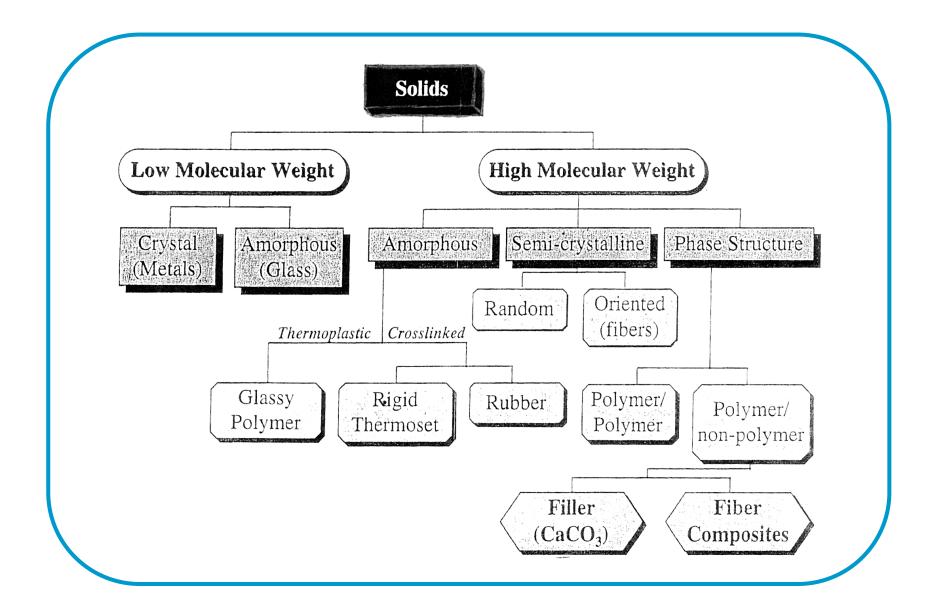
# Composite Materials

ALL REAL PROPERTY.

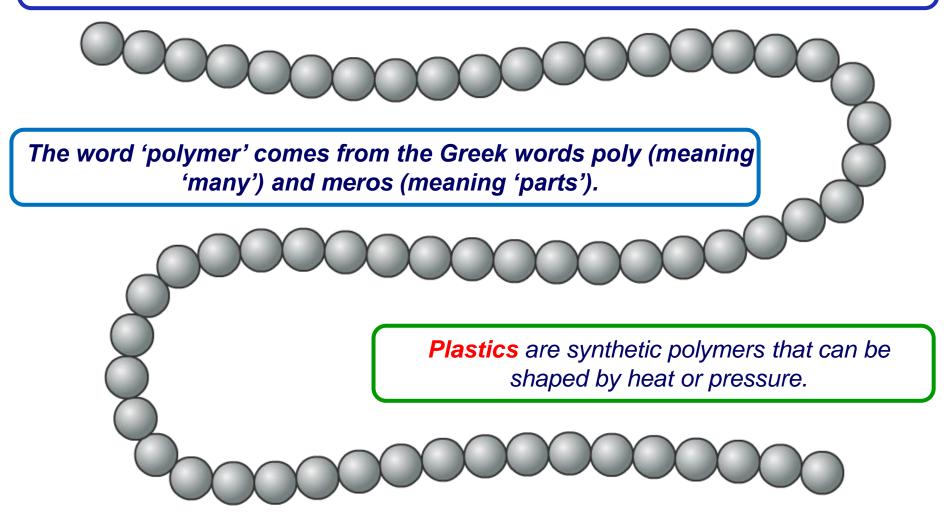
Polymer Matrix Composites and Polymer Basics

### Polymers



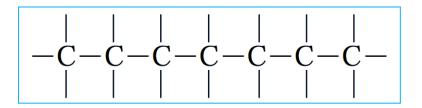
#### POLYMERS

**Polymers** are very large molecules made when hundreds of monomers join together to form long chains.



#### POLYMERS

- The molecules in polymers are gigantic in comparison to the hydrocarbon molecules, because of their size they are often referred to as macromolecules.
- Within each molecule, the atoms are bound together by covalent interatomic bonds. For most polymers, these molecules are in the form of long and flexible chains, the backbone of which is a string of carbon atoms; many times each carbon atom singly bonds to two adjacent carbons atoms on either side, represented schematically in two dimensions as follows:



#### **Polymer Classification**

#### Polymers (a)natural and (b) synthetic

*Naturally occurring polymers*—those derived from plants and animals—have been used for many centuries; these materials include lignin, rubber, hair, nails, skin, cotton, wool, leather, and silk.

Other natural polymers such as proteins, enzymes, starches, collagen and cellulose are important in biological and physiological processes in plants and animals.

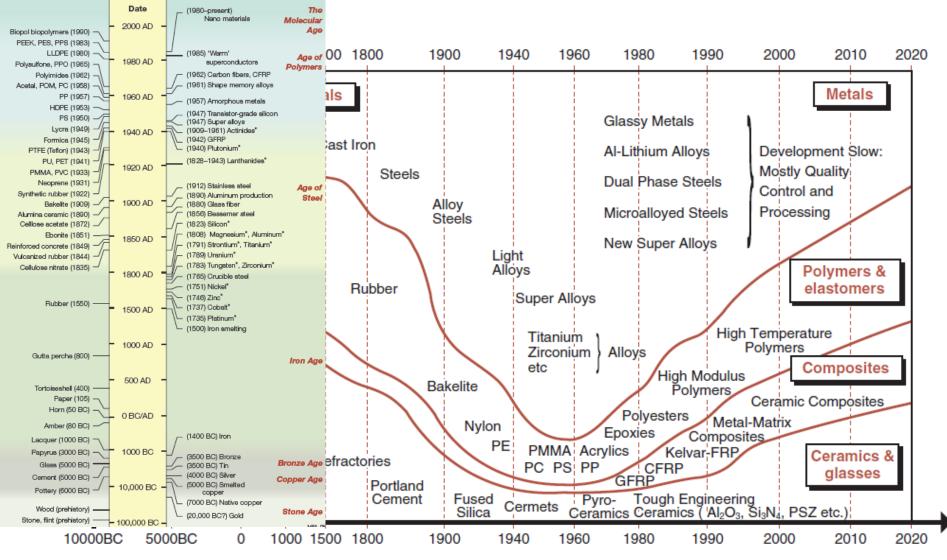
# **Polymer Classification**

Modern scientific research tools have made possible the determination of the molecular structures of this group of materials, and the development of numerous polymers, which are synthesized from small organic molecules.

Many of our useful plastics, rubbers, and fiber materials are synthetic polymers. In fact, since the conclusion of World War II, the field of materials has been virtually revolutionized by the advent of synthetic polymers.

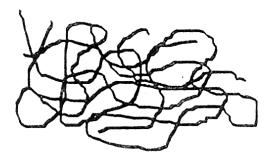
The synthetics can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts. In some applications metal and wood parts have been replaced by plastics, which have satisfactory properties and may be produced at a lower cost.

#### **Historical Evolution**



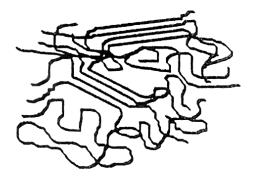
DATE

#### Microstructure



#### Amorphous

natural rubber polycarbonate (PC) acrylonitrile-butadiene-styrene (ABS) polystyrene



#### Semi-crystalline

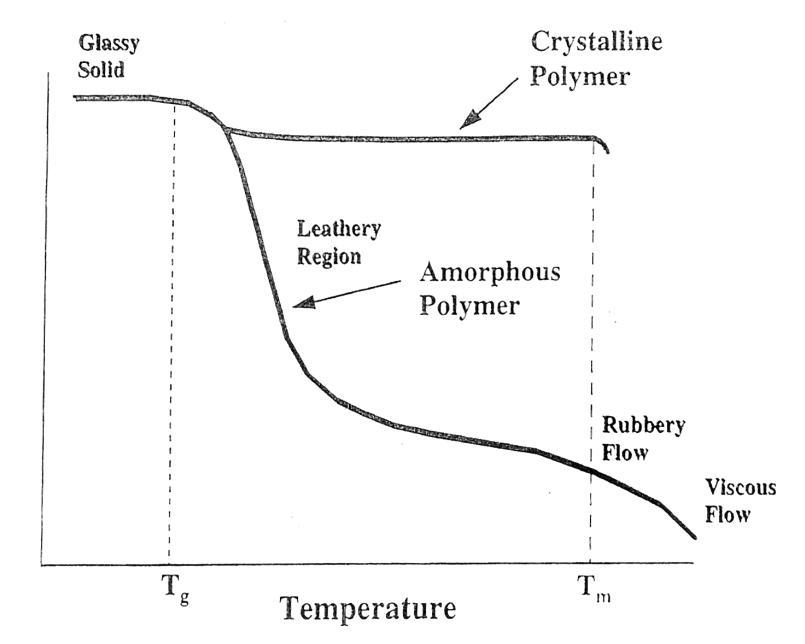
polyamide polyethylene terephthalate (PET) nylon



