO
- 加热速度较慢

Carbonization 碳化

- $1100^{o}C$ – $2800^{O}C$
- Only small diatomic molecules
  - H_2 N_2
  - Faster heating rate possible
- Graphitization above ~$1800^{o}C$
- Final C content: 80% to >99%
  - Temperature dependent
  - Overall Yield: 40-45%

- 1100oC - 2800OC
- 只有小的双原子分子
- H2 N2
- 加热速度更快
- 石墨化在~1800oC
- 最终C含量：80％至> 99％
- 温度依赖
- 产品总收率： 40-45％

Surface Treatment 表面处理

- Improves bonding with polymeric matrix materials
- Increases oxygenated groups at surface
  - Gassing at elevated temps.
  - Sodium hypochlorite solution
  - Nitric Acid

- 改善与聚合物基质材料的粘合
- 增加表面氧合基团
  - 在高温时充气
  - 次氯酸钠溶液
  - 硝酸

CF from PAN Precursor
来自PAN Precursor的CF

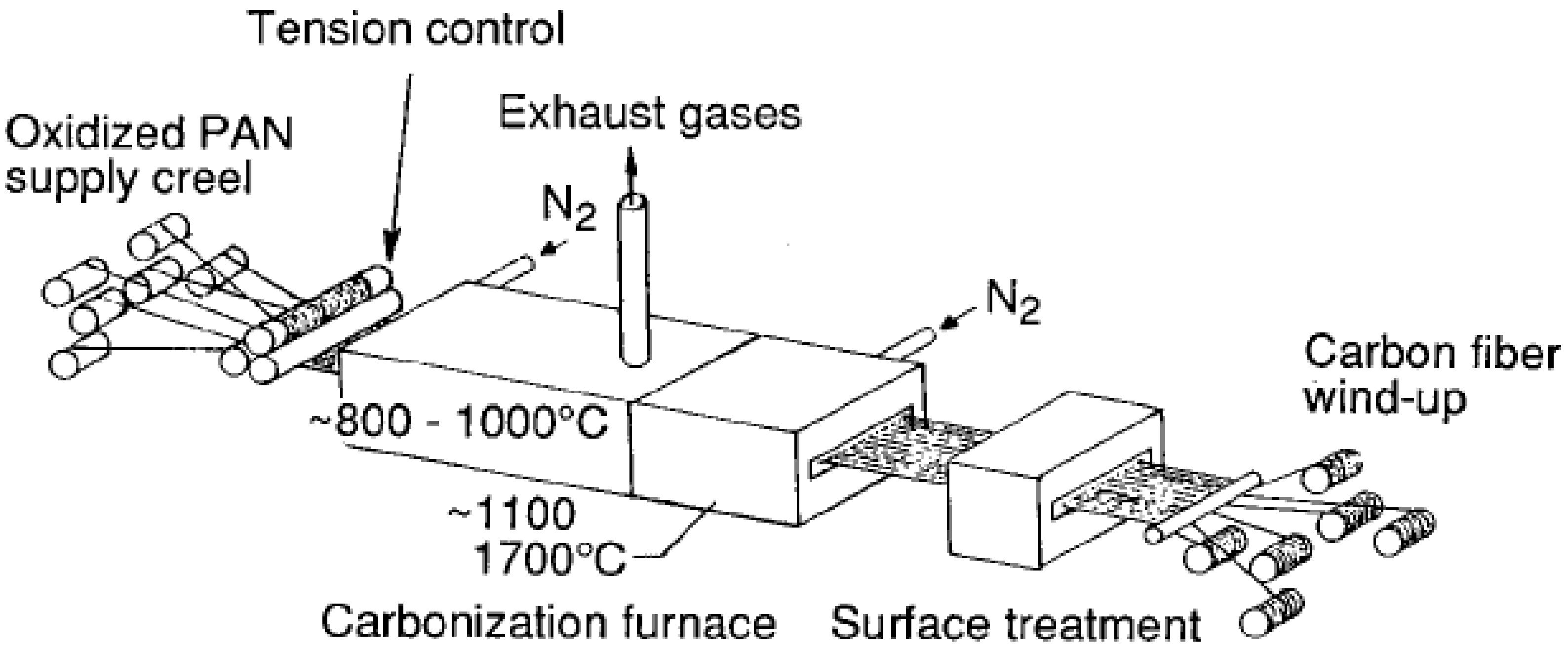
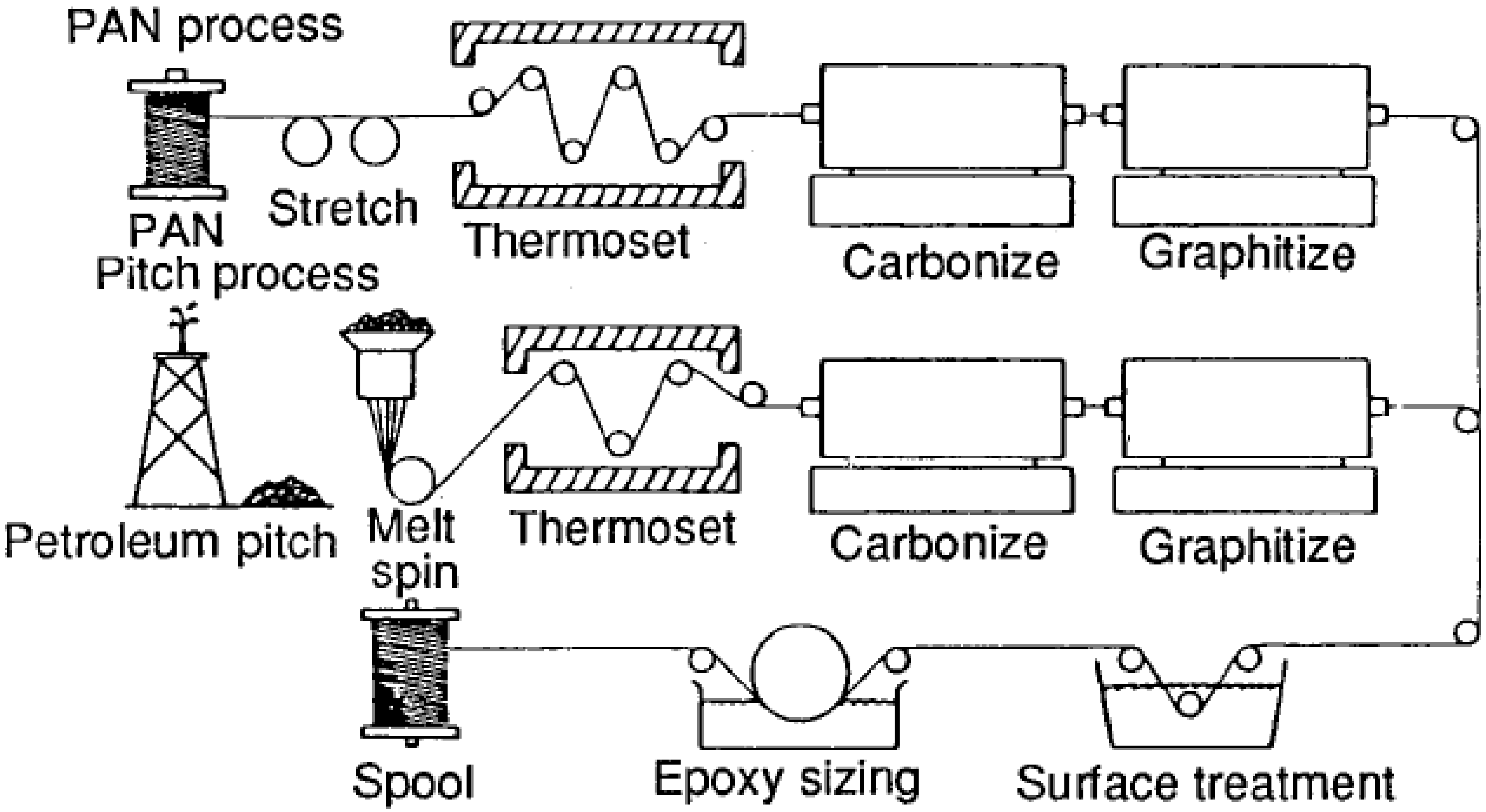


Figure 6. Schematic of carbon resistance furnace used to continuously carbonize stabilized precursor fiber.

