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- What are the basic microstructural features of a polymer?
- How are polymer properties affected by molecular weight?
- How do polymeric materials accommodate the polymer chain?
- What are the primary polymer processing methods?

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- Originally many natural polymers were used
 - Wood Rubber
 - Cotton Wool
 - Leather Silk
- Oldest known uses of "Modern Polymers"
 - Rubber balls used by Incas
 - Noah used pitch (a natural polymer)
 for the ark as had all ancient mariners!

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Most polymers are hydrocarbons – i.e. made up of H and C (we also recognize Si bearing or 'silicone polymers')

- Saturated hydrocarbons
 - Each carbon bonded to four other atoms



Name	Composition	Structure	Boiling Point (°C)
Methane	$\rm CH_4$	$\mathbf{H} - \mathbf{H}$	-164
Ethane	C_2H_6	$\begin{array}{ccc} H & H \\ I & I \\ H - C - C - H \\ I & I \\ H & H \end{array}$	-88.6
Propane	C_3H_8	$\begin{array}{cccc} \mathrm{H} & \mathrm{H} & \mathrm{H} \\ \mathrm{I} & \mathrm{I} & \mathrm{I} \\ \mathrm{H} - \mathrm{C} - \mathrm{C} - \mathrm{C} - \mathrm{H} \\ \mathrm{I} & \mathrm{I} & \mathrm{I} \\ \mathrm{H} & \mathrm{H} & \mathrm{H} \end{array}$	-42.1
Butane	C_4H_{10}		-0.5
Pentane	$C_{5}H_{12}$		36.1
Hexane	C_6H_{14}		69.0

Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

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- Double & triple bonds somewhat unstable
- Thus, can form new bonds

- Double bond found in ethylene or ethene - C_2H_4



- Triple bond found in acetylene or ethyne - C_2H_2

Lvrp hulvp

- Isomerism
 - two compounds with same chemical formula can have quite different structures

Ex: C₈H₁₈

• n-octane

$$H_3C + CH_2 + CH_3$$

2-methyl-4-ethyl pentane (isooctane)

$$\begin{array}{c} \mathsf{CH}_3\\ \mathsf{H}_3\mathsf{C}-\mathsf{CH}-\mathsf{CH}_2-\mathsf{CH}-\mathsf{CH}_3\\ \mathsf{CH}_2\\ \mathsf{CH}_2\\ \mathsf{CH}_3\end{array}$$

Name	Composition	Structure	Boiling Point (°C)
Methane	CH_4	$\mathbf{H} - \mathbf{H} = \mathbf{H}$	-164
Ethane	C_2H_6	$\begin{array}{ccc} H & H \\ I & I \\ H - C - C - H \\ I & I \\ H & H \end{array}$	-88.6
Propane	C_3H_8	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-42.1
Butane	C_4H_{10}		-0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Table 4.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

Family	Characteristic Unit		Representative Compound
Alcohols	R-OH	$\mathbf{H} - \mathbf{C} - \mathbf{O} \mathbf{H}$	Methyl alcohol
Ethers	R = O = R'	$\begin{array}{c} H & H \\ I - C - O - C - H \\ I & I \\ H & H \end{array}$	Dimethyl ether
Acids		H - C - C + O H	Acetic acid
Aldehydes	\mathbf{R}	$\mathbf{C} = \mathbf{O}$	Formaldehyde
Aromatic hydrocarbons	R	OH	Phenol
^{<i>a</i>} The simplified structure [denotes a ph	enyl group, $H C C C$ H C C C	

Table 4.2 Some Common Hydrocarbon Groups



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• Covalent chain configurations and strength:



Direction of increasing strength

Linear polymers

- polymers in which the mer units are connected end-to-end along the whole length of the chain
- These types of polymers are often quite flexible
 - Van der waal's forces and H-bonding are the two main types of interactions between chains
 - Some examples polyethylene, teflon, PVC, polypropylene



Branched polymers

• Polymer chains can branch:



- Or the fibers may aligned parallel, as in fibers and some plastic sheets.
- chains off the main chain (backbone)
 - This leads to inability of chains to pack very closely together
 - » These polymers often have lower densities
 - These branches are usually a result of side-reactions during the polymerization of the main chain
 - Most linear polymers can also be made in branched forms

Crosslinked polymers

- Molecular structure
 - adjacent chains attached via covalent bonds
 - Carried out during polymerization or by a non-reversible reaction after synthesis (referred to as crosslinking)
 - Materials often behave very differently from linear polymers
 - Many "rubbery" polymers are crosslinked to modify their mechanical properties; in that case it is often called vulcanization
 - Generally, amorphous polymers are weak and cross-linking adds strength: vulcanized rubber is polyisoprene with sulphur cross-links:



Network polymers

- polymers that are "trifunctional" instead of bifunctional
- There are three points on the mer that can react
- This leads to three-dimensional connectivity of the polymer backbone
 - Highly crosslinked polymers can also be classified as network polymers
 - Examples: epoxies, phenol-formaldehyde polymers



Fkhp lvwu #ri#Srop huv

• Free radical polymerization



• Initiator: example - benzoyl peroxide



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Example: ethylene

- Gas at STP
- To *polymerize* ethylene, typically increase T, P and/or add an initiator



poly-ethylene

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- Polymers are chain molecules. They are built up from simple units called *monomers*.
- E.g. polyethylene is built from ethylene units:

$$-CH_2-CH_2$$

which are assembled into long chains:



Polyethylene or **polythene** (<u>IUPAC</u> name **poly(ethene)**) is a <u>thermoplastic</u> commodity heavily used in consumer products (notably the <u>plastic shopping</u> <u>bag</u>). Over 60 million tons of the material are produced worldwide every year.



