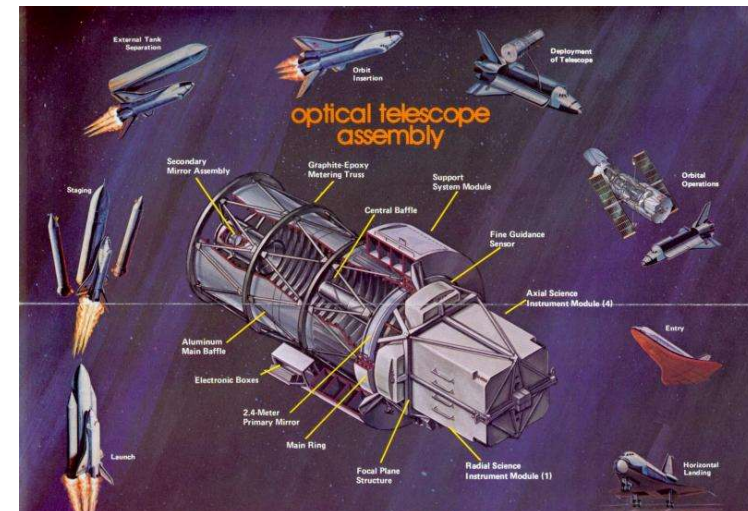


Carbon Fiber

Chemical Engineering on String



History

- Synthetic carbon industry begins in 1886 –National Carbon Company Cleveland Ohio makes carbon electrodes for street arc lamps
- 1879 Edison invents the first incandescent light bulb with carbon filaments derived from cellulose (cotton or bamboo that is carbonized). Tungsten filaments soon displace
- National Carbon merges with Union Carbide in 1917 to eventually form Union Carbide Corp
- Near the end of WWII UCC investigates carbonized rayon (cellulose based polymer) as a filament for vacuum tubes. In 1957 UCC develops a carbonized rayon cloth to be used in rocket nozzles and re-entry heat shields, but material has poor mechanical properties.
- 1958, while studying the triple point of graphite using carbon arcs, Roger Bacon discovered graphite whiskers being formed. Tensile of 20 GPa and modulus of 700 GPa (steel is ~2 GPa tensile and 200 Gpa). Whiskers were graphite sheets rolled into scrolls similar to nanotubes
- Published paper in 1960, Cost at the time was \$10 M per pound
- 1961 Japan begins development of carbon fibers from Polyacrylonitrile (PAN)
- 1964 British researchers push modulus of PAN fibers higher and start commercial production
- 1964 UCC scientists stretched carbon yarn while carbonizing to get orientation. 10X increase in modulus

From:<https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/carbonfibers.html>

History (continued)

- Leonard Singer with UCC discovers how to make carbon fiber from petroleum pitch. Patent follows in 1977
- 1970 Toray signs joint technology agreement with UCC after further improvements in the PAN process
- 1978 UCC licenses PAN process from Toray
- 1982 UCC starts up first US PAN based carbon fiber plant in Piedmont SC

Landmark Designation and Acknowledgments

Landmark Designation

The American Chemical Society designated the development of high performance carbon fibers at Union Carbide (now GrafTech International, Ltd.) in Parma, Ohio, as a National Historic Chemical Landmark on September 17, 2003. The plaque commemorating the development reads:

Scientists at the Parma Technical Center of Union Carbide Corporation (now GrafTech International) performed pioneering research on carbon fibers, for their weight the strongest and stiffest material known at the present time. In 1958 Roger Bacon demonstrated the ultrahigh strength of graphite in a filamentary form. Seven years later continuously processed high performance carbon yarn, from a rayon precursor, was commercialized. In 1970 Leonard Singer produced truly graphitic fibers, leading to the commercialization of carbon yarn derived from liquid crystalline pitch. Carbon fibers are used in aerospace and sports applications.

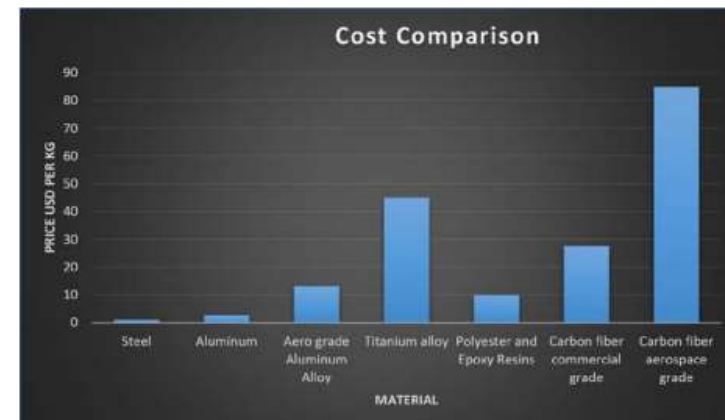
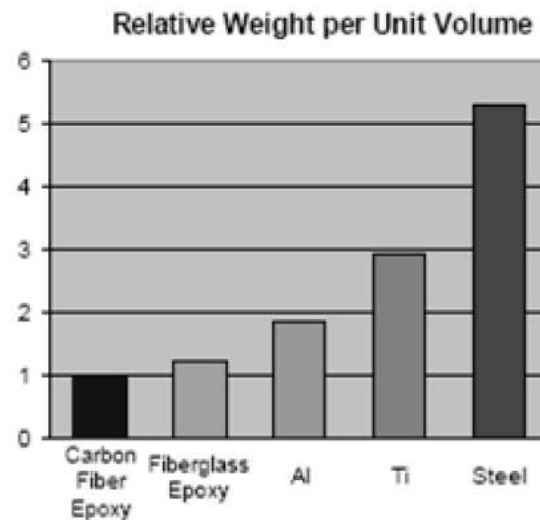
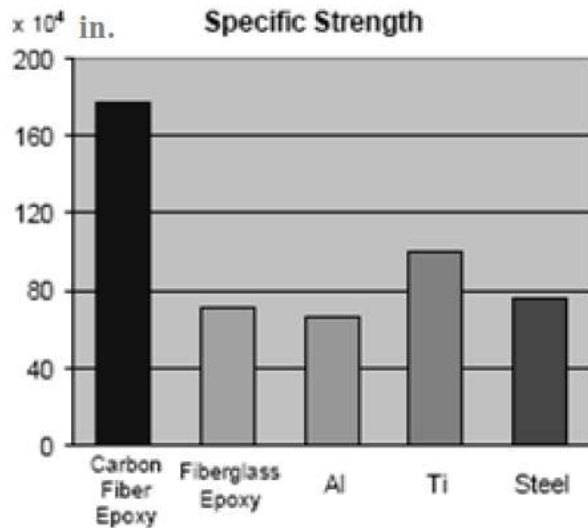