PAN and Pitch Processing
PAN和Pitch处理



Rayon (cellulose) Precursor Fibres
人造丝（纤维素）前体纤维

- Typically low modulus ($4x10^6$ psi)
- Fiber heated to 400ºC, pyrolization of cellulose
- Carbonization at >1000ºC
- Graphitized at >2000ºC
- High modulus obtained by stretching at final heat treatment stage

- 通常低模量（4x106 psi)
- 纤维加热至400ºC, 纤维素热解
- 碳化在> 1000ºC
- 石墨化在> 2000ºC
- 通过在最终热处理阶段拉伸获得的高模量

Mesophase Pitch Precursors
中间相沥青前体

- Same general process as PAN
- Low tensile strength of precursor fibers
- Melt-spin is used
- Do not require stretching process to maintain preferred alignment

- 与PAN相同的一般过程
- 前体纤维的拉伸强度低
- 使用熔体旋转
- 不需要拉伸过程来保持首选对齐

Final Carbon Fibre Forms
最终的碳纤维形式

- Woven, Braided, or Wound
  - Unidirectional lay-ups
  - Multi-directional weaves
- Strength limiting factors
  - Purity of precursor
  - Precursor void content
  - Temperature
  - Tension

- 编织， 编织或缠绕
  - 单向叠层
  - 多向编织
- 强度限制因素
  - 前体的纯度
  - 前体无效内容
  - 温度
  - 张力

CF from Differing Processes
来自不同流程的CF

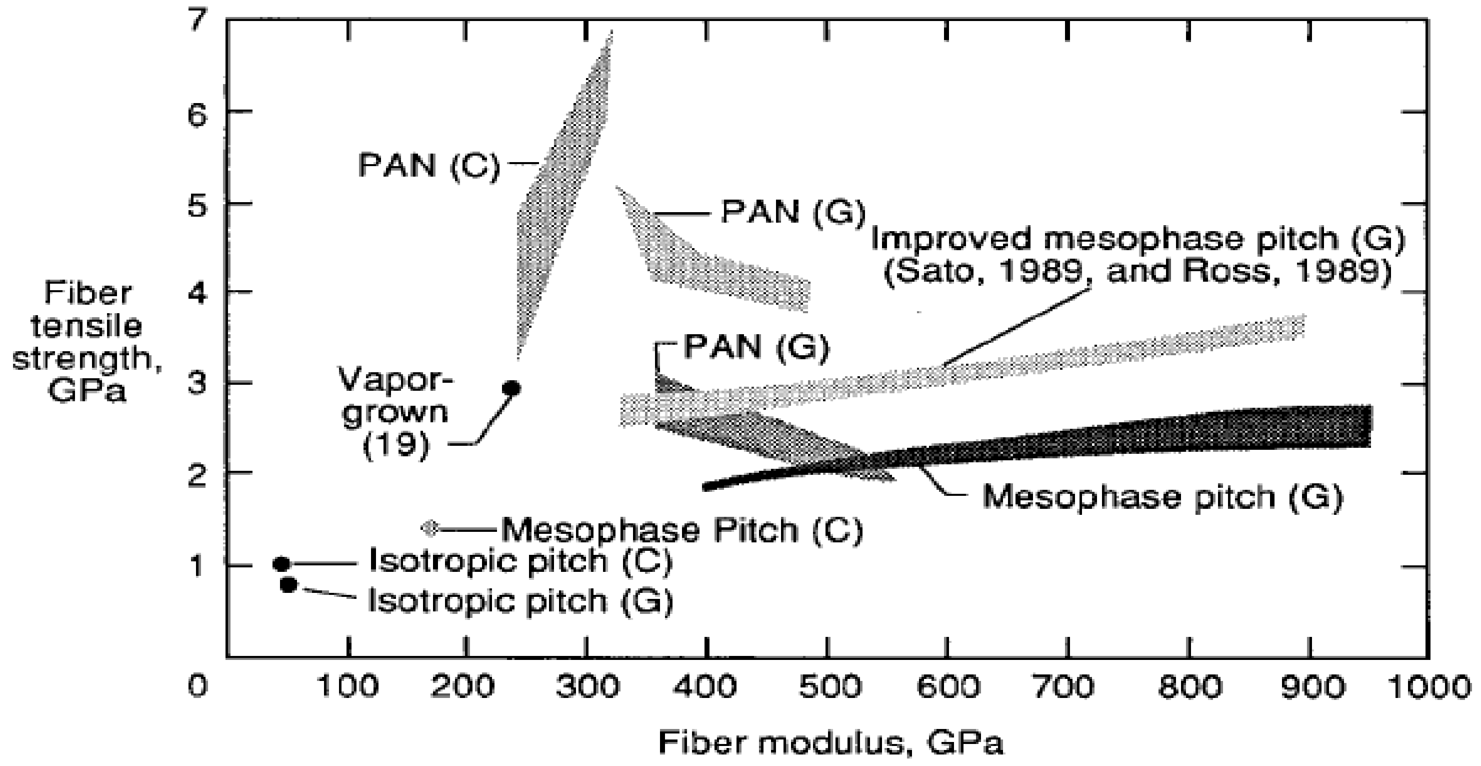


Figure 14. Tensile strength and modulus of various types of carbon fibers (ref. 19 and footnotes ∗, †, and ‡). G means the final heat treatment temperature is above 2000°C, and C indicates it is below 2000°C.

Carbon Fibre vs Steel
碳纤维与钢的比较

Material	Tensile Strength (GPa)	Tensile Modulus (GPa)	Density (g/cm)	Specific Strength (GPa)
Standard Grade CF	3.5	230.0	1.75	2.00
High Tensile Steel	1.3	210.0	7.87	0.17

