

Brief Overview of PMC Constituent Materials:

(a) Polymers(b) High-performance fibers



• The terms "plastics" and "polymers" are used interchangeably:

-"<u>Plastics</u>" from the Greek term "plastikos", meaning "capable of being shaped or molded" (not to be cunfused with "plastic deformation", the permanent change in shape caused by stresses above yielding)

- "Poly" from the Greek for "many"
 "Mers" from the Greek for "units"
 Polymer molecules have "many units"
- Polymers occur naturally (e.g., biological tissues, rubber, shellac, cellulose)
- First synthetic polymer was Bakelite, invented by Leo Baekland in 1907



- Scientific understanding of polymers evolved during the 1920s-30s, based largely on the work of William Carothers (Dupont); many polymers widely used today were developed during this time period:
 - Polystyrene
 - Polyvinyl chloride
 - Polyamides ("nylons")
 - Styrene-Butadeine Rubber (SBR)
- Understanding and use of polymers greatly expanded throughout the 1950s-60s (and continues today!)

"There's a great future in plastics," The Graduate (1967)





- The "mer" is the repeating unit in the polymer molecular chain
- For example, ethylene is the "mer" in "polyethylene":









• A few familiar polymer molecules:



Polytetraflouroethylene (Teflon; PTFE) lubricants, non-stick surfaces

Polyvinyl chloride (PVC) plumbing, structural plastics

Polypropylene (PP) fabrics, ropes, structural plastics





• The mer for polystyrene (often used to produce clear plastic cups):







• Many mers are more complex:



Polycarbonate Clear shatter-resistant plastic sheets





 Many mers may themselves be produced using other mers... a good example is "Nylon", used in a wide range of fabrics, gears, ropes, bushings...



Nylon 6



Nylon 6,6





 Many mers may themselves be produced using other mers... a good example is "Nylon", used in a wide range of fabrics, gears, ropes, bushings...



Nylon 6,10



Nylon 6,12



- "monomer" = a single mer
 "dimer" = two mers bonded together
 "trimer" = three mers bonded together
 "oligomer" = "a few" mers bonded together
 "polymer" = "many" mers bonded together
- "Degree of polymerization" (DP) = average number of mers in a molecular chain
- DPs from 1,000-5,000 is not uncommon:
 - polymer molecules are huge
 - polymers do not have a specific "molecular mass"...the DP depends on the polymerization process used....





-Fully polymerized molecules adopt a complex 3-D shape

-A bulk polymer sample is often compared to a bowl of cooked spaghetti



weight)

Three main types of polymer molecular structure





Fully polymerized thermoplastic vs. thermoset polymers

- Thermoplastic polymers (linear or branched) <u>can</u> be melted; thermoset polymers (crosslinked) <u>cannot</u> be melted
- At "low" temperatures, both thermoplastic and thermoset polymers are "glassy" solids
- As temperature is increased, both thermoplastic and thermoset polymers exhibit a characteristic "glass transition temperature" (T_g)...above the T_g the polymer is a "leathery" or "rubbery" solid (transition is more pronounced in thermoplastics than thermosets)
- As temperature is further increased:
 - Thermoplastic polymers *melt*
 - Thermosets further soften but *do not* melt
 - Both thermoplastics and thermosets are chemically destroyed if temperature increased too high





Constituents:

Polymer fundamentals



Some terms used to (approximately) describe the state of polymerization of a *thermoset*:

<u>A-stage</u>: an early stage in the polymerization process where few (or no) crosslinks have yet formed; resins typically low-viscosity fluid at room temperature

<u>B-stage</u>: an intermediate stage when resin is very viscous solid (or near-solid) at room temperature but softens and flows at elevated temperatures

<u>C-stage</u>: final stage of the polymerization process; resin fully crosslinked



Some terms used to describe the structure of thermoplastics

<u>Amorphous</u>: no longrange order (also applies to molecular structure of a thermoset)

<u>Semi-crystalline</u>: polymer chains aligned in an ordered way over a "long" distance





Some terms used to describe the structure of *thermoplastics*

A "<u>liquid crystal polymer</u>" (LCP) is a crystalline thermoplastic that maintains ordered (crystalline) regions in both solid and liquid form....