National Historic Chemical Landmark plaque for the Development of High Performance Carbon Fibers at the GrafTech International, Ltd., (formerly Union Carbide Corp.) in Parma, Ohio. Courtesy GrafTech International, Ltd.

Carbon fiber Supply and Demand

Carbon fiber demand and supply, metric tonnes (MT)			
	Carbon fiber demand	Carbon fiber supply (nameplate)	Carbon fiber supply (actual)*
2010	48,370	79,650	47,790
2015	82,400	143,595	93,171
2020 (est.)	150,200	180,600	129,965

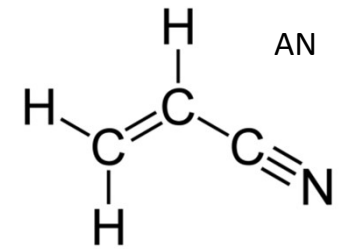
**Actual output is less than nameplate, due to capacity knockdown.*



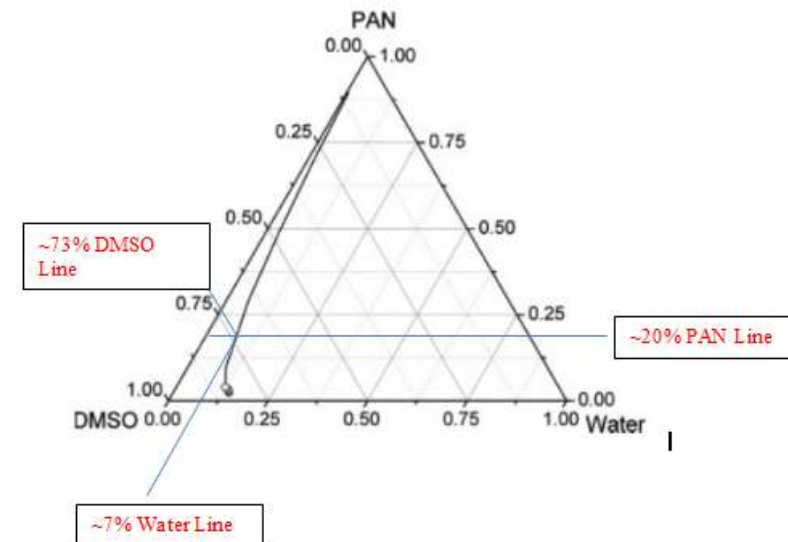
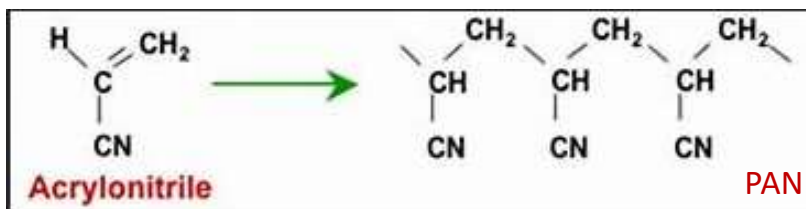
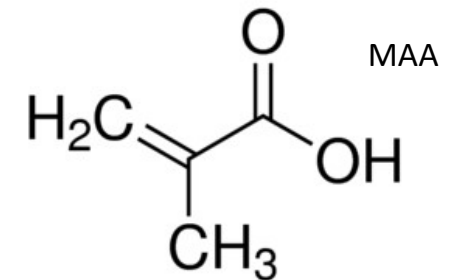
South Carolina Site History

- Leonard Singer with Union Carbide Corporation (UCC) discovers how to make carbon fiber from petroleum pitch. Patent follows.
- 1977-Union Carbide Pitch fiber plant built in Piedmont, SC
- 1970 Toray signs joint technology agreement with UCC after further improvements in the PAN process.
- 1978 Union Carbide Corporation (UCC) licenses PAN process from Toray
- 1982 UCC starts up first US PAN based carbon fiber plant in Piedmont SC
- 1986 Amoco acquires the carbon facility as Amoco Performance Products
- 1989 Second Production Line (GP2) developed and started up
- 1993 low carbon fiber demand causes six month shut down and furlough
- 1998 merger with BP
- 2001 BP sells facility to Cytec
- 2006 Third PAN production facility design begins
- 2009 Downturn causes project delay
- 2014 Third PAN production facility is put into service
- 2021 Facility shuts down due to low demand and COVID
- 2022 Facility is restarted and celebrates 40 years

PAN Fibers Chemistry



- Basis of PAN process is using acrylic precursor based on textile production
- Add a copolymer to aid in thermosetting, typically an organic acid
- Polymerize acrylonitrile-free radical
 - Solution polymerization
 - Batch polymerization
 - Reacted as polymer dope suitable for spinning
 - Suspension polymerization
 - Continuous polymerization
 - Polymer collected as slurry, washed and dried
 - Polymer dope made by mixing with solvent
- Polymer dope is typically 20% PAN in polar organic solvent such as DMF or DMSO
- Remove un-reacted acrylonitrile and gasses
- Wet spin or dry jet/wet spin and draw to orient