Modulus Classifications 模数分类

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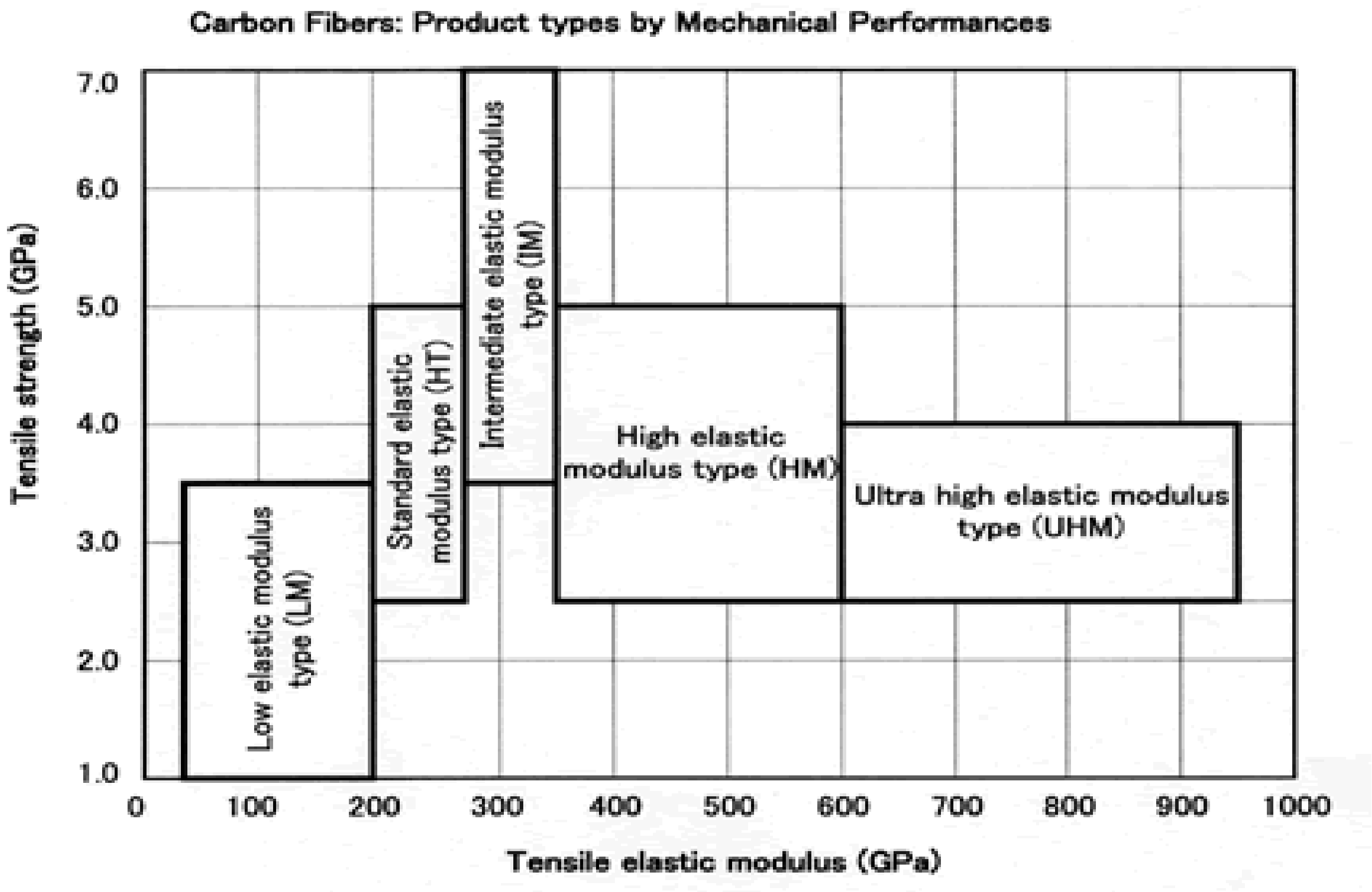
- Ultra high elastic modulus type (UHM)
- High elastic modulus type (HM)
- Intermediate elastic modulus type (IM)
- Standard elastic modulus type (HT)
- Low elastic modulus type (LM)

- 超高弹性模量型（UHM）
- 高弹性模量型（HM)
- 中间弹性模量型（IM）
- 标准弹性模量型（HT）
- 低弹性模量型（LM)

Carbon Fiber Modulus
碳纤维模量数据



http://www.carbonfiber.gr.jp/english/index.html

Carbon Fibres in Composites
复合材料中的碳纤维

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- Polymer-Matrix Composites
- Metal-Matrix Composites
- Carbon-Matrix Composites
- Ceramic-Matrix Composites
- Hybrid composites

- 聚合物 - 基质复合材料
- 金属基复合材料
- 碳基复合材料
- 陶瓷基复合材料
- 混合复合材料

Carbon-Carbon Composites
碳 - 碳复合材料

- Carbon substrate in Carbonaceous Matrix
- Carbon fibers continuous and woven
- Disadvantages
  - High fabrication cost
  - Poor oxidation resistance
  - Poor inter-laminar properties

- 碳质基质中的碳基质
- 碳纤维连续和编织
- 缺点
  - 制造成本高
  - 抗氧化性差
  - 层间性能差

Fabrication of C-C Composites
碳 - 碳复合材料的制备

- Liquid phase impregnation (LPI)
- Hot isostatic pressure impregnation carbonization (HIPIC)
- Hot pressing
- Chemical Vapor Infiltration (CVI)

- 液相浸渍（LPI）
- 热等静压浸渍碳化（HIPIC）
- 热压
- 化学气相渗透（CVI）

Applications of C-C Composites
碳 - 碳复合材料的应用

- Aircraft Brakes
- Heat Pipes
- Reentry vehicles
- Rocket motor nozzles
- Hip replacements
- Biomedical implants
- Tools and dies
- Engine pistons
- Electronic heat sinks
- Automotive and motorcycle bodies
- Bicycles