Tetrafluoroethylene monomer polymerize to form PTFE or polytetrafluoroethylene





poly(tetrafluoroethene) or **poly(tetrafluoroethylene)** (**PTFE**) is a synthetic <u>fluoropolymer</u>. PTFE is the <u>DuPont</u> brand name <u>Teflon</u>. Melting: 327C

Vinyl chloride monomer leads to poly(vinyl chloride) or PVC

PVC: manufacturing toys, packaging, coating, parts in motor vehicles, office supplies, insulation, adhesive tapes, furniture, etc. Consumers: shoe soles, children's toys, handbags, luggage, seat coverings, etc. Industrial sectors: conveyor belts,



printing rollers. Electric and electronic equipment: circuit boards, cables, electrical boxes, computer housing.



OC OH

Note: polyethylene is a long-chain hydrocarbon - paraffin wax for candles is short polyethylene



Polymer chemistry

- In polyethylene (PE) synthesis, the monomer is ethylene
- Turns out one can use many different monomers
 - Different functional groups/chemical composition polymers have very different properties!



Homopolymer and Copolymer

- Polymer chemistry
 - If formed from one monomer (all the repeat units are the same type) – this is called a <u>homopolymer</u>
 - If formed from multiple types of monomers (all the repeat units are <u>not</u> the same type) this is called a <u>copolymer</u>
- Also note the monomers shown before are referred to as bifunctional
 - Why? The reactive bond that leads to polymerization (the C=C double bond in ethylene) can react with *two* other units
 - Other monomers react with more than two other units
 e.g. trifunctional monomers

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- Some of the original monomer's materials are shed (condensed out) during polymerization process thus the name: Step Process
- Process is (typically) conducted in the presence of a catalyst to speed up the 'stepping'
- Water or CO₂ are commonly condensed out but other compounds can be condensed out including HCN, HCl and other acids

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Kevlar is <u>synthesised</u> in solution from the <u>monomers</u>: 1,4-<u>phenylene</u>-di<u>amine</u> (<u>para-phenylenediamine</u>) and <u>terephthaloyl chloride</u> in a <u>condensation reaction</u> yielding <u>hydrochloric acid</u> as a byproduct.

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A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer		Repeat Unit	
	Polyethylene (PE)	$\begin{array}{ccc} {}^{\mathrm{H}} {}^{H$	
	Poly(vinyl chloride) (PVC)	$\begin{array}{ccc} H & H \\ & \\ -C - C - \\ & \\ H & CI \end{array}$	
	Polytetrafluoroethylene (PTFE)	$ \begin{array}{ccc} \mathbf{F} & \mathbf{F} \\ & \\ -\mathbf{C} - \mathbf{C} - \\ & \\ \mathbf{F} & \mathbf{F} \end{array} $	
	Polypropylene (PP)	$\begin{array}{ccc} H & H \\ & \\ -C - C - \\ & \\ H & CH_3 \end{array}$	



A Listing of Repeat Units for 10 of the More Common Polymeric Materials

A Listing of Repeat Units for 10 of the More Common Polymeric Materials



Material Type	Trade Names	Major Application Characteristics	Typical Applications
		Thermoplastics	
Acrylonitrile- butadiene- styrene (ABS)	Abson Cycolac Kralastic Lustran Novodur Tybrene	Outstanding strength and toughness, resistant to heat distortion; good electrical properties; flammable and soluble in some organic solvents	Refrigerator linings, lawn and garden equipment, toys, highway safety devices
Acrylics [poly(methyl methacrylate)]	Acrylite Diakon Lucite Plexiglas	Outstanding light transmission and resistance to weathering; only fair mechanical properties	Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs
Fluorocarbons (PTFE or TFE)	Teflon Fluon Halar Hostaflon TF Neoflon	Chemically inert in almost all environ- ments, excellent electrical properties; low coefficient of friction; may be used to 260°C (500°F); relatively weak and poor cold-flow properties	Anticorrosive seals, chemical pipes and valves, bearings, antiadhesive coatings, high- temperature electronic parts
Polyamides (nylons)	Nylon Baylon Durethan Herox Nomex Ultramid Zytel	Good mechanical strength, abrasion resistance, and toughness; low coef- ficient of friction; absorbs water and some other liquids	Bearings, gears, cams, bushings, handles, and jacketing for wires and cables
Polycarbonates	Calibre Iupilon Lexan Makrolon Merlon	Dimensionally stable; low water absorption; transparent; very good impact resistance and ductility; chemical resistance not outstanding	Safety helmets, lenses, light globes, base for photo- graphic film
Polyethylene	Alathon Alkathene Fortiflex Hi-fax Petrothene Rigidex Rotothene Zendel	Chemically resistant and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering	Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials

Material Type	Trade Names	Major Application Characteristics	Typical Applications
Polypropylene	Herculon Meraklon Poly-pro Pro-fax Propak Propathene	Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light	Sterilizable bottles, packaging film, TV cabinets, luggage
Polystyrene	Carinex Dylene Hostyren Lustrex Styron Vestyron	Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive	Wall tile, battery cases, toys, indoor lighting panels, appliance housings
Vinyls	Darvic Exon Geon Pliovic Saran Tygon Vista	Good low-cost, general-purpose materials; ordinarily rigid, but may be made flexible with plasticizers; often copolymerized; susceptible to heat distortion	Floor coverings, pipe, electrical wire insulation, garden hose, phonograph records
Polyester (PET or PETE)	Celanar Dacron Eastapak Hylar Melinex Mylar Petra	One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity, acids, greases, oils, and solvents	Magnetic recording tapes, clothing, automotive tire cords, beverage containers
		Thermosetting Polymers	
Epoxies	Araldite Epikote Epon Epi-rez Lekutherm Lytex	Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties	Electrical moldings, sinks, adhesives, protective coat- ings, used with fiberglass laminates
Phenolics	Bakelite Amberol Arofene Durite Resinox	Excellent thermal stability to over 150°C (300°F); may be compounded with a large number of resins, fillers, etc.; inexpensive	Motor housings, telephones, auto distributors, electrical fixtures
Polyesters	Aropol Baygal Derakane Laminac Selectron	Excellent electrical properties and low cost; can be formulated for room- or high-temperature use; often fiber rein- forced	Helmets, fiberglass boats, auto body components, chairs, fans

Source: Adapted from C. A. Harper (Editor), *Handbook of Plastics and Elastomers*. Copyright © 1975 by McGraw-Hill Book Company. Reproduced with permission.

Chemical Type	Trade (Common) Names	Elongation (%)	Useful Temperature Range [°C (°F)]	Major Application Characteristics	Typical Applications
Natural poly- isoprene	Natural rubber (NR)	500–760	-60 to 120 (-75 to 250)	Excellent physical proper- ties; good resistance to cutting, gouging, and abrasion; low heat, ozone, and oil resistance; good electrical properties	Pneumatic tires and tubes; heels and soles; gaskets
Styrene- butadiene copolymer	GRS, Buna S (SBR)	450–500	-60 to 120 (-75 to 250)	Good physical properties; excellent abrasion resis- tance; not oil, ozone, or weather resistant; elec- trical properties good, but not outstanding	Same as natural rubber
Acrylonitrile- butadiene copolymer	Buna A, Nitrile (NBR)	400–600	-50 to 150 (-60 to 300)	Excellent resistance to vegetable, animal, and petroleum oils; poor low-temperature proper- ties; electrical properties not outstanding	Gasoline, chemical, and oil hose; seals and O-rings; heels and soles
Chloroprene	Neoprene (CR)	100-800	-50 to 105 (-60 to 225)	Excellent ozone, heat, and weathering resistance; good oil resistance; ex- cellent flame resistance; not as good in electrical applications as natural rubber	Wire and cable; chem. tank linings; belts, hoses, seals, and gaskets
Polysiloxane	Silicone (VMQ)	100-800	-115 to 315 (-175 to 600)	Excellent resistance to high and low tempera- tures; low strength; excellent electrical properties	High- and low- temperature insula- tion; seals, diaphragms; tubing for food and med- ical uses

Sources: Adapted from C. A. Harper (Editor), *Handbook of Plastics and Elastomers*. Copyright © 1975 by McGraw-Hill Book Company, reproduced with permission; and Materials Engineering's *Materials Selector*, copyright Penton/IPC.

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Molecular weight, *M*: Mass of a mole of chains.







Not all chains in a polymer are of the same length i.e., there is a distribution of molecular weights

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- The properties of a polymer depend on its length
- synthesis yields polymer distribution of lengths
- Define "average" molecular weight
- Two approaches are typically taken
 - Number average molecular weight (M_n)
 - Weight-average molecular weight (M_w)



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Example: average mass of a class

N _i	<i>M</i> _i	X _i	W _i
# of students	mass (lb)		
1	100	0.1	0.054
1	120	0.1	0.065
2	140	0.2	0.151
3	180	0.3	0.290
2	220	0.2	0.237
1	380	0.1	0.204
		\overline{M}_n	\overline{M}_{w}
		186 lb	216 lb

 $M_n = \sum x_i M_i$

 $\overline{M}_{w} = \sum W_{i}M_{i}$



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n = number of repeat units per chain $H = \frac{H}{C} + \frac{H}{C}$

where m = average molecular weight of repeat unit

$$\overline{m} = \Sigma f_i m_i$$
Chain fraction \overline{m} mol. wt of repeat unit
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Conformation – Molecular orientation can be changed by rotation around the bonds – note: no bond breaking needed



Figure 12.8 The length of kinked molecular chain is given by Equation 12.4, due to the free rotation of the C—C—C bond angle of 109.5°.