PAN Fibers Chemistry-cont'd

- Coagulation of the PAN in spinning is a diffusion process, solvent diffusing into the baths from the fiber and water diffusing into the filament
- Forms a spongy structure dependent on conditions
- PAN is a thermoplastic so we heat it to stretch and align the polymer molecules
- Apply finish to prevent sticking
- Drying collapses the fiber and anneals it
- More stretching
- Heat setting
 - Allows the polymer chains to relax slightly under control
- Wind up precursor fiber
- Typical filament size 10-12 microns

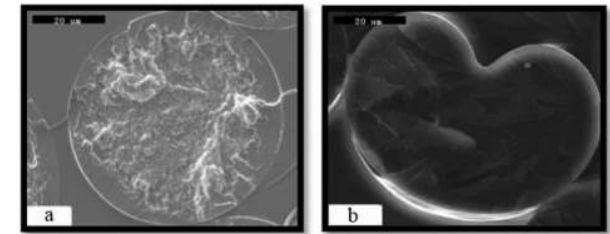
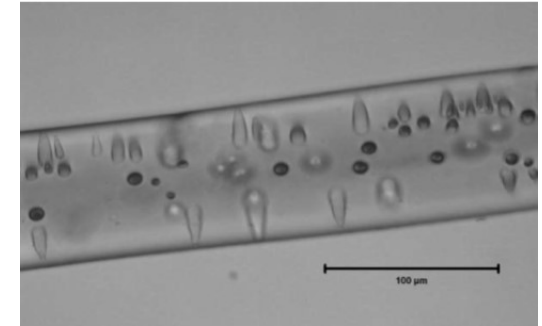
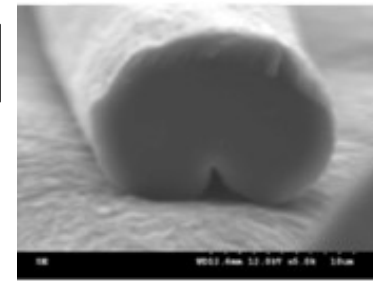


Figure 5. Effect of coagulation bath temperature on the shape of the precursor fibers, from Wang (89). (a) 60°C, (b) 40°C. (Reprinted with permission from *Journal of Applied Polymer Science*, Vol. 104, 3723-3729, (2007), John Wiley and Sons Publishers.)

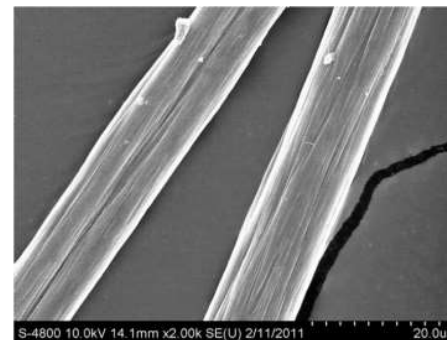


Figure 4.9. Fibrillar surface of wet-jet spun precursor fiber of 18 wt.% PAN-co-MA/DMAc

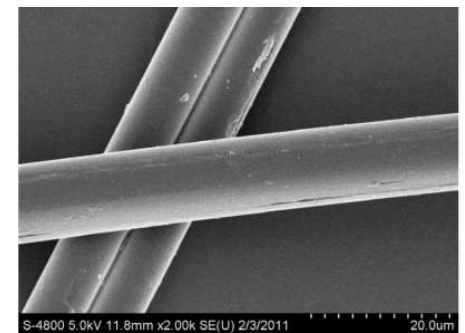


Figure 4.8. Smooth surface of dry-jet spun precursor of 20 wt.% PAN-co-MA/DMAc

PAN Fibers Process

- Polymer reaction is typical chemical engineering process done at $<100^{\circ}\text{C}$
- Dope prep requires precision to keep mass per unit length of fiber constant
- Must filter out particulates and gels to achieve high tensile strength
 - Tensile strength driven by flaws
 - Gels are polymer that comes out of solution
 - Sintered metal filters in down to single digit microns
- Solvent properties drive engineering considerations
 - DMSO freezes at 60°F
 - DMF liver toxin
 - Sodium Thiocyanate
- Remove unreacted acrylonitrile-cancer suspect
- Need precise temperature and composition control on the coagulation bath
 - Viscosity has strong temperature dependence-can double in 20°C
 - Precision metering pumps to spinnerets
- Spinnerets form multifilament tows (3K, 6K etc)
- Need De-ionized filtered water for washing
- Hot baths for washing – counter current extraction
- Large amount of ventilation
- Precision speed control

