INTRODUCTION TO POLYMERS AND FIBERS

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Dr. Liang appreciate the Tutorial for providing a good definition of fundamental concepts of polymer science and engineering, excellent description of liquid, injection, and compression molding of plastics and composites, and the relative advantages of various materials and techniques.

OVERVIEW

Concepts. Definitions. Technical terms

Polymer vs. Composite

Polymer

- **Thermoplastics vs. Thermosets**
- **Chemistry (polymerization, crosslinking)**
- **Physics (glass transition, stress-strain curve)**

Fibers

- **Types**
- **Fabric forms**
- **Selection tips**

Composite Properties

- **Rule of mixtures**

POLYMER

Polymer Basics

- poly = many

  mer = parts
- degree of polymerization = DP

Monomer *DP = 1*	+	Monomer *DP = 1*	→	Dimer *DP = 2*
Monomer *DP = 1*	+	Dimer *DP = 2*	→	Trimer *DP = 3*
n-mer *DP = n*	+	m-mer *DP = m*	→	(n+m)-mer *DP = (n+m)*

COMPOSITE

- A heterogeneous combination of two or more materials

- **reinforcing elements such as fibers, fillers**
- **binders such as resins or polymers**

- These materials differ in form or composition on a macroscale.

- There exists interface between these materials.

Role of Fibers and Resins in FRP Composites

Fiber:

- **Load-bearing component.**

Resin:

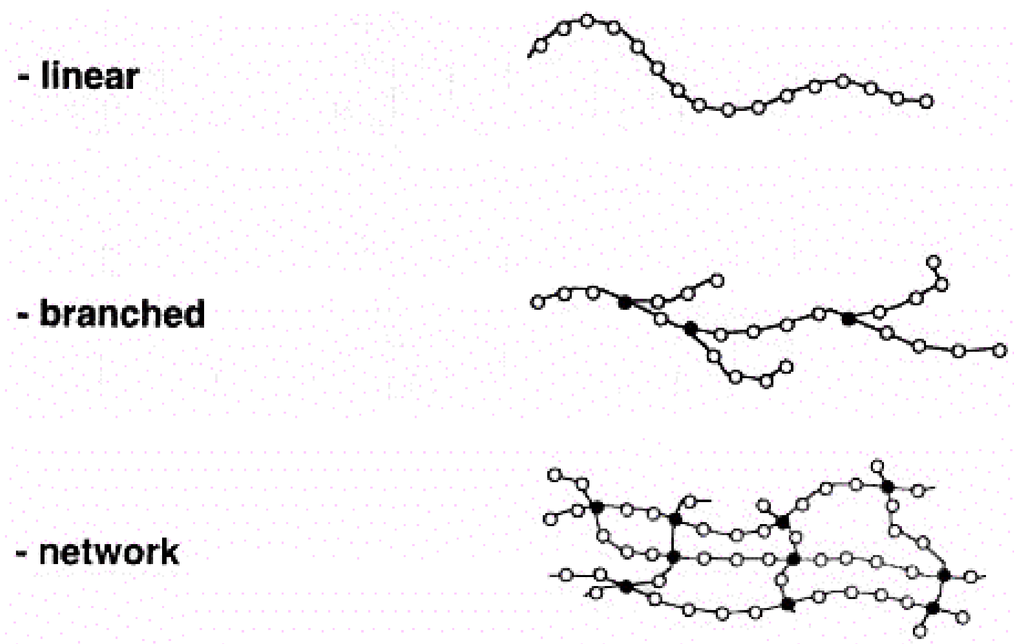
- **Dissipate loads to the fiber network**
- **Maintain fiber orientation**
- **Protect the fiber network from damaging environmental conditions such as humidity and high temperature**
- **Dictates the process and processing conditions**

POLYMER CONFIGURATIONS

Linear: **long, linear chains, e.g. most thermoplastics, such as HDPE**

Branched: long chains with arms coming from branch points, e.g., LDPE

Network: long chains linked together by crosslinking arms to form a network of chains, e.g., cured thermosets, such as vinyl ester