- 飞机刹车
- 热管
- 再入飞行器
- 火箭发动机喷嘴
- 髋关节置换术
- 生物医学植入物
- 工具和模具
- 发动机活塞
- 电子散热片
- 汽车和摩托车车身
- 自行车

Large and Small Tow Fibres
大型和小型拖曳纤维

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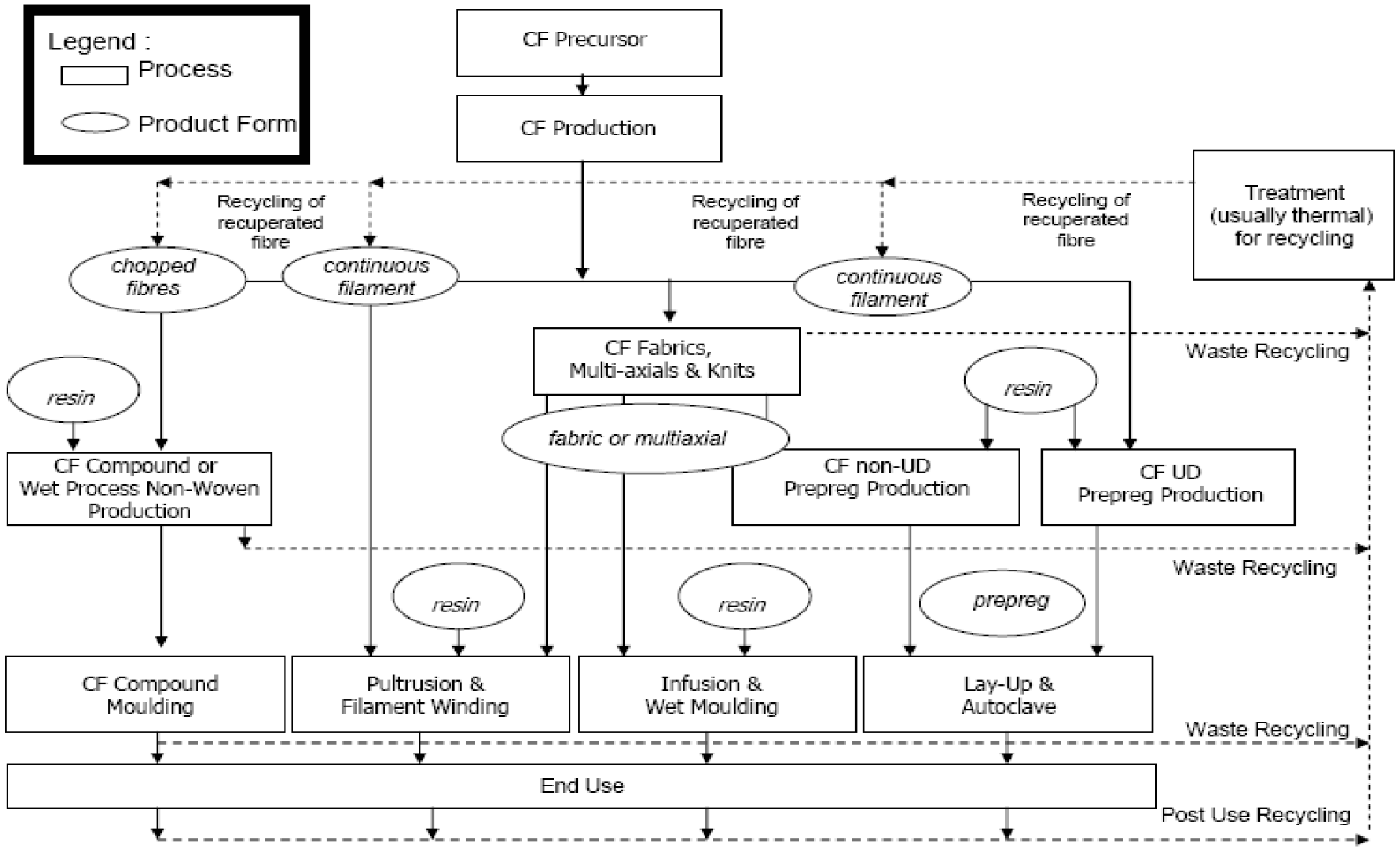
- Past focus on small tow (tow = number of individual fibres in a continuous bundle) for high-end applications
- 过去专注于小型丝束 (丝束=连续束中单根纤维的数量), 适用于高端应用
- Small tow products ranged from 1,000 to 24,000 filaments
- 小型丝束产品的长度范围为1,000至24,000根
- Lower cost CF industrial (non-aerospace) applications
- 碳纤维工业（非航空航天）应用具有较低的成本
  - Higher productivity processes (laying down more carbon/unit time) and a lower price of fibre
  - 更高的生产率工艺，每单位时间生产更多碳纤维，可降低纤维价格
  - Uses large tow products, usually > 24K
  - 使用大型丝束产品，通常> 24K