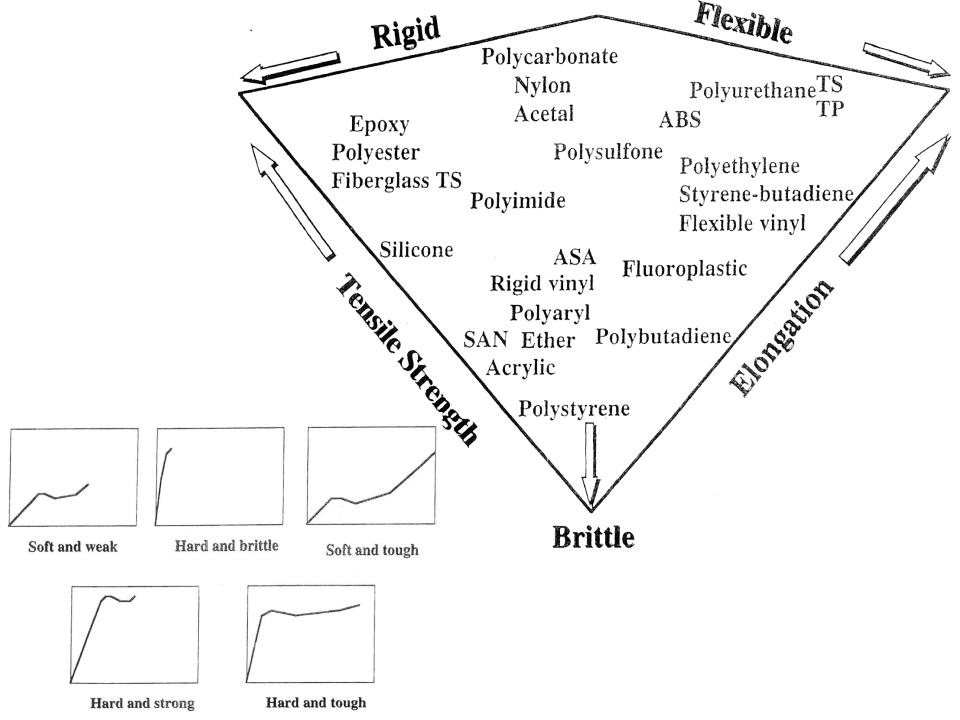
#### Crystalline

linear polyethylene polypropylene

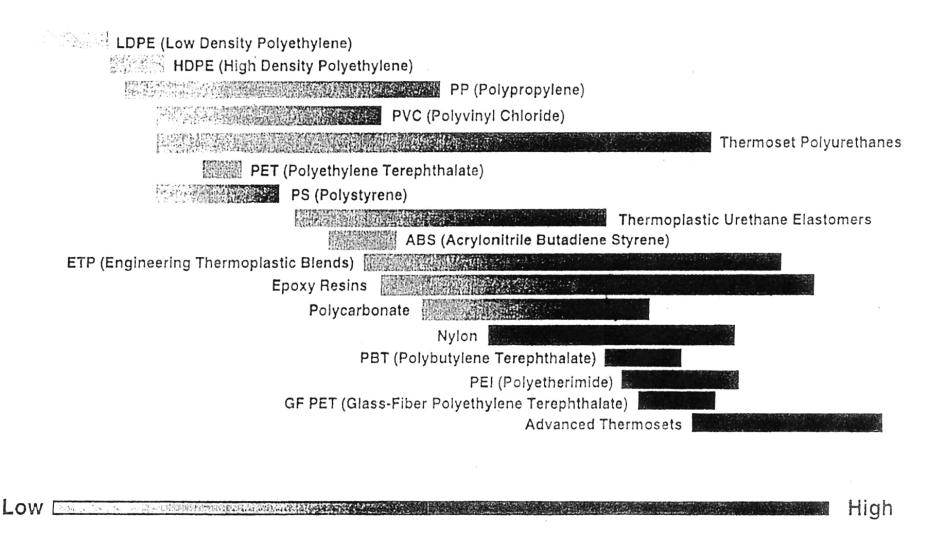
#### **Properties**



log (E)



# **Properties**

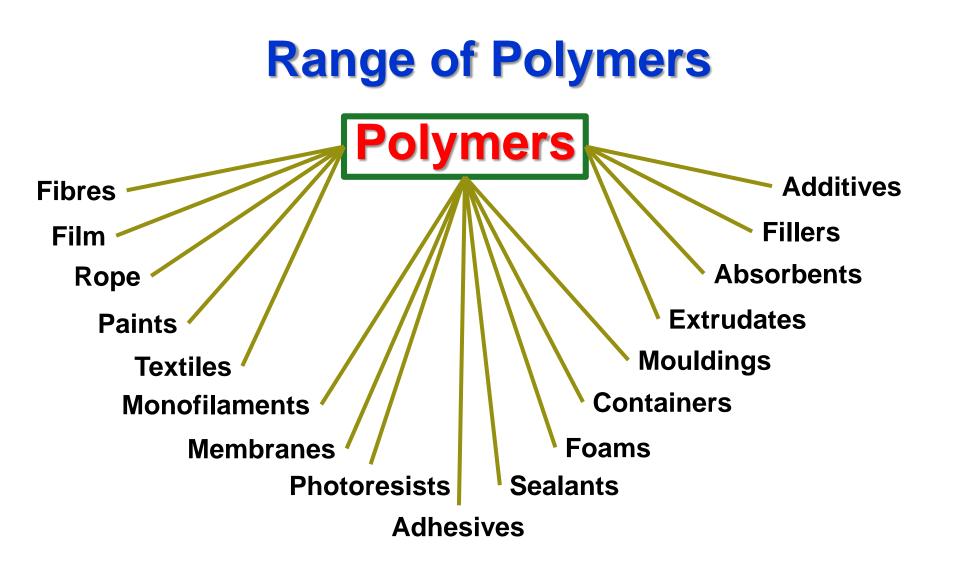


Performance Range

# **Applications of Polymers**

- Packaging (Film, Containers)
- Coatings
- Structural
- Adhesives
- Clothing
- Household Goods
- Electronics
- Sporting Goods
- Biomedical

## POLYMERS



#### POLYMERS



# Applications

#### **Polymer matrix composite**



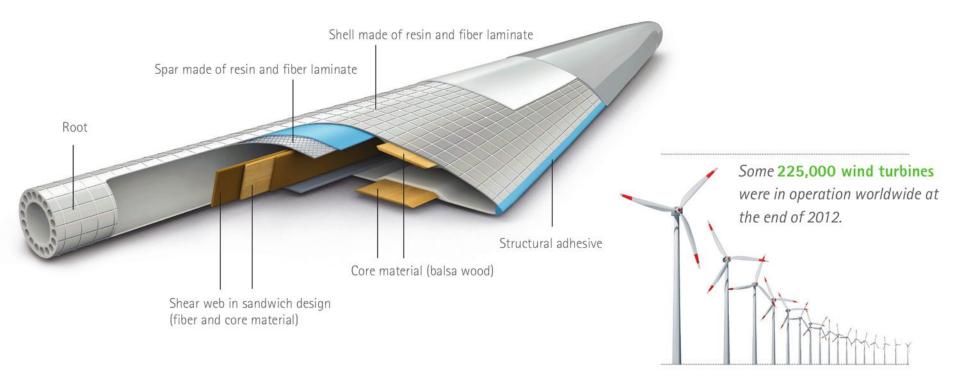
#### Minardi Formula

All Formula One race cars have a carbon fibre monocoque structure that protects the driver for all crashes