<u>Significant</u> confusion factor (especially for those of us who are not polymer chemists!):

- Some polymers can be produced as <u>either</u> a thermoplastic or thermoset
- Some thermoplastic polymers can be produced as:
 - Amorphous thermoplastic
 - Semi-crystalline thermoplastic
 - Liquid crystal thermoplastic
- prime example: polyester



Approximate T_g and T_m of polymers used in PMCs

Thermosets

```
TS Polyester (T_g \sim 300^\circ F)
Epoxy (T_g \sim 350^\circ F)
Bismaleimide (T_g > 450^\circ F)
Polyimide (T_q > 500^\circ F)
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Note: All temperatures approximate and depend on specific conditions used to polymerize the polymer....



- Characteristically, high-performance fibers:
 - Have small diameters (~5-30 μ m)
 - Exhibit high specific stiffness & specific strength (compared to structural metal alloys)

Specific stiffness =
$$\frac{E}{\rho}$$
 Specific strength = $\frac{\sigma^f}{\rho}$

- Are brittle (compared to structural metal alloys)







Advanced Materials in Transport Aircraft Structures

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- Three families of high performance fibers will be discussed:
 - Carbon/graphite fibers
 - Glass fibers
 - Aramid (Kevlar) fibers



<u>Warning</u>: the terms "carbon" and "graphite" are used in the next several slides.... depending on context, *these terms have different meanings*....

Constituents



- A few things about the element carbon
- Carbon (C) is the sixth element in the periodic table
- *Polymorphism* is the ability of a solid material to exist in more than one crystalline form
- There are several polymorphs of carbon; three polymorphs are diamond, graphite, and buckminsterfullerene (C₆₀)



(Y. Lu, University of Wisconsin)



- Both "carbon fibers" and "graphite fibers" are nearly pure carbon, arranged in the *graphite* crystalline structure (aside: structure of carbon nanotubes is similar to the buckminsterfullerene crystalline structure)
- Carbon (or graphite) fibers are commercially available with a wide range in mechanical properties



- In practice, the terms "carbon fibers" and "graphite fibers" are often used interchangeably
- A *suggested* standard definition:
 - "Graphite fiber" = fiber with carbon content > 95% (or 99%?)
 - "Carbon fiber" = fiber with carbon content < 95%</p>
- An alternate *suggested* standard definition is to refer to all forms as "carbon fibers", and to define:
 - Type I carbon fibers have higher modulus and lower strength
 - Type II carbon fibers have lower modulus and higher strength



- Graphite crystalline structure:
 - The "sheets" of carbon atoms are called "graphene"
 - Each C atom within graphene forms a covalent bond with 3 adjacent carbon atoms (results in hexagonal rings of C atoms)
 - Adjacent graphene sheets bonded by relatively weaker van der Waals forces
 - Graphene sheets define the socalled "basal plane" of the graphite crystalline structure
 - High fiber stiffness is achieved by aligning the basal plane with the fiber axis





<u>Graphitic graphite</u>: Closelypacked adjacent graphene sheets; sheet spacing 0.335 nm



<u>Turbostratic graphite</u>: Graphene sheets haphazardly packed; sheet spacing typically ~0.344 nm



Constituents

Carbon and Graphite Fibers



- In *high modulus* carbon fibers the structure is mostly graphitic graphite.
- In *low* and *intermediate* modulus fibers the structure is mostly turbostratic graphite.
- In either case the fiber is highly anisotropic (i.e., transverse stiffness/strength is much lower than axial stiffness/strength



- C = Core structure
- D = Defects (voids, irregular stacking, etc.)
- G = Graphite planes
- H = Highly oriented skin layer
- S = Stacked graphite planes



Processing

- Carbon fibers are manufactured from two types of precursors:
 - <u>Textile</u> precursors:
 Polyacrylonitrile (PAN) or
 rayon. PAN is the most
 common textile fiber precursor