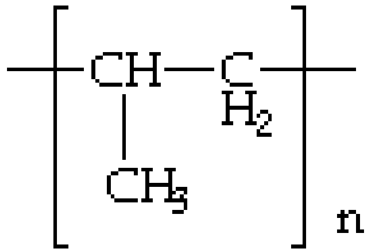


THERMOPLASTIC POLYMERS

Thermoplastic polymers: soften, melt and flow upon heating, e.g., LDPE, HDPE, PP, PS, PVC, Nylon, PMMA, PC, ABS, PET

Characteristics:

PP



- **Linear or branched structure**
- **Easy to process with application of heat**
- **Heat sensitive properties**
- **Individual polymer molecules are held together by weak secondary forces:**
    - **Van der Waal's forces**
    - **Hydrogen bonds**
    - **Dipole-dipole interactions**

THERMOPLASTIC POLYMERS (cont'd)

Advantages:

- **Unlimited shelf life -won't undergo reaction during storage**
- **Easy to handle (no tackiness)**
- **Shorter fabrication time**
- **Recyclable - they undergo melt and solidify cycles**
- **Easy to repair by welding, solvent bonding, etc.**
- **Postformable**
- **Higher fracture toughness and better delamination resistance under fatigue than epoxy**

Disadvantages:

- **Poor creep resistance**
- **Poor thermal stability**
- **Poor melt flow characteristics (high viscosity ~ 1,000,000 cP)**

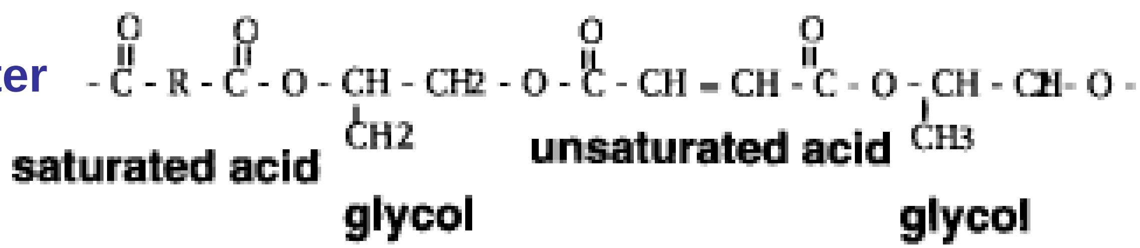
THERMOSET POLYMERS

Thermosets: do not flow upon reheating, e.g. unsaturated polyesters, vinyl esters, epoxies, phenol formaldehyde, urethane

Characteristics:

- **Upon application of heat, liquid resin becomes cured / rigid**
- **End polymer is less temp. sensitive than thermoplastics**
- **Crosslinked network structure (formed from chemical bonds, i.e. primary forces) exists throughout the part**
- **Crosslinking provides thermal stability such that polymer will not melt or flow upon heating.**

Polyester

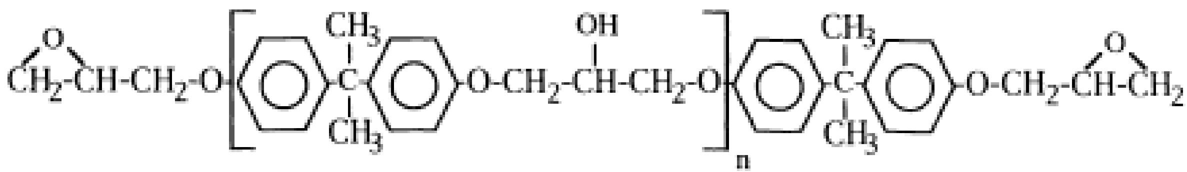


THERMOSET POLYMERS (cont'd)

Advantages:

- Low resin viscosity (~20 – 500cP)
- Good fiber wet-out
- Excellent thermal stability once polymerized
- Chemically resistant
- Creep resistant

Epoxy



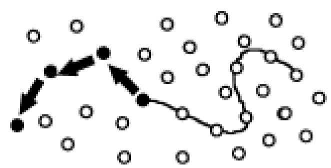
Disadvantages:

- Brittle (low strain-at-break)
- Long fabrication time in the mold
- Limited storage life at room temperature before curing
- Non-recyclable via standard techniques
- Molding in the shape of a final part - not postformable

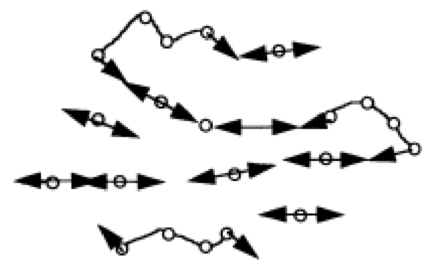
POLYMERIZATION REACTIONS

Thermoplastics: polymerized prior to molding the final part
Thermosets: polymerized during the molding process

Chain Polymerization



Step Polymerization



Polymers formed via chain reaction:	Polymers formed via step reaction:
Polyethylene	Nylon
Polypropylene	Polycarbonate
Polystyrene	Polyethylene terephthalate
Polyvinyl chloride	Epoxy
Polymethyl methacrylate	Phenol formaldehyde
Acrylonitrite-butadiene-styrene	Urethane
	Unsaturated polyesters
	Vinyl esters

CHAIN (OR ADDITION) POLYMERIZATION

Initiators /Catalysts

Benzoyl peroxide (BPO)   Dicumyl peroxide (DCP)

Methyl ethyl ketone peroxide (MEKP)

Upon heating, these peroxides dissociate to form two radicals which attack the monomer double bonds and add to them (addition). This forms a reactive radical center which can propagate to form a polymer.

Inhibitors and Retarders

Used to suppress polymerization in order to improve processability

Inhibitors stop all radical polymerization until consumed.

Retarders stop only a portion of the radicals from propagating.

Promoters and Accelerators

Used to help initiate cure at room temperature, e.g. Cobalt naphthenate, DMA

STEP (OR CONDENSATION) POLYMERIZATION

No special activation needed to allow a monomer to react with any nearby monomer.

Condensation: water liberated when the polymer bonds form.

Polyester formation: The acid groups in diacids react with the alcohol groups in diols to form ester linkages.

Curing Agents

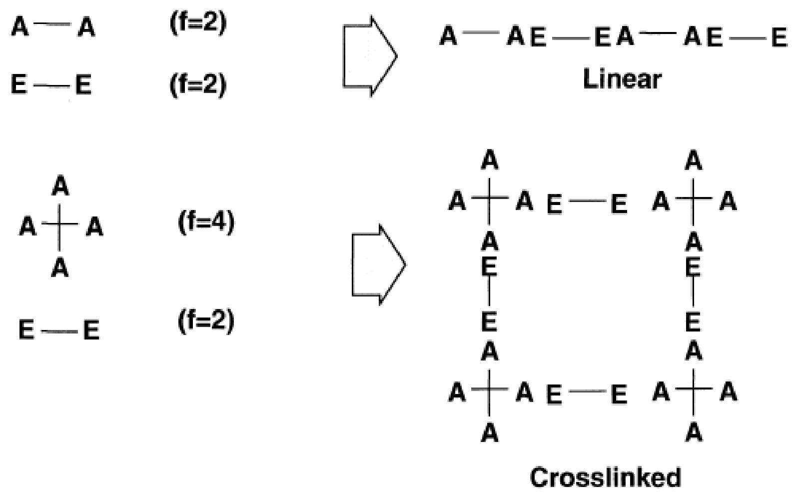
Importance of curing agents (also called crosslinking agents, hardeners, or catalysts):

- **determines the type of curing reaction**
- **influences the processing cycle: viscosity versus time, gelation**
- **affects properties of the cured system: Tg, modulus, strength**

Examples of curing agents for epoxies:
aliphatic amine (DETA), aromatic amine (MPDA), cyclic anhydrides (NMA)

CROSSLINKING IN STEP POLYMERIZATION

Crosslinks are formed with the use of monomer of multi functional groups



Functionality (f): the number of reactive groups of monomer.