#### BMC frame with carbon/epoxy pre-preg

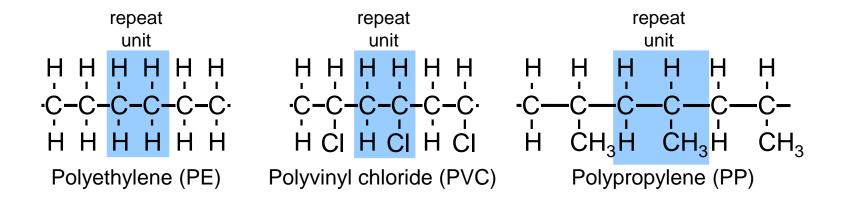
One of the most well-known composite applications in sports is the so-called "carbon bike". The frame consists of carbon fibre-reinforced epoxy which makes the frame very stiff and lightweight. 13

# Applications



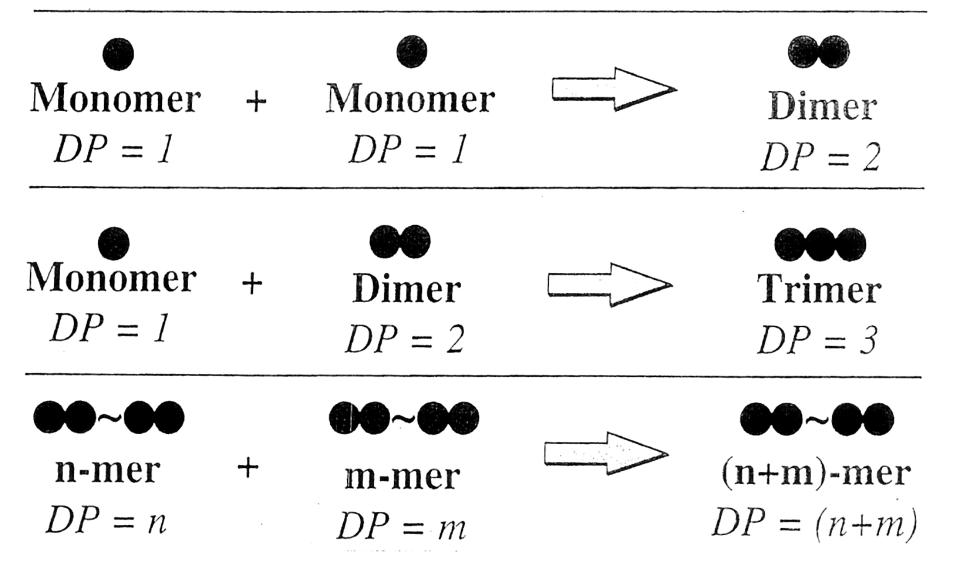
#### What is a polymer?



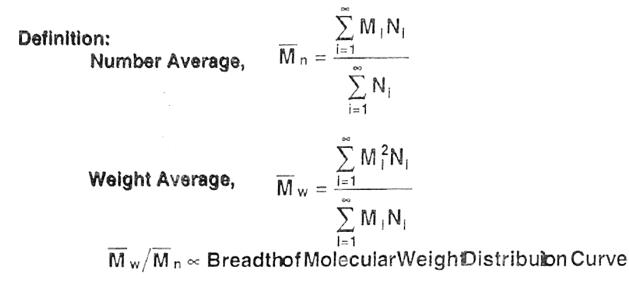


Adapted from Fig. 14.2, Callister 7e.

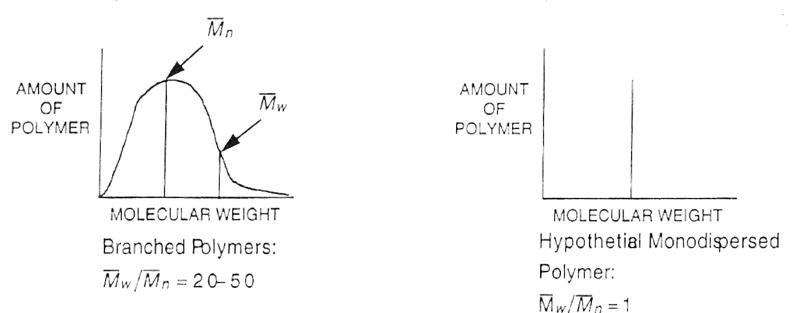
#### degree of polymerization = DP



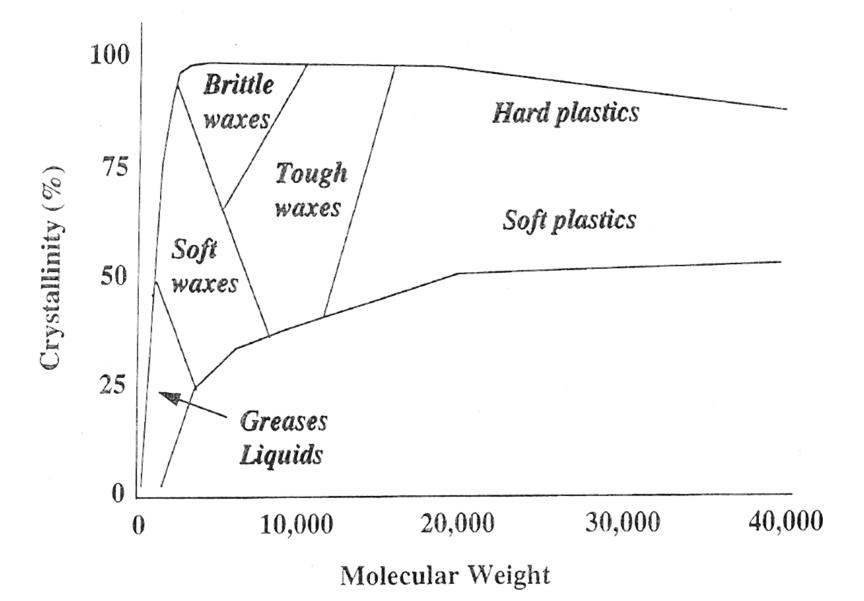
#### **Molecular Weight Distribution**



Examples:



# **Physical Characterization of PE**



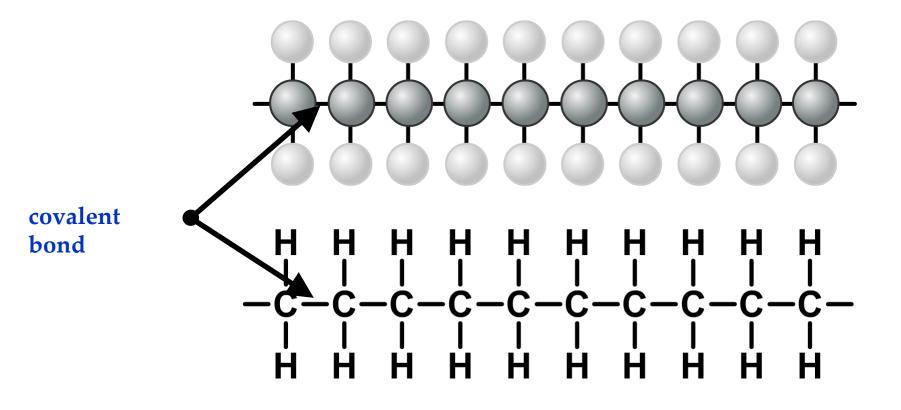
When all the repeating units along a chain are of the same type, the resulting polymer is called a *homopolymer*.

There is no restriction in polymer synthesis that prevents the formation of compounds other than homopolymers; and, in fact, chains may be composed of two or more different mer units, in what are termed *copolymers*.

### What keeps the chain together?

**Polymerization** is the reaction used to convert monomers into polymers. The monomers in a polymer are joined together by covalent bonds between atoms.

In a covalent bond, each atom shares one or more electrons with another atom. The bonds are sometimes shown as lines.