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Configurations – to change must break bonds

• Stereoisomerism



Polymer Molecular Configurations

ĭ#Jhjxodulw|#dqg#v|pphwu|#ri#vlgh#jurxsv#diihfw#surshuwlhv



ĭ₩whuhrlvrp hulvp =#fdq#dgg#jhrp hwulf#vrp hulvp #vrr,



- Conversion from one stereoisomerism to another is *not* possible by simple rotation about single chain bond; bonds must be severed first, then reformed!

Polymer Geometrical Isomerism

ĭ#IJhjxodulw|#dqg#v|pphwu|#ri#vlgh#jurxsv#diihfw#surshuwlhv



cis-structure

trans-structure

with R= CH3to form rubberCis-polyisoprenetrans-polyisoprene

-Conversion from one *isomerism* to another is *not* possible by simple rotation about chain bond because double-bond is too rigid!

-See Figure 4.8 for taxonomy of polymer structures

Tacticity

Tacticity – stereoregularity of chain



cis/trans Isomerism





cis-isoprene (natural rubber)

bulky groups on same side of chain



trans

trans-isoprene (gutta percha)

bulky groups on opposite sides of chain

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two or more monomers polymerized together

A –

- random A and B randomly vary in chain
- alternating A and B alternate in polymer chain
- block large blocks of A alternate with large blocks of B
- graft chains of B grafted on to A backbone

B –



Thermoplastics vs. Thermosets

- Thermoplastics:
 - -- little crosslinking
 - -- ductile
 - -- soften w/heating
 - -- polyethylene polypropylene polycarbonate polystyrene



• Thermosets:

- -- large crosslinking (10 to 50% of mers)
- -- hard and brittle
- -- do NOT soften w/heating
- -- vulcanized rubber, epoxies, polyester resin, phenolic resin

Adapted from Fig. 15.19, *Callister 7e.* (Fig. 15.19 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

Polymer Additives

Improve mechanical properties, processability, durability, etc.

- Fillers
 - Added to improve tensile strength & abrasion resistance, toughness & decrease cost
 - ex: carbon black, silica gel, wood flour, glass, limestone, talc, etc.
- Plasticizers
 - Added to reduce the glass transition temperature T_{α}
 - commonly added to PVC otherwise it is brittle

Polymer Additives

- Stabilizers
 - Antioxidants
 - UV protectants
- Lubricants
 - Added to allow easier processing
 - "slides" through dies easier ex: Na stearate
- Colorants
 - Dyes or pigments
- Flame Retardants
 - CI/F & B

Polymer Types: Elastomers

Elastomers – rubber

- Crosslinked materials
 - Natural rubber
 - Synthetic rubber and thermoplastic elastomers

SBR- styrene-butadiene rubber

styrene



Polymer Types: Fibers

Fibers - length/diameter >100

- Textiles are main use
 - Must have high tensile strength
 - Usually highly crystalline & highly polar
- Formed by spinning
 - ex: extrude polymer through a spinnerette
 - Pt plate with 1000's of holes for nylon
 - ex: rayon dissolved in solvent then pumped through die head to make fibers
 - the fibers are drawn
 - leads to highly aligned chains- fibrillar structure

Polymer Types

- Coatings thin film on surface i.e. paint, varnish
 - To protect item
 - Improve appearance
 - Electrical insulation
- Adhesives produce bond between two adherands
 - Usually bonded by:
 - 1. Secondary bonds
 - 2. Mechanical bonding
- Films blown film extrusion
- Foams gas bubbles in plastic

Processing of Plastics

- Thermoplastic -
 - can be reversibly cooled & reheated, i.e. recycled
 - heat till soft, shape as desired, then cool
 - ex: polyethylene, polypropylene, polystyrene, etc.
- Thermoset
 - when heated forms a network
 - degrades (not melts) when heated
 - mold the prepolymer then allow further reaction
 - ex: urethane, epoxy

Processing Plastics - Molding

- Compression and transfer molding
 - thermoplastic or thermoset



Processing Plastics - Molding

- Injection molding
 - thermoplastic & some thermosets





Processing Plastics – Extrusion



Encyclopædia Britannica, 1997.)

Blown-Film Extrusion



(from Encyclopædia Britannica, 1997.)