- **f equal to 2:** **linear polymer**
- **f greater than 2:** **branched or crosslinked polymer**

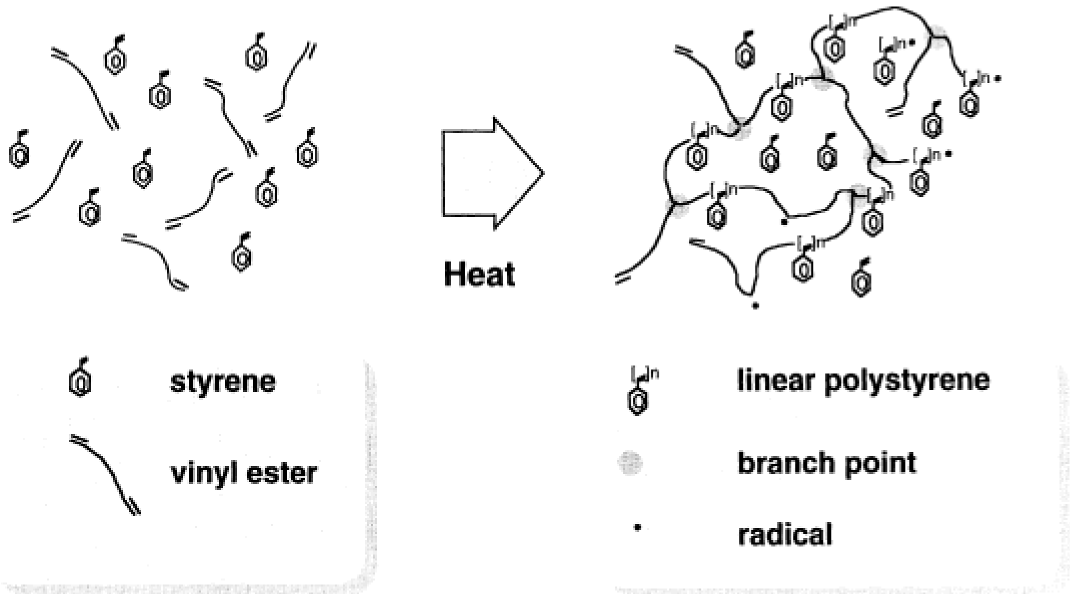
Thermosets cured via this process include

Epoxies **Phenol formaldehyde** **Urethane**

CROSSLINKING IN CHAIN POLYMERIZATION

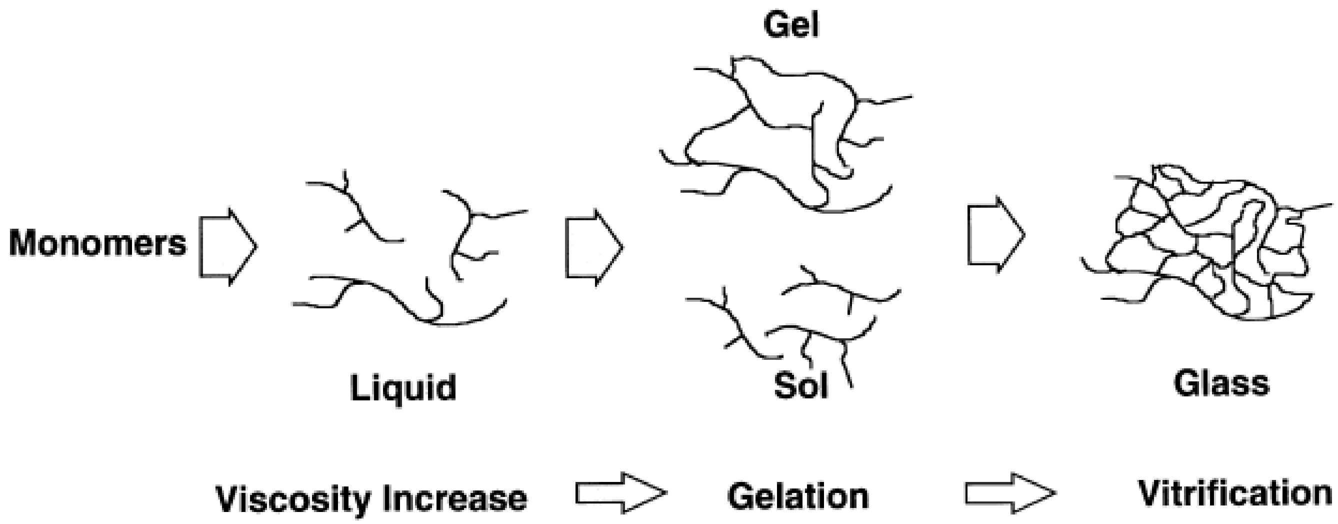
Monomers with two or more double bonds (for example, divinyl monomers) may lead to crosslinking.