#### HYDROCARBON MOLECULES

- Most polymers are organic in origin, and many organic materials are hydrocarbons; that is, they are composed of hydrogen and carbon.
- Furthermore, the intramolecular bonds are covalent. Each carbon atom has four electrons that may participate in covalent bonding, whereas every hydrogen atom has only one bonding electron. A single covalent bond exists when each of the two bonding atoms contributes one electron. Double and triple bonds between two carbon atoms involve the sharing of two and three pairs of electrons, respectively. For example, in ethylene, which has the chemical formula C<sub>2</sub>H<sub>4</sub>, the two carbon atoms are doubly bonded together, and each is also singly bonded to two hydrogen atoms, as represented by the structural formula

$$\begin{matrix} H & H \\ | & | \\ C = C \\ | & | \\ H & H \end{matrix}$$

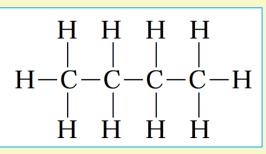
#### HYDROCARBON MOLECULES

Compositions and Molecular Structures for Some of the Paraffin Compounds: C<sub>n</sub>H<sub>2n+2</sub>

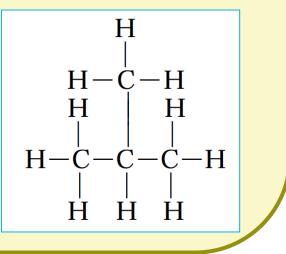
Name	Composition	Structure	Boiling Point (°C)
Methane	$CH_4$	H   H-C-H   H	-164
Ethane	$C_2H_6$	H H     H-C-C-H     H H	-88.6
Propane	$C_3H_8$	H H H       H-C-C-C-H       H H H	-42.1
Butane Pentane Hexane	$\begin{array}{c} C_{4}H_{10} \\ C_{5}H_{12} \\ C_{6}H_{14} \end{array}$		$-0.5 \\ 36.1 \\ 69.0$

#### **HYDROCARBON MOLECULES**

- Hydrocarbon compounds with the same composition may have different atomic arrangements, a phenomenon termed isomerism.
- For example, there are two iso mers for butane; normal butane has the structure



• whereas a molecule of isobutane is represented as follows:



Some Common Hydrocarbon Groups						
Family	Characteristic Representative Unit Compound					
Alcohols	R—OH	н н—С—он н	Methyl alcohol			
Ethers	R—O—R'	H H       H-C-O-C-H   H H	Dimethyl ether			
Acids	R-C	H H H H H	Acetic acid			
Aldehydes	R C=0	H H H	Formaldehyde			
Aromatic hydrocarbons		ОН	Phenol			
"The simplified structure denotes a phenyl group, H C C C H						

#### **Polymer Classification**

It is useful to classify polymers in order to make generalizations regarding physical properties, formability, and reactivity.

The appropriate classification scheme can change, however, because there are several different ways in which to classify polymers.

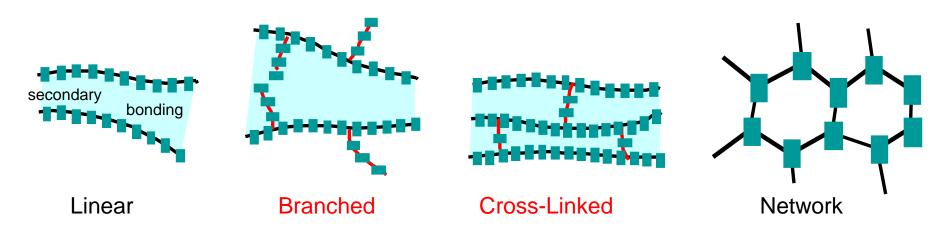
The first scheme groups polymers according to their chain chemistry. Carbonchain polymers have a backbone composed entirely of carbon atoms. In contrast, heterochain polymers have other elements in the backbone, such as oxygen in a polyether, -C-O-C-.

We can also classify polymers according to their macroscopic structure—that is, independent of the chemistry of the chain or functional groups. There are three categories of polymers according to this scheme: linear, branched, and networked (crosslinked) polymers.

# **Polymer Classification**

Classification of polymers according to macroscopic structure:

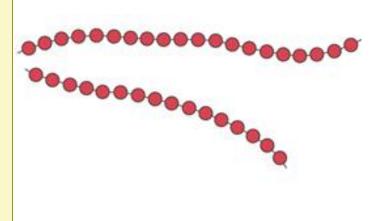
#### **Molecular Structures for Polymers**

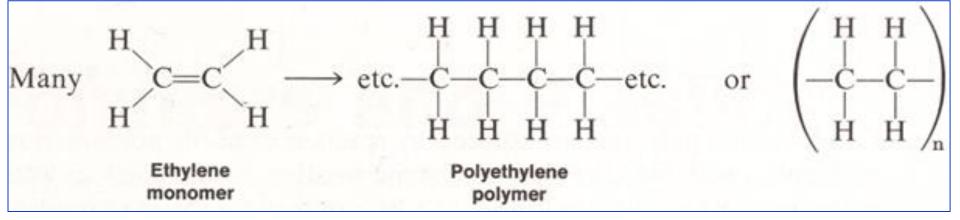


Adapted from Fig. 4.7, Callister & Rethwisch 3e.

# **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





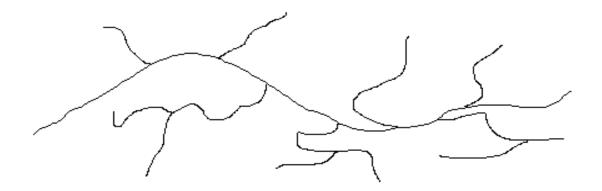
#### **Branched Polymers**

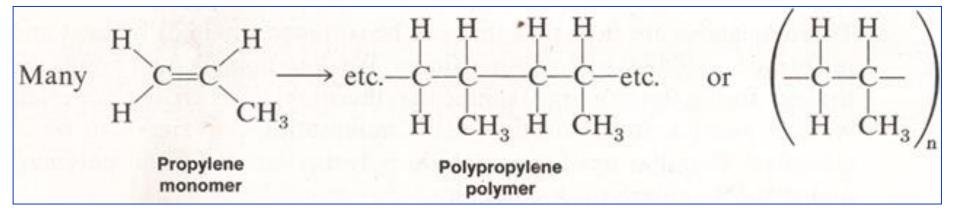
#### **Polymer chains can branch:**

- 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

#### **Branched Polymers**

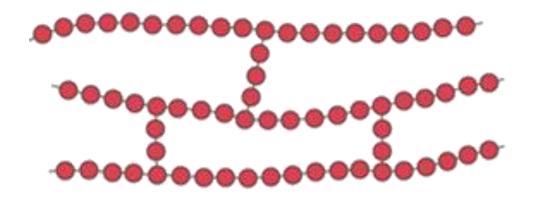
• Polymer chains can branch:



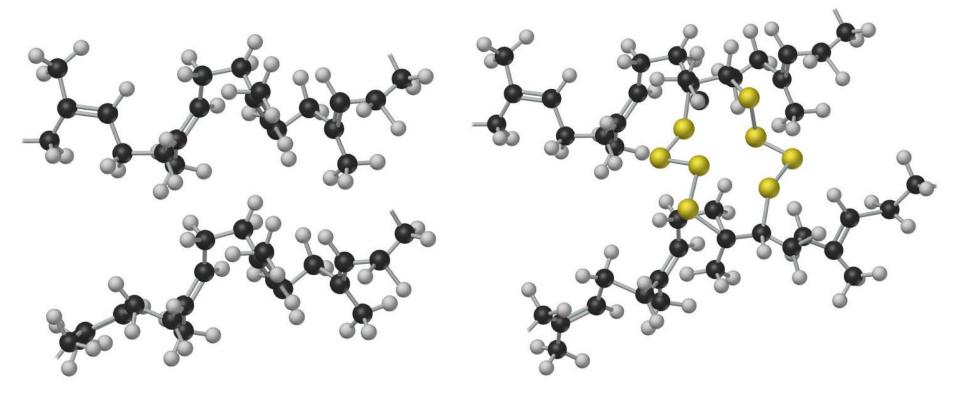


#### **Molecular structure**

- 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:



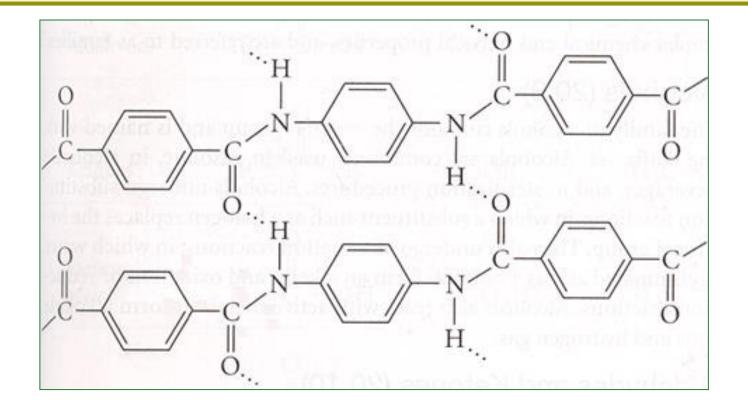
#### **Cross-Linking Polymers**



Kevlar is a cross-linked polymer.