TABLE 12.10

The Relationship of Processing, Molecular Structure, and Mechanical Behavior for Polymers

Category	Processing technique	Molecular structure	Mechanical effect
Thermoplastic polymers	Addition agent	Branching	Increased strength and stiffness
	Vulcanization	Cross-linking	Increased strength and stiffness
	Crystallization	Increased crystallinity	Increased strength and stiffness
	Plasticizer	Decreased molecular weight	Decreased strength and stiffness
	Filler	Restricted chain mobility	Increased strength and stiffness
Thermosetting polymers	Setting at elevated temperatures	Network formation	Rigid (remaining upon cooling)

Advanced Polymers

- Ultrahigh molecular weight polyethylene (UHMWPE)
 - Molecular weight ca. 4 x 10⁶ g/mol
 - Excellent properties for variety of applications
 - bullet-proof vest, golf ball covers, hip joints, etc.





The Stem, femoral head, and the AC socket are made from Cobalt-chrome metal alloy or ceramic, AC cup made from polyethylene

ABS – A Polymerized "Alloy"

ABS, Acrylonitrile-Butadiene-Styrene

Made up of the 3 materials: acrylonitrile, butadiene and styrene. The material is located under the group styrene plastic. Styrene plastics are in volume one of the most used plastics.

Properties

The mechanical properties for ABS are good for impact resistance even in low temperatures. The material is stiff, and the properties are kept over a wide temperature range. The hardness and stiffness for ABS is lower than for PS and PVC.

Weather and chemical resistance

The weather resistance for ABS is restricted, but can be drastically improved by additives as black pigments. The chemical resistance for ABS is relatively good and it is not affected by water, non organic salts, acids and basic. The material will dissolve in aldehyde, ketone, ester and some chlorinated hydrocarbons.

Processing

ABS can be processed by standard mechanical tools as used for machining of metals and wood. The cutting speed need to be high and the cutting tools has to be sharp. Cooling is recommended to avoid melting of the material. If the surface finish is of importance for the product, the ABS can be treated with varnish, chromium plated or doubled by a layer of acrylic or polyester. ABS can be glued to it self by use of a glue containing dissolvent. Polyurethane based or epoxy based glue can be used for gluing to other materials.

A Processing Movie:



Summary - Polymers

- General drawbacks to polymers:
 - -- E, σ_y , K_c , $T_{application}$ are generally small.
 - -- Deformation is often *T* and time dependent.
 - -- Result: polymers benefit from composite reinforcement.
- Thermoplastics (PE, PS, PP, PC):
 - -- Smaller *E*, σ_y , *T*_{application}
 - -- Larger K_c
 - -- Easier to form and recycle
- Elastomers (rubber):
 Large reversible strains!
- Thermosets (epoxies, polyesters):
 - -- Larger *E*, σ_y , *T*_{application}
 - -- Smaller Kc

Composites:

- A Composite material is a material system composed of two or more macro constituents that differ in shape and chemical composition and which are insoluble in each other. The history of composite materials dates back to early 20th century. In 1940, fiber glass was first used to reinforce epoxy.
- Applications:
 - Aerospace industry
 - Sporting Goods Industry
 - Automotive Industry
 - Home Appliance Industry

Advanced Aerospace Application:

Boeing 767 (and in 777, 787 airplanes w/ the latest, full wing box is composite):



Figure 12.22 A bar graph plot of the data of Table 12.8 illustrates the substantial increase in specific strength (strength-toweight ratio) possible with composites.



Terminology/Classification

- Composites:
 - -- Multiphase material w/significant proportions of each phase.
- Matrix
 - -- The continuous phase
 - -- Purpose is to:
 - transfer stress to other phases
 - protect phases from environment
 - -- Classification: MMC, CMC, PMC

metal ceramic polymer

- Dispersed phase:
 - Purpose: enhance matrix properties.
 MMC: increase σ_y, *TS*, creep resist.
 CMC: increase K_c
 PMC: increase E, σ_y, *TS*, creep resist.
 - -- Classification: Particle, fiber, structural



Reprinted with permission from D. Hull and T.W. Clyne, *An Introduction to Composite Materials*, 2nd ed., Cambridge University Press, New York, 1996, Fig. 3.6, p. 47.

TABLE 12.2

Polymeric Matrix Materials for Fiberglass			
Polymer	Characteristics and applications		
Thermosetting			
Epoxies	High strength (for filament-wound vessels)		
Polyesters	For general structures (usually fabric reinforced)		
Phenolics	High-temperature applications		
Silicones	Electrical applications (e.g., printed-circuit panels)		
Thermoplastic			
Nylon 66			
Polycarbonate	Less common, especially good ductility		
Polystyrene			

Source: Data from L. J. Broutman and R. H. Krock, Eds., Modern Composite Materials, Addison-Wesley Publishing Co., Inc., Reading, MA, 1967, Chapter 13.

TABLE 12.3

Advanced	Composite	Systems	Other Than	Fiberglass
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Class	Fiber/Matrix		
Polymer matrix	Para-aramid (Kevlar ^a)/epoxy Para-aramid (Kevlar ^a)/polyester C (graphite)/epoxy C (graphite)/polyester C (graphite)/polyetheretherketone (PEEK) C (graphite)/polyphenylene sulfide (PPS)		
Metal matrix	B/A1 C/A1 Al ₂ O ₃ /A1 Al ₂ O ₃ /Mg SiC/A1 SiC/Ti (alloys)		
Ceramic matrix	Nb/MoSi ₂ C/C C/SiC SiC/Al ₂ O ₃ SiC/SiC SiC/Si3N ₄ SiC/Li–Al–silicate (glass-ceramic)		

^aTrade name, Du Pont.