Examples of this type of systems: unsaturated polyesters, vinyl esters



- **Vinyl ester with unsaturations is formed via step polymerization;**
- **The unsaturated sites are reacted with styrene to produce crosslinked structure via chain reaction with using peroxide initiator.**

CURE OF THERMOSETTING RESINS



A thermosetting system is set to cure when a crosslinked network of polymer chains is formed.

Gel point: The onset of gelation when the material won't flow, i.e. molecular weight approaches infinity.

TYPICAL VINYL ESTER AND POLYESTER RESIN FORMULATION

Resin/ pre-polymer- 40 to 100% (typically (55-65%)

- **Provides polymer properties, including modulus, toughness, glass transition temperature, and durability.**

Reactive diluent or monomer (styrene commonly)- 0-60% (typically 35-45%)

- **Viscosity control**
- **Lower cost**
- **Improve wetting behavior**

Initiator (catalyst)--1 to 3%

- **Peroxide necessary to begin chemical reaction**

Inhibitors--less than 100 ppm

- **Aid in processing**
- **Improve shelf life**

GLASS TRANSITION TEMPERATURE

T < Tg: Glassy state - brittleness, stiffness, and rigidity

T >Tg: Rubber state - softening and flow

Molecular Interpretation:

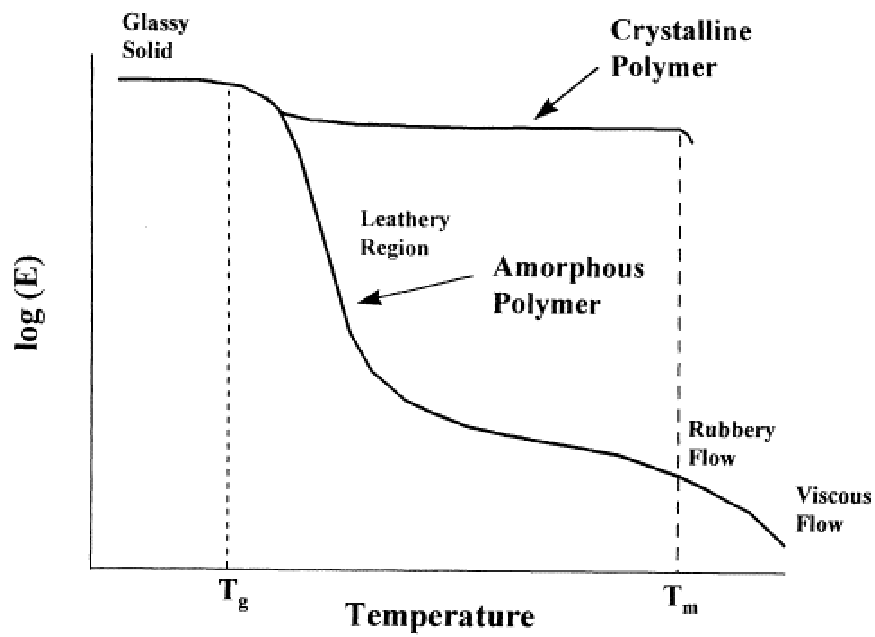
In glassy state

- **No large scale molecular motions**
- **Atoms move against restraint of secondary bond forces**