Polymer chains of Kevlar crystallize in parallel, like dry spaghetti noodles in a box. These parallel chains are cross-linked with hydrogen bonds.

As a result, Kevlar is 5 times stronger that steel.

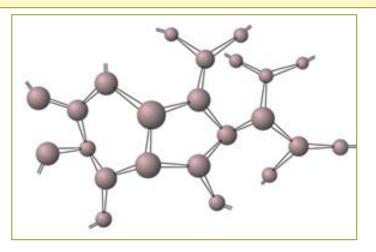


Kevlar is used in bulletproof vests, helmets, suspension bridge cables, and radial tires.



# **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

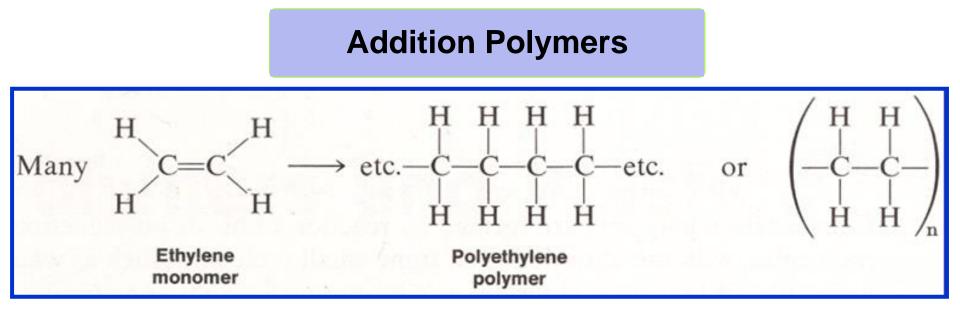


**Classifying Polymers by Synthesis** 

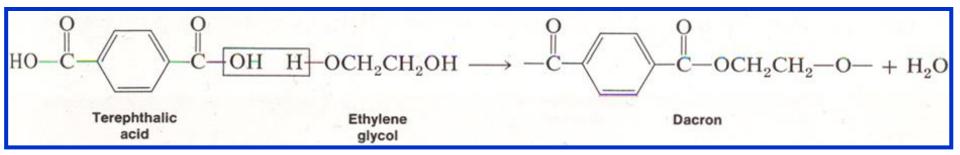
#### **Addition Polymers**

#### **Condensation Polymer**

These polymers are made from monomers that link together without losing any atoms. These monomers typically have at least one carbon-carbon double bond. Polyethylene is an addition polymer. These polymers are made from monomers that link together and lose small molecules such as water ( $H_2O$ ), ammonia ( $NH_3$ ), or hydrogen chloride (HCI). These monomers have 2 or more reactive functional groups. Most condensation polymers are copolymers.



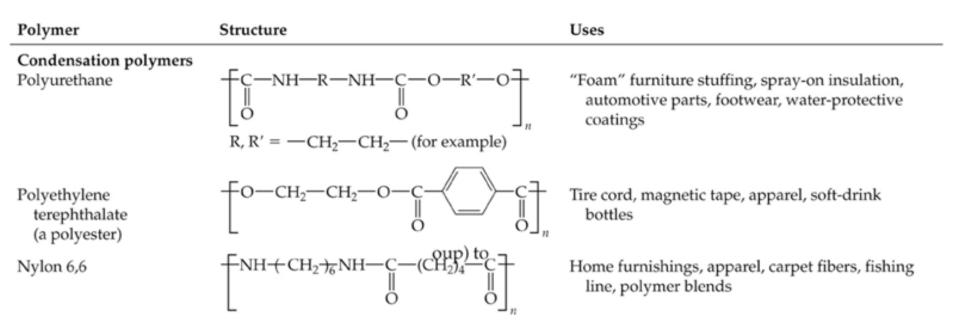
#### **Condensation Polymer**

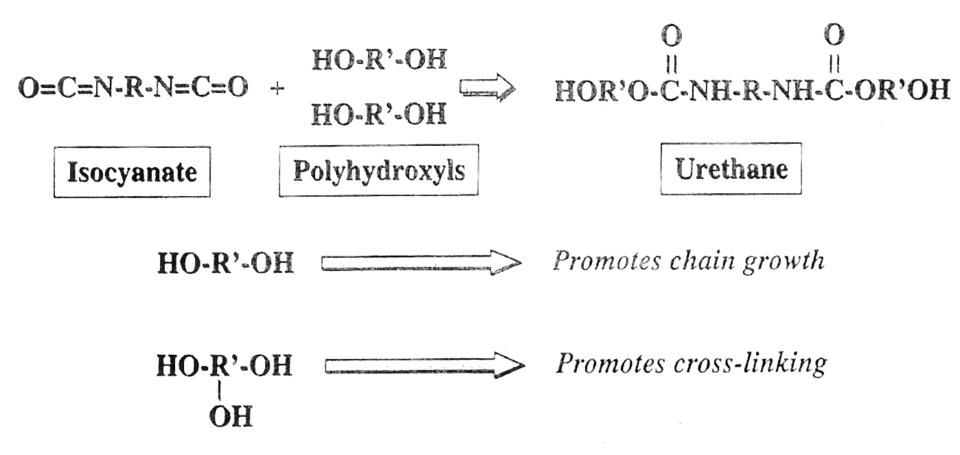


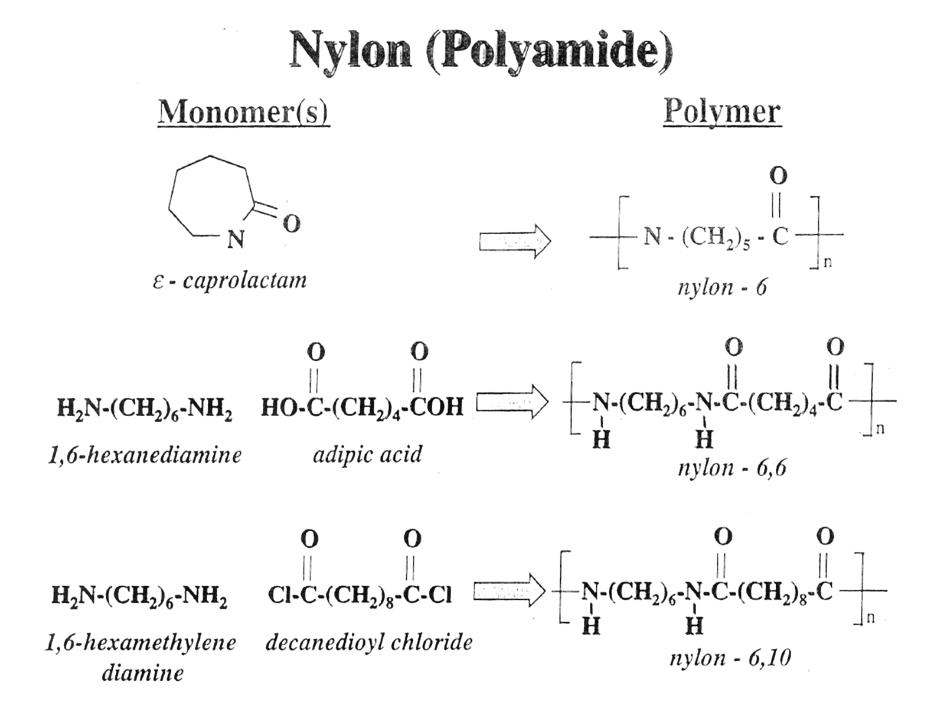
### **Addition Polymers**

Polymer	Structure	Uses
Addition polymers Polyethylene	$-CH_2-CH_2$	Films, packaging, bottles
Polypropylene	$\begin{bmatrix} CH_2 - CH \\ I \\ CH_3 \end{bmatrix}_n$	Kitchenware, fibers, appliances
Polystyrene	CH <sub>2</sub> -CH	Packaging, disposable food containers, insulation
Polyvinyl chloride	$\begin{bmatrix} CH_2 - CH \\ I \\ CI \end{bmatrix}_n$	Pipe fittings, clear film for meat packaging