Source: Data from K. K. Chawla, University of Alabama, Birmingham; A. K. Dhingra, the Du Pont Company; and A. J. Klein, ASM International.

Composite Survey



Composite Benefits



TABLE 12.7

Mechanical Properties of Common Composite Systems

Class	E [MPa (ksi)]	T.S. [MPa (ksi)]	Flexural strength [MPa (ksi)]	Compressive strength [MPa (ksi)]	Percent elongation at failure	$K_{ m IC}^{ m a}$ (MPa $\sqrt{ m m}$)
Polymer-matrix						
E-glass (73.3 vol %) in epoxy (parallel loading of continuous fibers) ^b	$56\times 10^3 (8.1\times 10^3)$	1,640 (238)	-	9 8-13	2.9	42-60
Al ₂ O ₃ whiskers (14 vol %) in epoxy ^b	$41 \times 10^3 (6 \times 10^3)$	779 (113)				
C (67 vol %) in epoxy (parallel loading) ^c	$221 \times 10^3 (32 \times 10^3)$	1,206 (175)	2 <u>7 - 7</u> 4	9 1 - 51		2 1 - 11
Kevlar ^d (82 vol %) in epoxy (parallel loading) ^c	$86\times 10^3 (12\times 10^3)$	1,517 (220)				
B (70 vol %) in epoxy (parallel loading of continuous filaments) ^b	$210-280 \times 10^{3}$ (30-40 × 10 ³) ^c	1,400–2,100 (200–300)°		9 8-33		46
Metal matrix						
Al ₂ O ₃ (10 vol %) dispersion- strengthened aluminum ^b	20	330 (48)		9 8-33		9 8-33
W (50 vol %) in copper (parallel loading of continuous filaments) ^b	$260\times10^3(38\times10^3)$	1,100 (160)	-	—	-	
W particles (50 vol %) in copper ^b	$190 \times 10^3 (27 \times 10^3)$	380 (55)	2 <u>1</u>	3 <u></u>	<u>1010</u>	
Ceramic-matrix						
SiC whiskers in Al ₂ O ^e ₃	9 7 - 73	17 17	800 (116)	95-53		8.7
SiC fibers in SiC ^e	1 <u>1-22</u>	3214	750 (109)	2 <u>12 - 221</u>		25.0
SiC whiskers in reaction-bonded $Si_3N_4^e$	8	1 	900 (131)	10 1		20.0

^aSource: Data from M. F. Ashby and D. R. H. Jones, *Engineering Materials—An Introduction to Their Properties and Applications*, Pergamon Press, Inc., Elmsford, NY, 1980. ^bL. J. Broutman and R. H. Krock, Eds., *Modern Composite Materials*, Addison-Wesley Publishing Co., Inc., Reading, MA, 1967.

^cA. K. Dhingra, Du Pont Company.

^dTrade name, Du Pont.

^eA. J. Klein, Advanced Materials and Processes 2, 26 (1986).
Composite Survey: Particle-I



Composite Survey: Particle-II

Particle-reinforced

Fiber-reinforced

Structural

Concrete – gravel + sand + cement

- Why sand and gravel? Sand packs into gravel voids

Reinforced concrete - Reinforce with steel rebar or remesh

- increases strength - even if cement matrix is cracked

Prestressed concrete - remesh under tension during setting of concrete. Tension release puts concrete under compressive force

- Concrete much stronger under compression.
- Applied tension must exceed compressive force

Post tensioning – tighten nuts to put under rod under tension but concrete under compression





- Application to other properties:
 - -- Electrical conductivity, σ_e : Replace *E* in the above equations with σ_e .
 - -- Thermal conductivity, k: Replace E in above equations with k.



- Fibers themselves are very strong
 - Provide significant strength improvement to material
 - Ex: fiber-glass
 - Continuous glass filaments in a polymer matrix
 - Strength due to fibers
 - Polymer simply holds them in place and environmentally protects them

Composite Survey: Fiber

Particle-reinforced Fiber-reinforced

Structural

Fiber Materials

- Whiskers Thin single crystals large length to diameter ratio
 - graphite, SiN, SiC
 - high crystal perfection extremely strong, strongest known materials!
 - very expensive
 - Fibers
 - polycrystalline or amorphous
 - generally polymers or ceramics
 - Ex: Al₂O₃, Aramid, E-glass, Boron, UHMWPE
 - Wires
 - Metal steel, Mo, W

Fiber Loading Effect under Stress:



Composite Survey: Fiber



• Ex: **For fiberglass**, a fiber length > 15 mm is needed since this length provides a "Continuous fiber" based on *usual glass fiber properties*