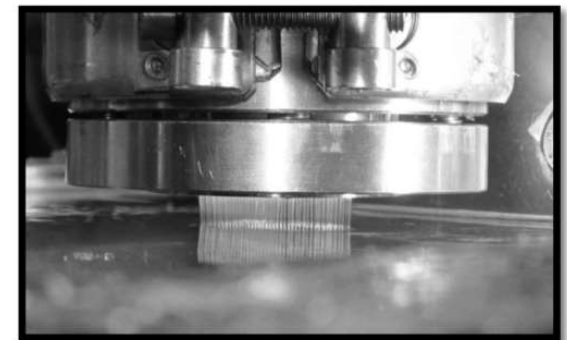
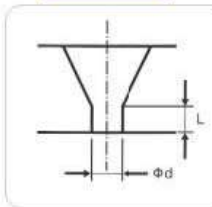
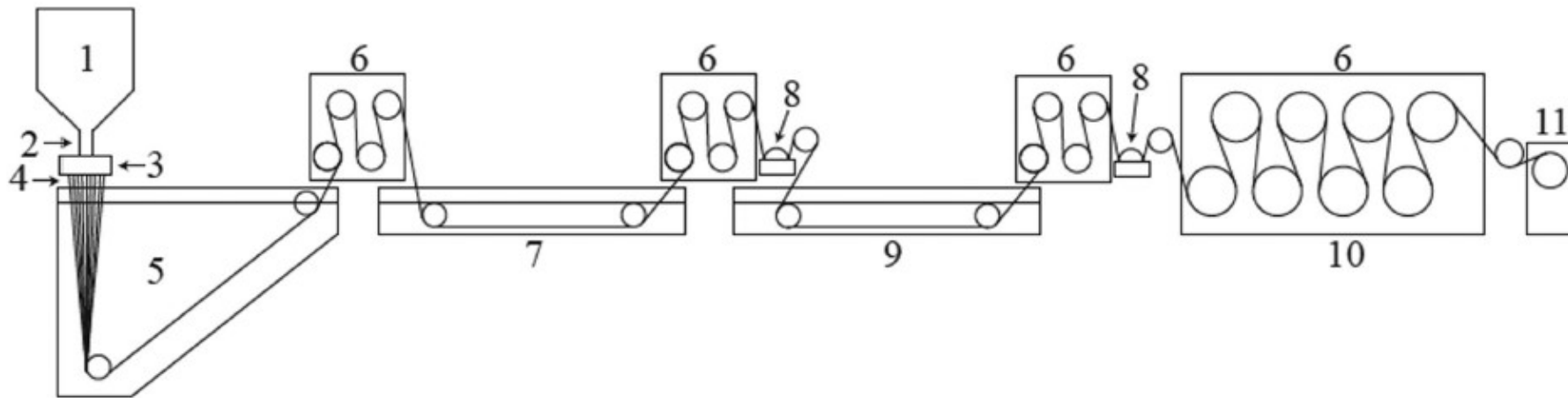


Figure 1. Multi-filament air-gap (5 mm) spinning of PAN polymer solution into a DMAC/H₂O coagulation bath at the University of Kentucky Center for Applied Energy Research.

PAN Fibers Process



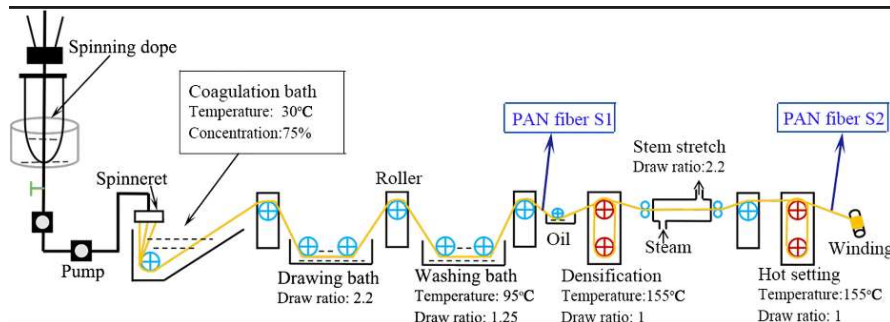
1 - spinning solution
2 - filtration
3 - spinnerette
4 - air gap

5 - coagulation bath
6 - driven rollers
7 - washing bath(s)
8 - spin finish application

9 - stretching bath(s)
10 - drying, collapsing, and heat setting
11 - traversing takeup

PAN Fibers Process

- Drive stands must support draw tensions
 - Usually cantilevered rolls
 - Top speed <1000 ft/min
- Wind as large a spool as possible
- Wash water plus solvent sent to recovery system
 - Recover solvent to recycle back to reactor
 - Distillation processes
- Utilities required
 - Air
 - De-ionized Water
 - Cooling water
 - Blanket nitrogen
 - Steam
 - Water treatment
 - Vapor collection and treatment

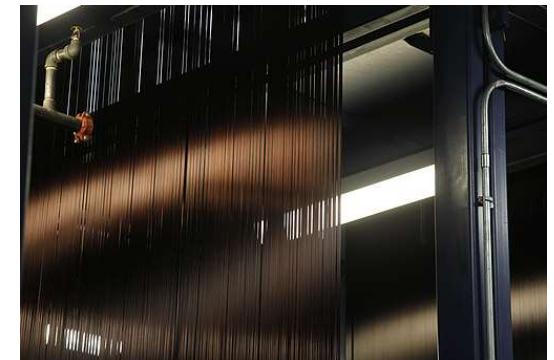
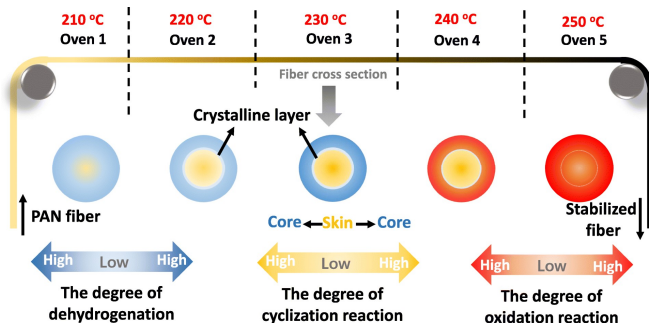
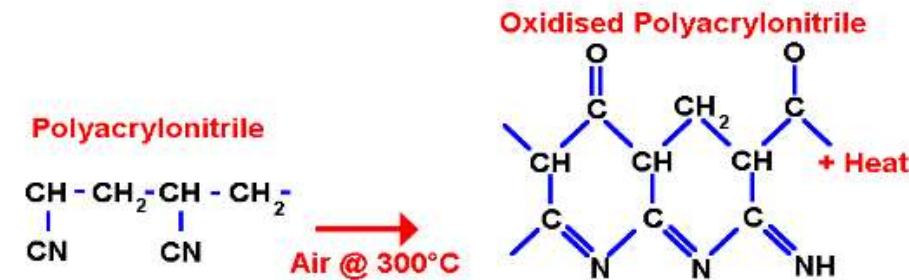
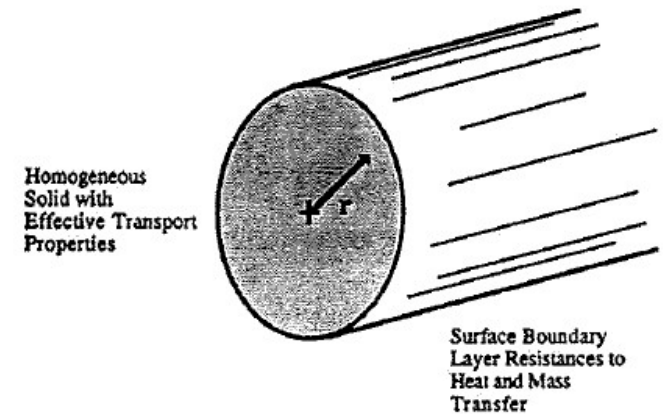