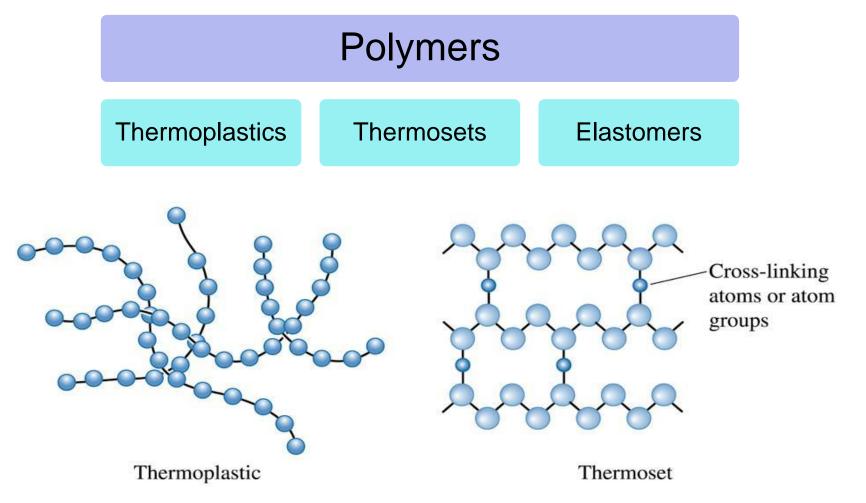
#### **Condensation Polymer**







Finally, polymers can be classified according to their formability.



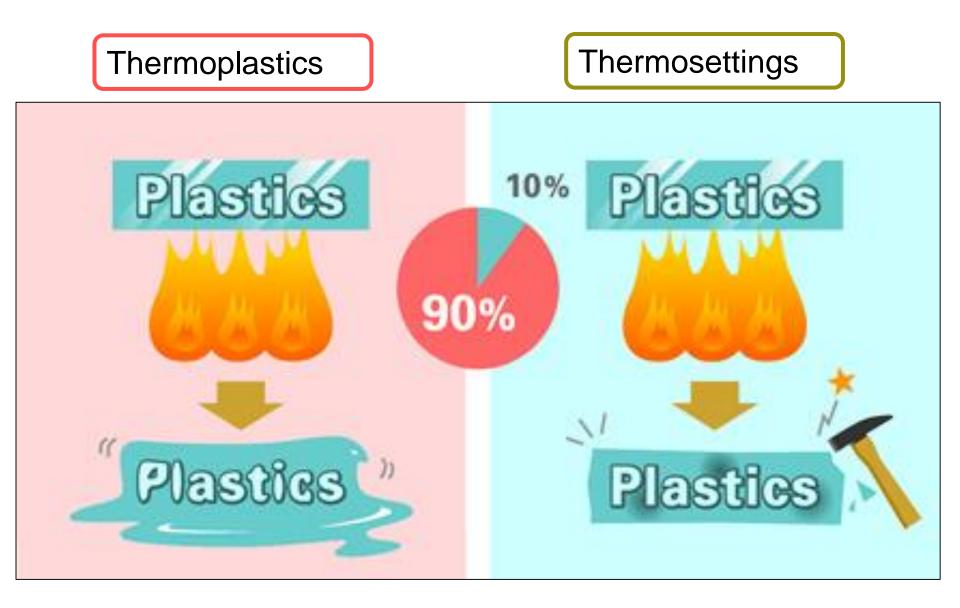
Polymers that can be repeatedly shaped and reshaped are called *thermoplastics*, whereas those polymers that cannot be reshaped at any temperature once they are set are termed *thermosets*.

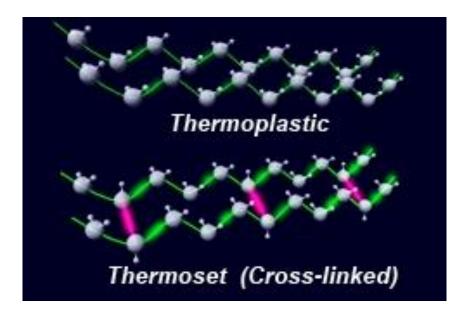
**Thermoplastics** - reversible in phase by heating and cooling. Solid phase at room temperature and liquid phase at elevated temperature.

**Thermosets** - irreversible in phase by heating and cooling. Change to liquid phase when heated, then follow with an irreversible exothermic chemical reaction. Remain in solid phase subsequently.

Often times network polymers are thermosets, and linear and branched polymers are thermoplastics. Hence, the thermoplastic/thermoset distinction is worthy of some elaboration.

**Elastomers** – Rubbers. material that is elastic in some way. If a moderate amount of deforming force is added, the elastomer will return to its original shape. Useful for fibers.





Thermoset and thermoplastic materials are found in the insulation and jacketing of many cables on the market today. **Thermoplastic materials** consist of chains of molecules which separate when heat is applied. This molecular construction gives thermoplastics the ability to melt and remold time and time again. On the other hand, **thermoset materials** consist of polymer structures which are cured. Irradiation, heat, or chemical reactions can be used to cure the material. During the curing process, polymer chains are cross-linked with other molecules which is why thermoset materials are also known as **cross-linked materials** 

# Curing

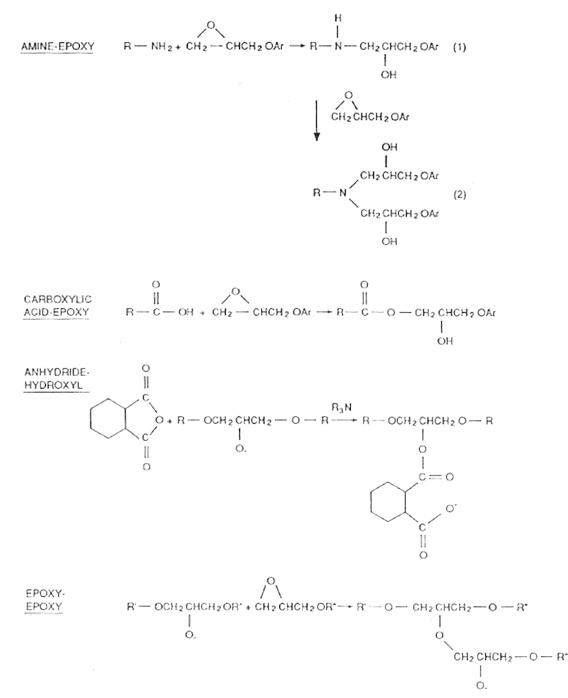


FIGURE 3.3-18. Basic curing reactions.

Thermoplastic resins and thermosetting resins, both types become soft when heated, but they differ in their behavior after they cool to a solid.

While thermoplastic resins become soft again when heated once more, thermosetting resins do not change their form any more even if they are heated again. The reason why a plastic cup placed inadvertently near the fire becomes deformed is that it is made of a thermoplastic resin.

Handles of frying pans and knobs of pot lids are made of thermosetting resins. Because these resins have good electrical characteristics, they were used for switches and sockets of electric lamps. However, because of their poor productivity, they have been replaced gradually by thermoplastic resins. Today, thermoplastic resins make up nearly 90% of these electrical components. Thermoplastic resins are further divided into "general-purpose plastics" and high-performance "engineering plastics" Thermoplastic resins are divided into crystalline and noncrystalline resins.