Fiber Load Behavior under Stress:



Behavior under load for Fibers & Matrix





Composite Strength: Longitudinal Loading

- Continuous fibers Estimate fiber-reinforced composite strength for long continuous fibers in a matrix
- Longitudinal deformation

$$\sigma_{c} = \sigma_{m} V_{m} + \sigma_{f} V_{f}$$

•

 $\varepsilon_c = \varepsilon_m = \varepsilon_f$ isostrain

$$E_{ce} = E_m V_m + E_f V_f$$

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m}$$

longitudinal (extensional) modulus

f = fiberm = matrix Remembering: $E = \sigma/\epsilon$ and note, this model corresponds to the "upper bound" for particulate composites



Composite Strength: Transverse Loading

• In transverse loading the fibers carry less of the load and are in a state of 'isostress'

$$\sigma_c = \sigma_m = \sigma_f = \sigma \qquad \varepsilon_c = \varepsilon_m V_m + \varepsilon_f V_f$$



transverse modulus

Remembering: E = σ/ϵ and note, this model corresponds to the "lower bound" for particulate composites

An Example:

Example: Given an epoxy/carbon unidirectional continuous fiber composite with $V_f = .60$ and the following fiber and matrix properties:

	Ultimate Strength o _u psi	Modulus E _L psi	UTS, SI	Modulus, SI
Ероху	$\sigma_{som} = 8400$	$E_m = 550,000$	57.9 MPa	3.8 GPa
Carbon Fibers	$\sigma_{\rm uf} = 305,000$	$E_f = 58,000,000$	2.4 GPa	399.9 GPa

a) Calculate the longitudinal stiffness (moduli) of the composite (E_{eL}) :

$$E_{cL} = E_f V_f + E_{nL} V_n = 58,000,000(.60) + 550,000(.40) = 35,020,000 \text{ psi}$$
 (241.5 GPa)

b) Calculate the transverse stiffness (moduli) of the composite (E_{eT}) :

$$E_{cT} = \frac{E_f E_m}{V_f (E_m - E_f) + E_f} = \frac{58,000,000 \cdot 550,000}{.60(550,000 - 58,000,000) + 58,000,000} = 1,355,716 \text{ psi}$$
(9.34 GPa)

The transverse moduli ($E_{cT} = 1,355,716$ psi) is only 3.9% of the longitudinal moduli ($E_{cL} = 35,020,000$ psi).

Note: 6870 N/m² (pascal) per psi!

Composite Strength

Particle-reinforced

Fiber-reinforced

- Structural
- Estimate of *Ec* and *TS* for **discontinuous** fibers:
 - -- valid when fiber length > $15 \frac{\sigma_f d}{\tau_c}$
 - -- Elastic modulus in fiber direction:

 $E_c = E_m V_m + K E_f V_f$

efficiency factor:

- -- aligned 1D: K = 1 (aligned ||)
- -- aligned 1D: K = 0 (aligned \perp)
- -- random 2D: *K* = 3/8 (2D isotropy)
- -- random 3D: K = 1/5 (3D isotropy)
- -- *TS* in fiber direction:

 $(TS)_c = (TS)_m V_m + (TS)_f V_f$

From: H. Krenchel, *Fibre Reinforcement*, Copenhagen: Akademisk Forlag, 1964.

(aligned 1D)

Looking at strength:

$$l > l_{C}$$

$$\sigma_{cd}^{*} = \sigma_{f}^{*} V_{f} \left(1 - \frac{l_{C}}{2l} \right) + \sigma_{m}^{'} \left(1 - V_{f} \right)$$

where σ_{f}^{*} is fiber fracture strength & $\sigma_{m}^{'}$ is matrix stress when composite fails $l < l_{C}$ $\sigma_{cd'}^{*} = \frac{l\tau_{C}}{d}V_{f} + \sigma_{m}^{'}(1-V_{f})$

where: d is fiber diameter &

 au_c is smaller of Matrix Fiber shear strength or matrix shear yield strength

Composite Survey: Structural



Composite Manufacturing Processes

- Particulate Methods: Sintering
- Fiber reinforced: Several
- Structural: Usually Hand lay-up and atmospheric curing or vacuum curing



Irwin/McGraw-Hill

Open Mold Processes

Only one mold (male or female) is needed and may be made of any material such as wood, reinforced plastic or , for longer runs, sheet metal or electroformed nickel. The final part is usually very smooth.

Shaping. Steps that may be taken for high quality

- 1. Mold release agent (silicone, polyvinyl alcohol, fluorocarbon, or sometimes, plastic film) is first applied.
- 2. Unreinforced surface layer (gel coat) may be deposited for best surface quality.

Hand Lay-Up: The resin and fiber (or pieces cut from prepreg) are placed manually, air is expelled with squeegees and if necessary, multiple layers are built up.