PAN FIBER INDUSTRIAL PRODUCTION



PAN Carbon Fibers Chemistry

- PAN is thermoplastic, must thermoset it to be able to convert it to carbon fiber
- Heating PAN in air thermosets the PAN via crosslinking to drive up the molecular weight and melting point. Reaction occurs in the solid state.
- Air diffuses into the filament and reacts
- First order reaction kinetics
 - $$\frac{-d[\text{PAN}]}{dt} = k [\text{PAN}][\text{O}_2]$$
- Exothermic
 - Temperature profile to prevent self heat
 - Temperatures 200°C to 300°C
- Some shrinkage as bonds form
 - Tension controlled by roll speeds
 - Too low tension lose orientation
- Fiber density correlates to extent of reaction
- Off gas from oven
 - Contains low amounts of cyanide
 - Contains low amounts of spin finish



PAN Carbon Fibers Chemistry-cont'd

- Thermoset PAN is now suitable for conversion to carbon fiber
- Two steps
 - Dehydrogenation
 - Denitrogenation
 - In inert atmosphere
 - Lose ~50% of material
 - Large amount of HCN and tars evolved
 - Nitrogen and CO evolved
 - Temperature profile critical to property development
 - Forming chemical bonds-fiber shrinking
- Next step is surface treatment
 - Graphite is inert so need to alter the surface
 - Add oxygen in surface treatment
 - Electrolysis/wash (electrochemistry)
 - Plasma
 - Improves interlaminar shear strength
- Size fiber to protect in weaving
- Dry
- Wind-Final filament size 5-7 microns

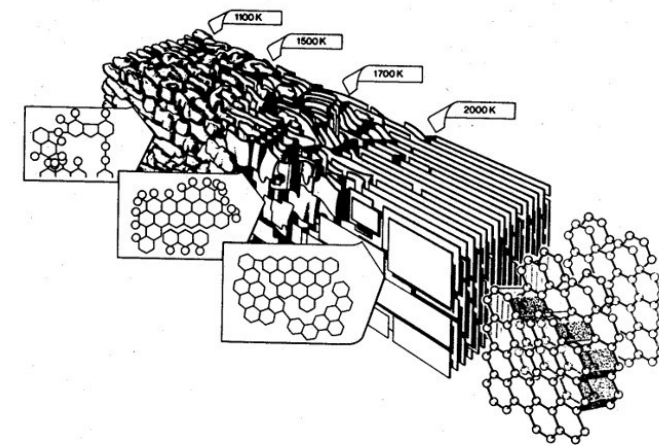
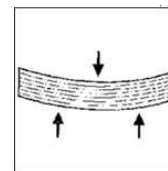
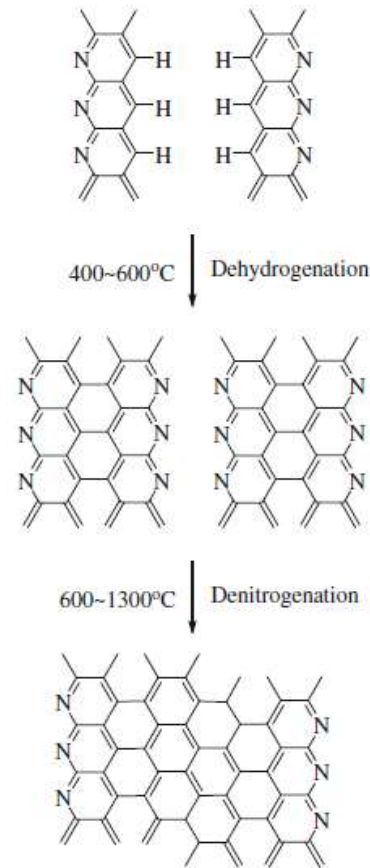
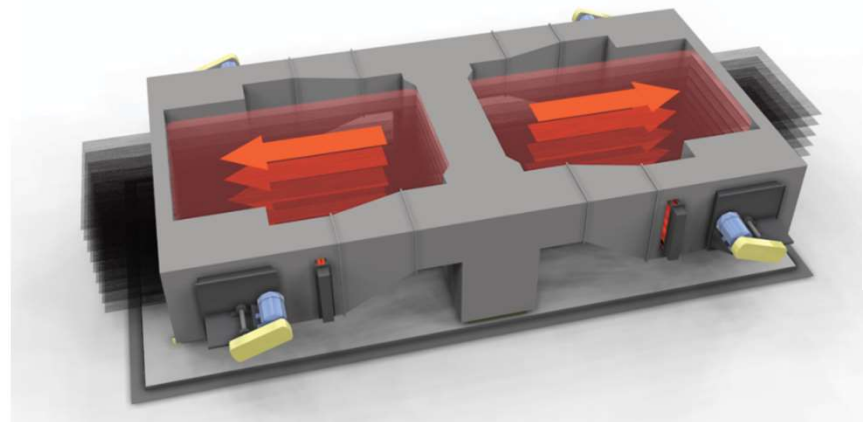
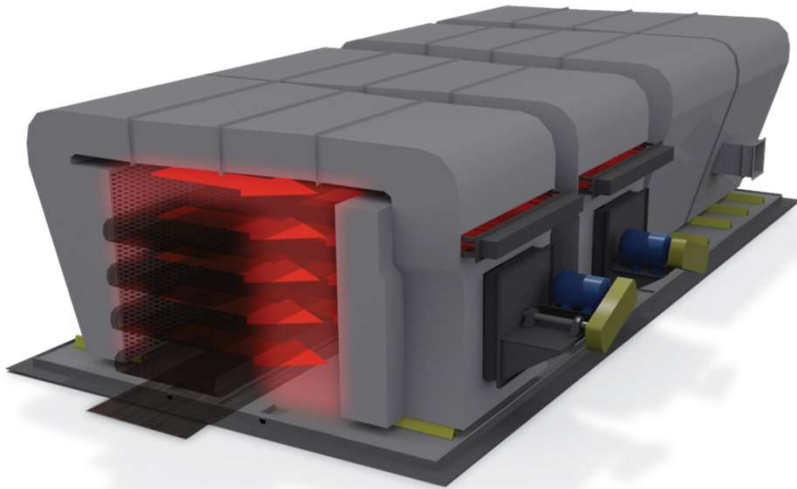