 - <u>Pitch</u> precursors: Petroleum asphalt, coal tar. Pitch must first be converted to a suitable fiber.





Processing

- Preferential alignment of graphene layers with the fiber axis accomplished by
 - Orientation of polymer precursor by spinningstretching-drawing.
 - Orientation by stretching during graphitization.





- First produced in 1932
- Wide range of applications (insulation; electronics; textiles; reinforcements in concrete, ceramics and polymers)
- All glasses have an amorphous crystalline structure with no long-range order; hence glass fibers are *isotropic*



(chemical structure of standard plate glass)



- Eight types of glass fibers are commercially available (described in ASTM C 162)
 - In all cases greatest weight % is silica (SiO₂); various oxides added to provide specific properties in different fibers.
 - Only three types of glass fibers used in polymeric composites: E-glass, C-glass, and S-glass.



Composition of E-, S-, and C-glass fibers (ASTM C162)

	E-Glass	S-Glass	C-Glass
Oxide	weight % weight %		weight %
SiO ₂	52-56 64-66		64-68
AI_2O_3	12-16	24-25	3-5
B_2O_3	5-10		4-6
CaO	16-25	0-0.2	11-15
MgO	0-5	9.5-10	2-4
Na ₂ O + K ₂ O	0-2	0-0.2	7-10
Fe ₂ O ₃	0-0.8	0-0.1	0-0.8
F ₂	0-1		



- Raw materials blended to form a batch; melted in furnace; refined during gravity flow in forehearth Molten glass fed into a series of
- Molten glass fed into a series of platinum bushings; each has hundreds of holes in its base.
- Filaments drawn mechanically as glass extrudes through holes.





- Viscosity of glass (temperature)
- Diameter of holes in bushing
- Winding speed
- \bullet E-glass fiber diameter 8-15 μm



- Kevlar is an "aramid" fiber produced by the DuPont Co.
- Aramid is a generic name for a class of synthetic organic polymeric fibers (also called aromatic polyamide fibers)
- Repeat unit is called paraphenylene terephthalamide (PPT)





- A hydrogen bond (a type of van der Waals force) forms between H and O atoms in adjacent chains
- High fiber stiffness and strength achieved by aligning the molecular chains with fiber axis





- Kevlar fibers are anisotropic:
 - High axial stiffness/strength
 - Low transverse stiffness/strength
- Relatively good resistance to temperature, despite being a polymer:
 - Max temp (long term) ~300°F
 ~150°C
 - Decomposes (air) at ~800°F
 ~430°C





- (At least) eight grades of Kevlar fibers (with differing combinations of stiffness, strength, % elongation, cost, etc) are commercially available
- Kevlar 49 is probably most widely used in structural composite materials



Nominal properties of some common fibers

Fiber	Typical Diameter (μm)	Specific gravity	Tensile modulus, GPa (Msi)	Tensile strength, GPa (ksi)	Strain to failure, (%)	Coefficient of Thermal expansion (10 ⁻⁶ /°C)	Poisson's ratio
E-glass	10 (round)	2.54	72.4 (10.5)	3.4 (500)	4.8	5	0.2
PAN carbon T-300	7 (round)	1.76	231 (33.5)	3.65 (530)	1.4	-0.6 (longitudinal) 7 – 12 (radial)	0.2
Pitch carbon P-55	10	2.0	380 (55)	1.90 (275)	0.5	-1.3 (longitudinal)	
Aramid Kevlar 49	11.9 (round)	1.45	131 (19)	3.62 (525)	2.8	-2 (longitudinal) 59 (radial)	0.35

Constituents

High Performance Fibers



- All high performance fibers are commercially available as
 - Short (chopped) fibers
 - Roving spools (resembles a spool of thread); 2k, 4k, 6k, 12k, etc
 - Fabrics produced from roving:
 - Unidirectional
 - Woven
 - Braided





Constituents Some Common Fabrics





Unidirectional



Simple Weave



Crowfoot Satin Weave



1x1 Biaxial Bias Braid



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Constituents Unidirectional Fabric





Constituents Woven Fabric





http://www.nauticexpo.com/prod/nida-core-corporation/glass-fiber-fabric-multiaxial-27841-192139.html

Constituents Braided Fabric







Megabraiders (up to 800 carriers)



Braided Tubular Sleeves



Sleeves may be slit.....to produce various widths (A&P Technologies: www.braider.com) 47