Polymer Matrix Composites Value Chain
聚合物基复合材料价值链



Polymer Matrix Composite Production
聚合物基复合材料生产

- Value chain starts with production of CF precursor (mostly PAN)
- 价值链始于CF前体（主要是PAN）的生产
- Oxidation/carbonisation process converts precursor into CF
- 氧化/碳化过程将前体转化为CF.
- Next is production of woven or multi-axial type fabrics , 下一步是生产织造或多轴型织物
    - 3D knitted CF shapes produced,　生产3D针织CF形状
    - Reinforcement placed exactly where needed in 3D shapes
    - 钢筋准确放置在3D形状所需的位置
- Prepreg production is the next key step, 预浸料生产是下一个关键步骤
    - Unidirectional (UD) prepregs directly make use of continuous filament CF
    - 单向（UD）预浸料直接使用连续长丝CF
    - Fabric based prepregs mainly based on epoxy resin
    - 基于织物的预浸料主要基于环氧树脂
    - Some thermoplastic prepregs PEEK and PPS for temperature resistance
    - 一些热塑性预浸料PEEK和PPS用于耐温

Properties Polymer Matrix Composites
性能聚合物基复合材料

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Typical Composite Properties (at Room Temperature)	U.S. Units	SI Units	Test Method
0º Tensile Strength	370 ksi	2,550 MPa	ASTM D3039
0º Tensile Modulus	21.0 Msi	145 GPa	
0º Tensile Strain	1.6%	1.6%	
0º Short Beam Shear Strength	18.5 ksi	128 MPa	ASTM D2344
0º Compressive Strength	270 ksi	1,862 MPa	ASTM Mod. D695
Fiber Volume	60%	60%	

Applications of Polymer Matrix Composites 聚合物基复合材料的应用

- Aerospace
  - Enable weight reduction
  - Allow aircraft to travel further, faster and/or carry more passengers
  - Use less fuel
- Automotive
  - Enable weight reduction
  - Increase fuel efficiency

Aerospace Products 航空航天产品

- AS507 CF是一种连续，高强度，高应变，PAN基纤维，可提供12,000（12K）长丝数丝束。经过表面处理后，它的尺寸可以改善其层间剪切性能，处理特性和结构性能。该产品适用于织造，预成型，长丝缠绕，编织和拉挤成型

- AS102 12k（0.5％）碳纤维符合NMS 818碳纤维规范（NCAMP）
- 符合行业标准的航空航天级CF.

UK Production of CF Composites
英国CF复合材料生产

UK production of CF composite parts by product form and end use – 2008 (in tons of composite)					
Product Form	CF Compound (Thermoset or Thermoplastic)	Continuous CF Filament	CF Fabric, Multixial and Knitted	CF Prepreg (UD and fabric based)	Total By End Use
End Use					
Aerospace/Defence	20	50	-	700	770
Automotive	10	50	40	150	250
Marine	-	60	100	-	160
Wind Energy	-	650	-	50	700
Industrial	10	50	40	50	150
Sports	5	20	-	20	45
Other	5	20	20	10	55
Total	**50**	**900**	**200**	**980**	**2,130**

谢谢
Thank You

如需进一步信息和讨论，请联系

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