## Thermoplastics

#### Acetals

- Acrylics PMMA
- Acrylonitrile-Butadiene-Styrene ABS
- Cellulosics
- Fluoropolymers PTFE , Teflon
- Polyamides (PA) Nylons, Kevlar
- Polysters PET
- Polyethylene (PE) HDPE, LDPE
- Polypropylene (PP)
- Polystyrene (PS)
- Polyvinyl chloride (PVC)

## Thermoplastics

Material	Uses	Notes	Material	Uses	Notes
Acrylic (PMMA)		Stiff, hard and uniform strength. Scratches easily. Clear; has good optical properties. Non-toxic.	Acrylo- nitrile butadiene- styrene (ABS)		High impact strength. Tough and scratch resistant. Resistant to chemicals
		Good insulator, easily machined and polishes well	Polyvinyl chloride (PVC)	<b>O</b>	Chemical and weather resistant. Needs a stabiliser for outdoor
Rigid polystyrene		Light, hard, stiff, often transparent. Brittle			use. Good electrical insulator
(HDPS)		with low impact strength. Water resistant. The toughened type can be coloured	Polyethyl- ene tereph- thalate (PET)		Used extensively for mineral water bottles. Clear and very tough
Expanded polystyrene (LDPS)		Buoyant, lightweight. A good sound and heat insulator	Polyethyl- ene (poly- thene, PE)	8	Tough, very popular. Quite cheap. Available in a wide range of
Polyamide (nylon)	<b>Horizon</b>	Usually creamy in colour. Hard, tough and resistant to wear. Low friction. Machines well, but very difficult to join			colours. Fairly low melting point

# Thermoplastics



## Thermosets

- Amino resins
- Epoxies
- Phenolics
- Polyesters
- Polyurethanes
- Silicones



## Thermosets

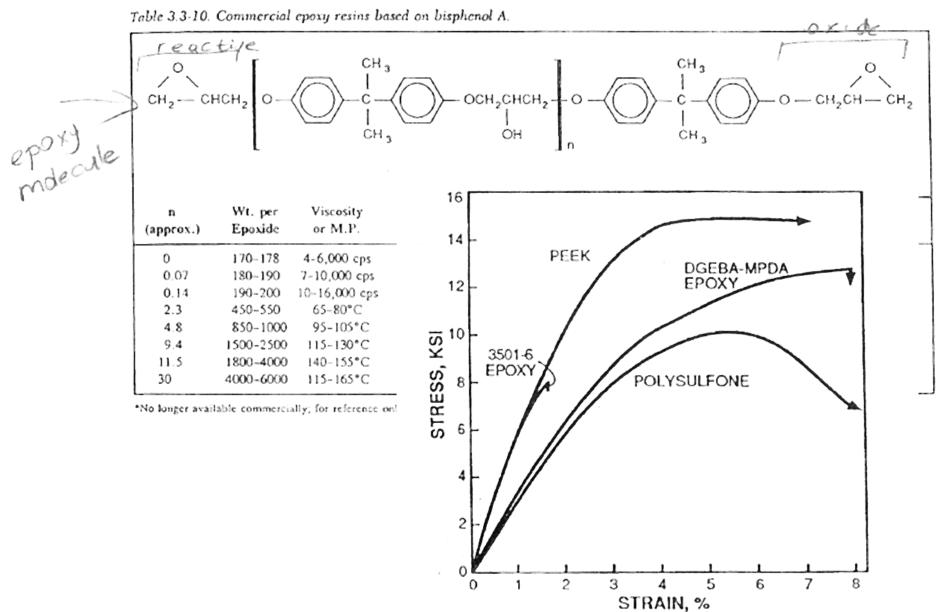


FIGURE 3.3-23. Tensile stress vs. strain for thermoplastic and

## Thermosets

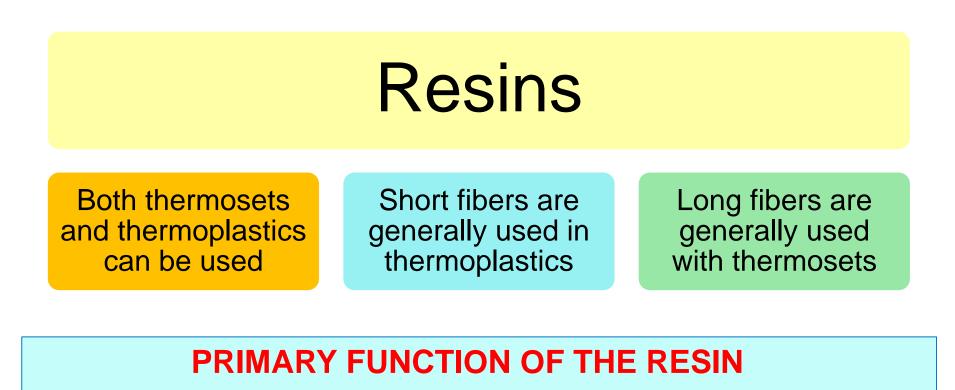
Material	Uses	Notes	Material	Uses	Notes
Polyester resin (GRP)		Stiff, hard and brittle. Used for casting and, when reinforced by glass fibres, produces GRP. Easy to colour. Excellent for outdoor uses	Epoxy resin	Contraction of the second seco	Very strong, especially when reinforced by glass or carbon fibres. Used as an adhesive for unlike materials e.g. metals to plastics
Urea formal- dehyde (UF)		Stiff, hard and brittle. Excellent electrical insulator. Used as an adhesive	Melamine formal- dehyde (MF)		Stiff, hard and strong. Scratch resistant. Low water absorption. Stain resistant. No odour. Available in a wide range of colours

## Elastomers

#### Natural rubber

#### Synthetic rubbers

- butadiene rubber
- butyl rubber
- chloroprene rubber
- ethylene-propylene rubber
- isoprene rubber
- nitrile rubber
- polyurethanes
- silicones
- styrene-butadiene rubber
- thermoplastic elastomers



"TO TRANSFER STRESS BETWEEN REINFORCING FIBERS AND TO PROTECT THEM FROM MECHANICAL AND ENVIRONMENTAL DAMAGE"

- By far the most common type of composite material.
- Matrix is relatively soft and flexible.
- Reinforcement must have high strength and stiffness
- As the load must be transferred from matrix to reinforcement, the reinforcement-matrix bond must be strong.

#### **Attractive features of FRP (Fiber Reinforced Polymers)**

- High strength-to-weight ratio
- High modulus-to-weight ratio
- Low specific gravity
- Good fatigue strength
- Good corrosion resistance, although polymers are soluble in various chemicals
- Low thermal expansion, leading to good dimensional stability
- Significant anisotropy in properties

Roughly 95% of the composite market uses thermosetting polymers

Thermoseting polymers are polymerized in two ways:

By adding a catalyst to the resin causing the resin to 'cure', basically one must measure and mix two parts of the resin and apply it before the resin cures

By heating the resin to its cure temperature

## Resins

### **Thermoset Advantages**

- Thermal Stability
- Chemical Resistance
- Reduced Creep and Stress Relaxation
- Low Viscosity- Excellent for Fiber Orientation
- Common Material

#### **Common thermosetting plastics**

**Phenolics:** good electrical properties, often used in circuit board applications

**Epoxies:** low solvent emission (fumes) upon curing, low shrink rate upon polymerization which produces a relatively residual stress-free bond with the reinforcement, it is the matrix material that produces the highest strength and stiffness, often used in aerospace applications

**Polyester:** most commonly used resin, slightly weaker than epoxy but about half the price, produces emission when curing, used in everything from boats to RVs to piping to Corvette bodies

## **Polymer Matrices**

Matrix	Characteristics
Epoxy	<ul> <li>Most widely used matrix for composites</li> <li>Can be toughened with the addition of rubber plasticizers to the matrix</li> <li>Cures at 120-175°C; 175°C max service temperature</li> <li>May be cured in oven or autoclave</li> <li>3501-6 (non-toughened) and 977-2 (toughened) are most widely used</li> </ul>
Bismaleimide	<ul> <li>Improved thermal stability over epoxies</li> <li>175-230°C cure and service temp</li> <li>Must be cured at high pressure (autoclave)</li> <li>More brittle than epoxy</li> <li>5250 most widely used</li> </ul>
Polyimide	<ul> <li>Maximum temperature stability</li> <li>260-315°C cure and service temperature</li> <li>Cure is complicated and some forms give off toxic fumes</li> <li>Must be cured in autoclave</li> <li>PMR-15 is most widely used</li> </ul>

## Resins

## **Thermoplastic Advantages**

- Room Temperature Material Storage
- Rapid, Low Cost Forming
- Reformable
- Tough

Properties and Processing	Characteristics of Key	Thermoplastic Resins
---------------------------	------------------------	----------------------

Properties	PEEK	PPS	Nylon	PEI	РР	PMMA
Service temperature	250°C (480°F)	220°C (430°F)	70°C (160°F)	170°C (340°F)	55°C (130°F)	65°C (150°F)
Density (g/cc)	1.32	1.35	1.15	1.27	0.91	1.19
Processing temperature	385°C (725°F)	330°C (625°F)	275°C (525°F)	315°C (600°F)	175°C (350°F)	205°C (400°F)
Moisture absorption	Very low	Very low	High	Average	Low	Very low
Bonding characteristics	Poor	Poor	Poor	Good	Poor	Good