Fig: Molecular structure of carbon fiber

Carbon Fiber Process

- Creel
 - Collect precursor fiber from high-speed spinning
 - Pay off in a web up to 3m wide (dictated by furnace width)
 - Hundreds of positions depending on tow size and width
 - Up to ~ 10 m/min line speeds
- Oxidation
 - Various oven designs depending on air flow desired



a. Parallel flow of air,

$$Nu = \frac{1}{2} 0.035 Re^{0.59}$$

b. Cross-flow of air,

$$Nu = \frac{1}{2} 0.065 Re^{0.57}$$

$$Re = 2R_b \rho_{air} v / \mu$$

- Typical air flows max 10 fps (7 mph)
- Air both heats and cools the fiber
- Need ~ 1 hr residence time
- Fire protection systems
- Drive stands
- Multiple temperature stages
- Electric or gas fired



Carbon Fiber Process

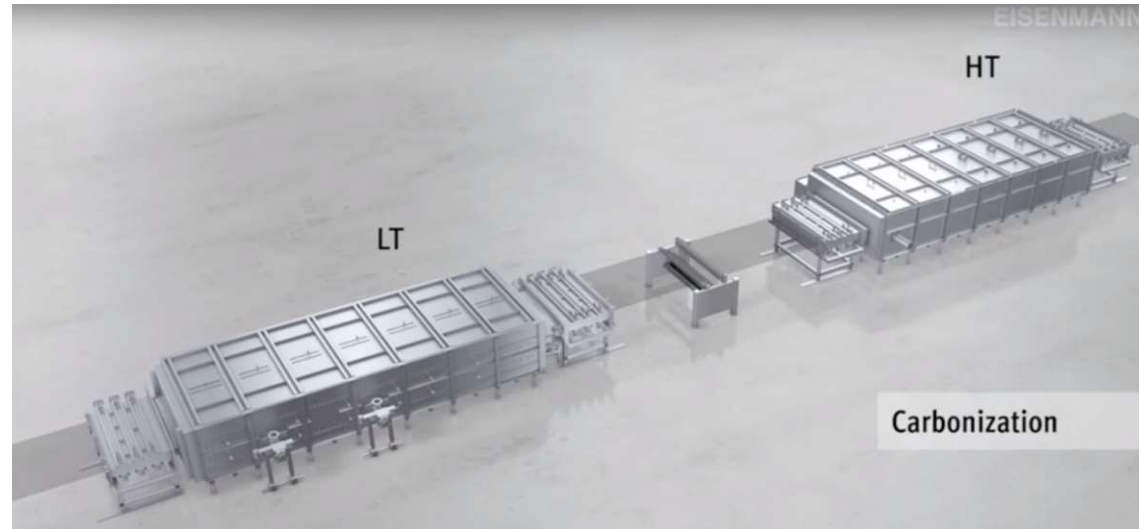
- Two furnaces to convert to carbon fiber

- LT

- Capable up to 800°C
- Steel muffle
- Electric or gas heat
- End seals
- Off gas connections
 - Heated
- Precise pressure control
- Atmosphere monitoring

- HT

- Capable up to 1,800°C
- Graphite construction
- Electric
- End seals
- Off gas connections
 - Heated
- Precise pressure control
- Atmosphere monitoring
 - Oxygen
 - Water
 - CO
- Water cooling for shell and cables



Carbon Fiber Process

- Surface treatment
 - Electrolysis method most common
 - Current drives the reaction
 - Electrolyte carries current to fiber
- Washing to remove electrolyte
 - Can react with sizing or matrix
 - Acid hydrolyzes epoxy
- Apply sizing
 - Coupling agent?
 - Matrix compatible
- Dry sizing
 - Typically done in hot air
- Wind
 - Good package build
 - Large as possible for prepreg creel