- · Hardening is at room temperature but may be improved by heating.
- Void volume is typically 1%.
- Foam cores may be incorporated (and left in the part) for greater shape complexity. Thus essentially all shapes can be produced.
- Process is slow (deposition rate around 1 kg/h) and labor-intensive
- Quality is highly dependent on operator skill.
- Extensively used for products such as airframe components, boats, truck bodies, tanks, swimming pools, and ducts.

SPRAY-UP MOLDING

A spray gun supplying resin in two converging streams into which roving is chopped

- · Automation with robots results in highly reproducible production
- · Labor costs are lower



Tape-Laying Machines (Automated Lay-Up)

Cut and lay the ply or prepreg under computer control and without tension; may allow reentrant shapes to be made.

- · Cost is about half of hand lay-up
- Extensively used for products such as airframe components, boats, truck bodies, tanks, swimming pools, and ducts.



PREPREG PRODUCTION PROCESSES

- Prepreg is the composite industry's term for continuous fiber reinforcement pre-impregnated with a polymer resin that is only partially cured.
- Prepreg is delivered in tape form to the manufacturer who then molds and fully cures the product without having to add any resin.
- * This is the composite form most widely used for structural applications

PrePreg Process

- Manufacturing begins by collimating a series of spool-wound continuous fiber tows.
- Tows are then sandwiched and pressed between sheets of release and carrier paper using heated rollers (calendering).
- The release paper sheet has been coated with a thin film of heated resin solution to assure thorough impregnation of the fibers.

PrePreg Process

- The final prepreg product is a thin tape consisting of continuous and aligned fibers embedded in a partially cured resin
- Prepared for packaging by winding onto a cardboard core.
- Typical tape thicknesses range between 0.08 and 0.25 mm
- Tape widths range between 25 and 1525 mm.
- Resin content lies between about 35 and 45 vol%

PrePreg Process

- The prepreg is stored at 0°C (32 °F) or lower because matrix undergoes curing reactions at room temperature. Also the time in use at room temperature must be minimized. Life time is about 6 months if properly handled.
- * Both thermoplastic and thermosetting resins are utilized: carbon, glass, and aramid fibers are the common reinforcements.
- Actual fabrication begins with the lay-up. Normally a number of plies are laid up to provide the desired thickness.
- * The lay-up can be by hand or automated.

- Filament Winding
 - Ex: pressure tanks
 - Continuous filaments wound onto mandrel



Filament Winding Characteristics

- * Because of the tension, only relatively simple shapes can be produced.
- CNC winding machines with several degrees of freedom (sometimes 7) are frequently employed.
- * The filament (or tape, tow, or band) is either precoated with the polymer or is drawn through a polymer bath so that it picks up polymer on its way to the winder.
- Void volume can be higher (3%)
- The cost is about half that of tape laying
- * Productivity is high (50 kg/h).
- Applications include: fabrication of composite pipes, tanks, and pressure vessels. Carbon fiber reinforced rocket motor cases used for Space Shuttle and other rockets are made this way.

Composite Production Methods:

Pultrusion

 Continuous fibers pulled through resin tank, then into preforming die & oven to cure



- Production rates around 1 m/min.
- Applications are to sporting goods (golf club shafts), vehicle drive shafts (because of the high damping capacity), nonconductive ladder rails for electrical service, and structural members for vehicle and aerospace applications.

Summary: Composites

- Composites are classified according to:
 - -- the matrix material (CMC, MMC, PMC)
 - -- the reinforcement geometry (particles, fibers, layers).
- Composites enhance matrix properties:
 - -- MMC: enhance σ_y , *TS*, creep performance
 - -- CMC: enhance K_c
 - -- PMC: enhance E, σ_y , TS, creep performance
- Particulate-reinforced:
 - -- Elastic modulii can be estimated.
 - -- Properties are isotropic.
- Fiber-reinforced:
 - -- Elastic modulus and *TS* can be estimated wrt fiber dir.
 - -- Properties can be isotropic or anisotropic.
- Structural:
 - -- Based on build-up of sandwiches in layered form.

Summary

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- ŬWkh‡pruh‡Šoxps|õ#dqg≢eudqfkhgwkh#sro|phu/#wkh#bhvv# ghqvh#dqg#bhvv#fu|vwdoodqh1
- Wkh#pruh#urvvolqnlqjwkh#wilihuwkh#srophul#pqg/#
 qhwzrunhgsrophuv#duh#onh#khdylop#urvvolqnhg#rqhv1
- Pdq #rqj0fkdlqhg#srop huv#u vwd@l>h#z lwk#d#vskhuxdwh# p lfurvwuxfwxuh 0udgldd#u vwd@lwhv#vhsdudwhg#e |# dp ruskrxv#uhjlrqv1
- ^{*} R swlfdd#surshuwlhv=##u|vwdodqh#A#vfdwwhu#djkw#Eudjj, dp ruskrxv#A#wdqvsduhqwl P rvw#ryddhqwp rdhfxdhv#devrue#djkw#*rxwlgh#ylvledh#vshfwxp /*# h1j1#SPPD#cxflwh,#v#d#kljk#cdulw|#wdqsduhqwp dwhuldov1