# **Polymer Matrices**

Matrix	Characteristics
Cyanate	<ul> <li>Moderate temperature stability with significantly reduced outgassing</li> <li>200-260°C cure and service temperature</li> <li>Virtually zero outgassing</li> <li>Used for satellite applications where sensitive optics are present</li> </ul>
Polyester	<ul> <li>Low cost matrix not used in aerospace</li> </ul>
Phenolic	<ul> <li>Low cost matrix with low mechanical properties used in the production of rocket nozzles</li> </ul>
PEEK	<ul> <li>Thermoplastic matrix of interest because it can be re- molded by the subsequent application of heat and pressure</li> </ul>

Potential for commercial resins-property/process characteristics

Property	Thermoset	Thermoplastic
Modulus	High	Medium
Service temperature	High	Medium
Toughness	Medium	High
Viscosity	Low	High
Processing temperature	Low	High
Recyclability	Limited	Good

J. A. E. Månson, M. D. Wakeman, and N. Bernet, "Composite processing and manufacturing—an overview," in Comprehensive Composite Materials, A. Kelly and C. Zweben, Eds., vol. 2, chapter 2, pp. 577–607, Elsevier, Amsterdam, The Netherlands, 2000.

General Properties of Thermoset and Thermoplastic Composites			
Property	Thermoset Composites	Thermoplastic Composites	
Fiber volume	Medium to high	Low to medium	
Fiber length	Continuous and discontinuous	Continuous and discontinuous	
Molding time	Slow: 0.5 to 4 h	Fast: less than 5 min	
Molding pressure	Low: 1 to 7 bars	High: greater than 14 bars	
Material cost	Low to high	Low to medium	
Safety/handling	Good	Excellent	
Solvent resistance	High	Low	
Heat resistance	Low to high	Low to medium	
Storage life	Good (6 to 24 months with refrigeration)	Indefinite	

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.

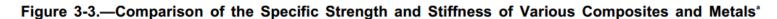
#### Reinforcement

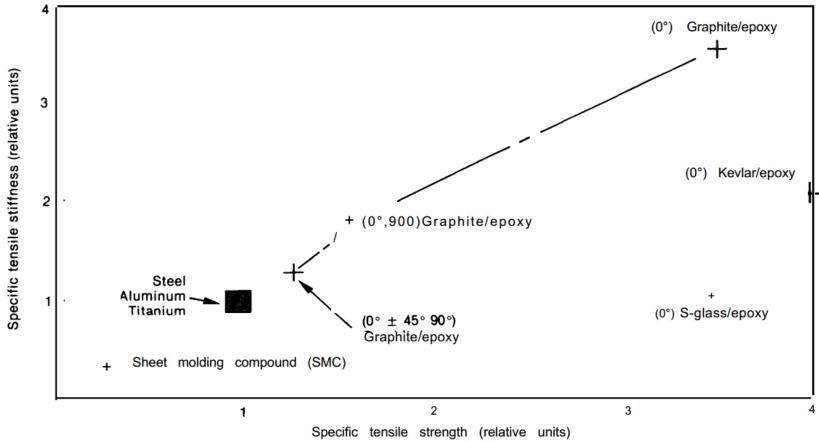
The continuous reinforcing fibers of advanced composites are responsible for their high strength and stiffness. The most important fibers in current use are glass, graphite, and aramid. Other organic fibers, such as oriented polyethylene, are also becoming important. PMCs contain about 60 percent reinforcing fiber by volume. The strength and stiffness of some continuous fiber reinforced PMCs are compared with those of sheet molding compound and various metals For instance, unidirectional, high strength graphite/epoxy has over three times the specific strength and stiffness (specific properties are ordinary properties divided by density) of common metal alloys.

#### Reinforcement

Of the continuous fibers, glass has a relatively low stiffness; however, its tensile strength is competitive with the other fibers and its cost is dramatically lower. This combination of properties is likely to ensure that glass fibers remain the most widely used reinforcement for high-volume commercial PMC applications. Only when stiffness or weight are at a premium would aramid and graphite fibers be used.







Specific properties are ordinary properties divided by density; angles refer to the directions of fiber reinforcement \*Steel: AISI 4340; AlumInum: 7075-T6; Titanium: Ti-6AI-4V.

SOURCE: Carl Zweben, General Electric Co.

#### Interphase

The interphase of PMCs is the region in which loads are transmitted between the reinforcement and the matrix. The extent of interaction between the reinforcement and the matrix is a design variable, and it may vary from strong chemical bonding to weak frictional forces. This can often be controlled by using an appropriate coating on the reinforcing fibers.

Generally, a strong interracial bond makes the PMC more rigid, but brittle

#### Short fiber composites

- Less than 0.2 inches (whiskers)
- Processed through standard thermoplastic processes
  - Must pass through gates, runners, and gap between processing screw and barrel walls
- Thermoplastics generally benefit greatly from even the short reinforcement materials

#### Intermediate length fiber reinforcement

The longer the fibers, the more difficult it is to coat the fibers enough to reap strength benefits

Low viscosity thermosets "wet-out" the materials better than high viscosity thermoplastics

Generally use unsaturated polyester and vinylester resins for FRP

#### Very long fibers or continuous fibers

Typically used with thermosets, also for "wet-out" reasons
 Used generally in advanced composite parts and have greater material property requirements

Generally use epoxy resins

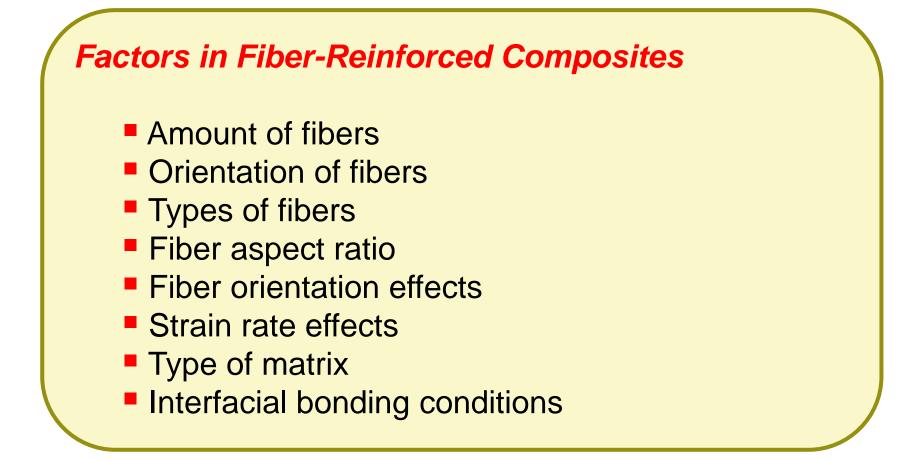
## **Hybrids**

When two or more fibers materials are combined in the composite.

 Intraply hybrids (within) - Alternate strands of different fibers in a single layer or ply.

Interply hybrid (across) – Different plies of different fibers.

The most widely used form is a laminar structure, made by stacking and bonding thin layers of fiber and polymer until the desired thickness is obtained.



#### Examples of fiber-reinforced materials and applications

# MaterialApplicationsBorsic aluminum<br/>Kevlar TM-epoxy and<br/>Kevlar TM-polyesterFan blades in engines, other aircraft and aerospace applications<br/>(including space shuttle), boat hulls, sporting<br/>goods (including tennis rackets, golf club shafts, fishing rods), flak jackets<br/>Aerospace and automotive applications, sporting goods<br/>Lightweight automotive applications, water and marine applications, corrosion-<br/>resistant applications, sporting goods equipment, aircraft and aerospace<br/>components

In order to select the most efficient manufacturing process, the manufacturing team considers several factors such as

- user needs
- performance requirements,
- size of the product,
- surface complexity,
- appearance,
- production rate,
- total production volume,
- economic targets/limitations,
- Iabor, materials,
- tooling/assembly, and equipment.

The method of manufacturing composites is very important to the design and outcome of the product

With traditional materials one starts out with a blank piece of material ie: rod, ingot, sheet, etc and works it to produce the desired part.

However, this is not the case with polymer-matrix composites.

With these composites the material and the component are being produced at the same time, therefore we aim for the product to be a net or near net shape with little to no post processing.