42

2 Precursors and Manufacturing of Carbon Fibers

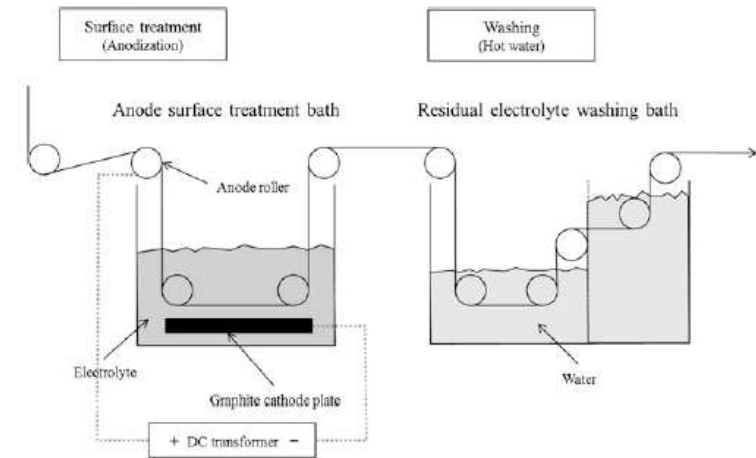
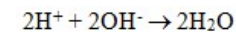
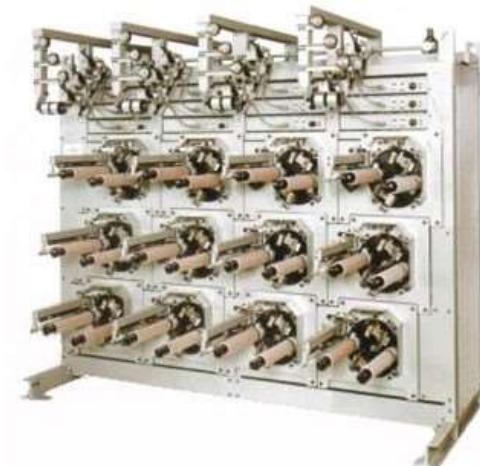
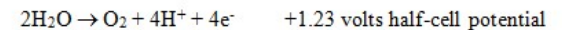


Fig. 2.7 Schematic of surface treatment and washing baths

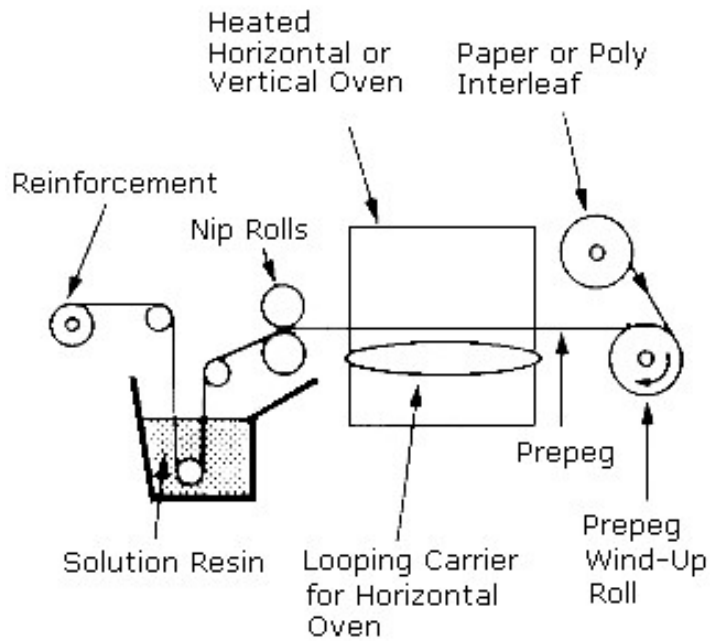
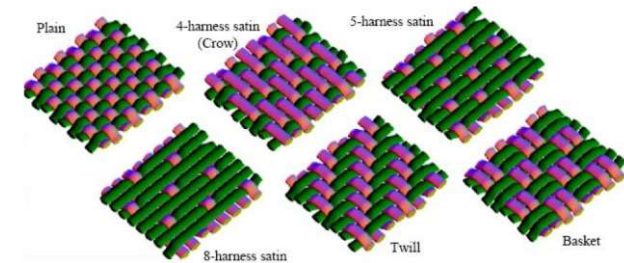
At the cathode:



At the anode:



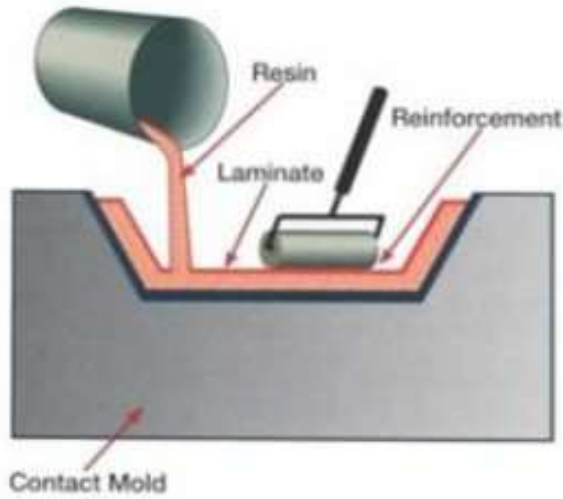
Weaving and Prepreg



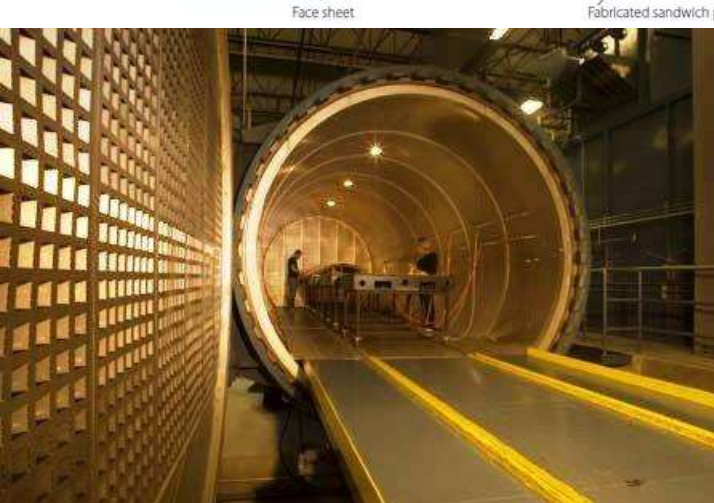
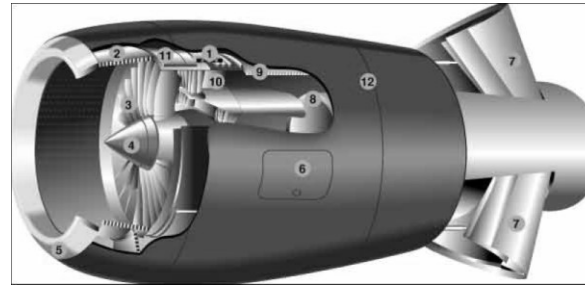
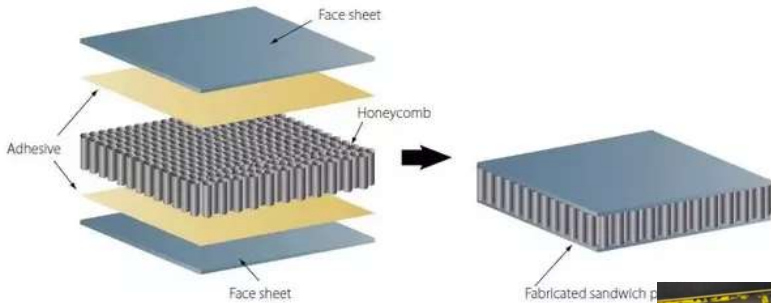
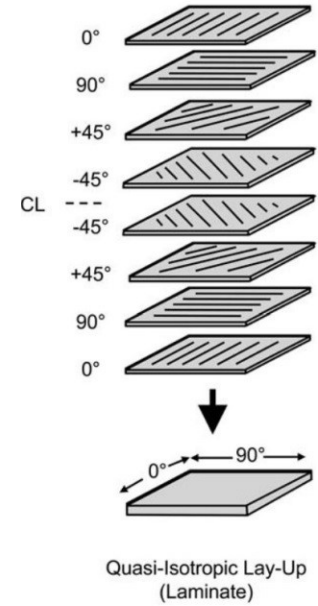
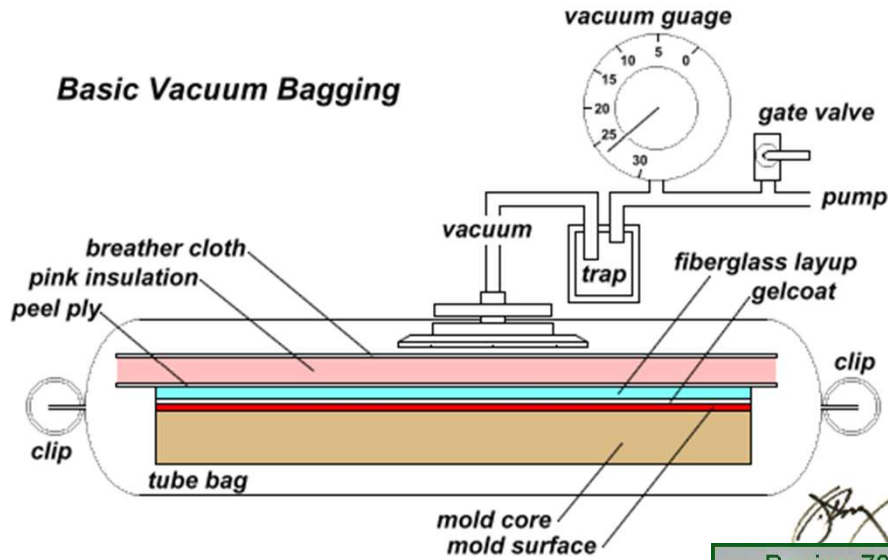
PREPREG PRODUCTION PROCESS

Making Parts

Hand Lay-Up



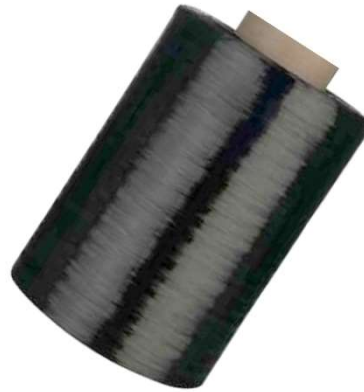
Basic Vacuum Bagging



CCF Carbon Fiber Products

GP1, GP2, GP3 PAN Fiber:

- T-300 3K, 6K, 12K
- T-650/35 3K, 6K, 12 K
- T-40/800



Rock Hill PAN Fiber:

- T-300 1K, 3K, 6K, 12 K
- T-650/35 3K, 6K
- T-40/800 6K, 12K

THORNEL® P25 Pitch and Resin B

THORNEL® P25 is a continuous pitch-based carbon fiber. THORNEL P25 is offered both with and without sizing. It is offered in both twisted and never-twisted forms. THORNEL® P25 is typically used on aircraft brakes.

Pitch Fiber

- P-25 2K, 4K
- GPC-10

THORNEL® T300 3K

Oxidation ovens, Carbonization Furnaces, Size Dryer

THORNEL® T300 3K is a standard modulus fiber supplied with epoxy-compatible sizing. It is offered in both twisted and never-twisted forms. THORNEL® T300 3K is used on secondary structures including aircraft flaps, slats, and spoilers.