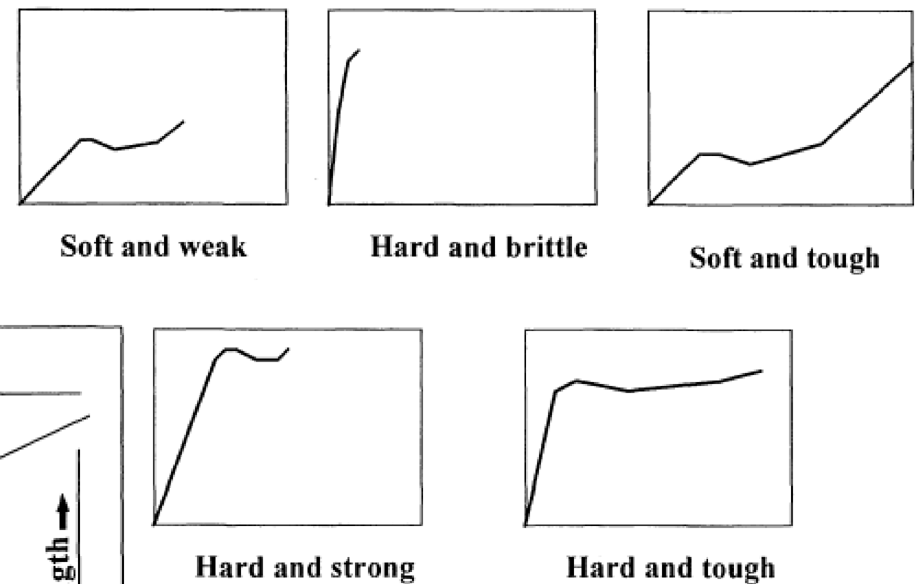
At glass transition temperature

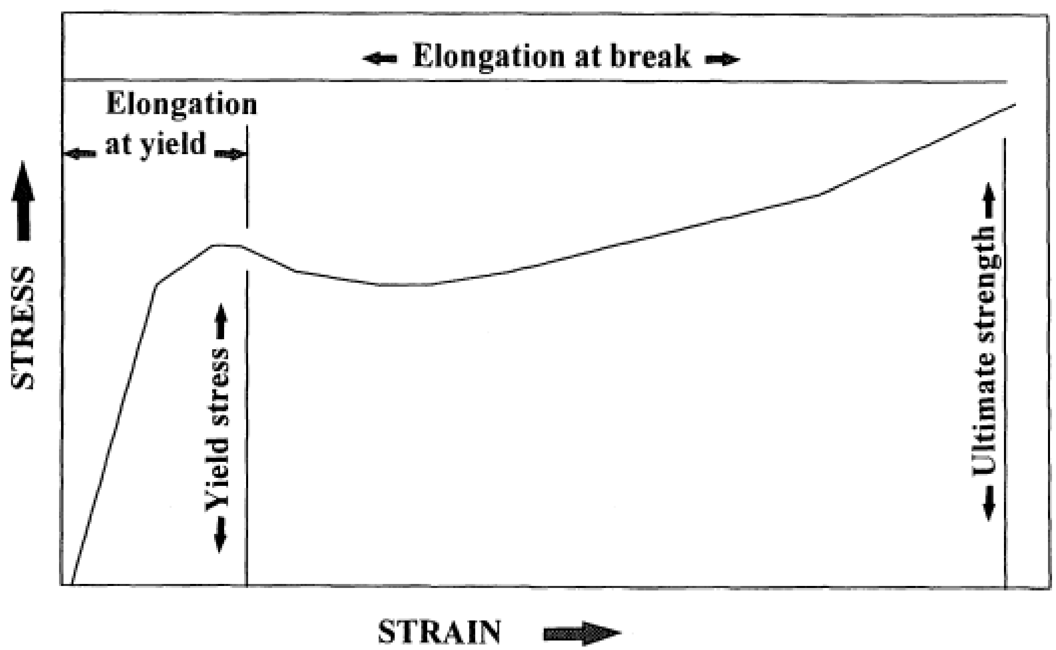
- **Onset of liquid-like motion of long molecular segments**
- **More free volume**

Thermal Transitions

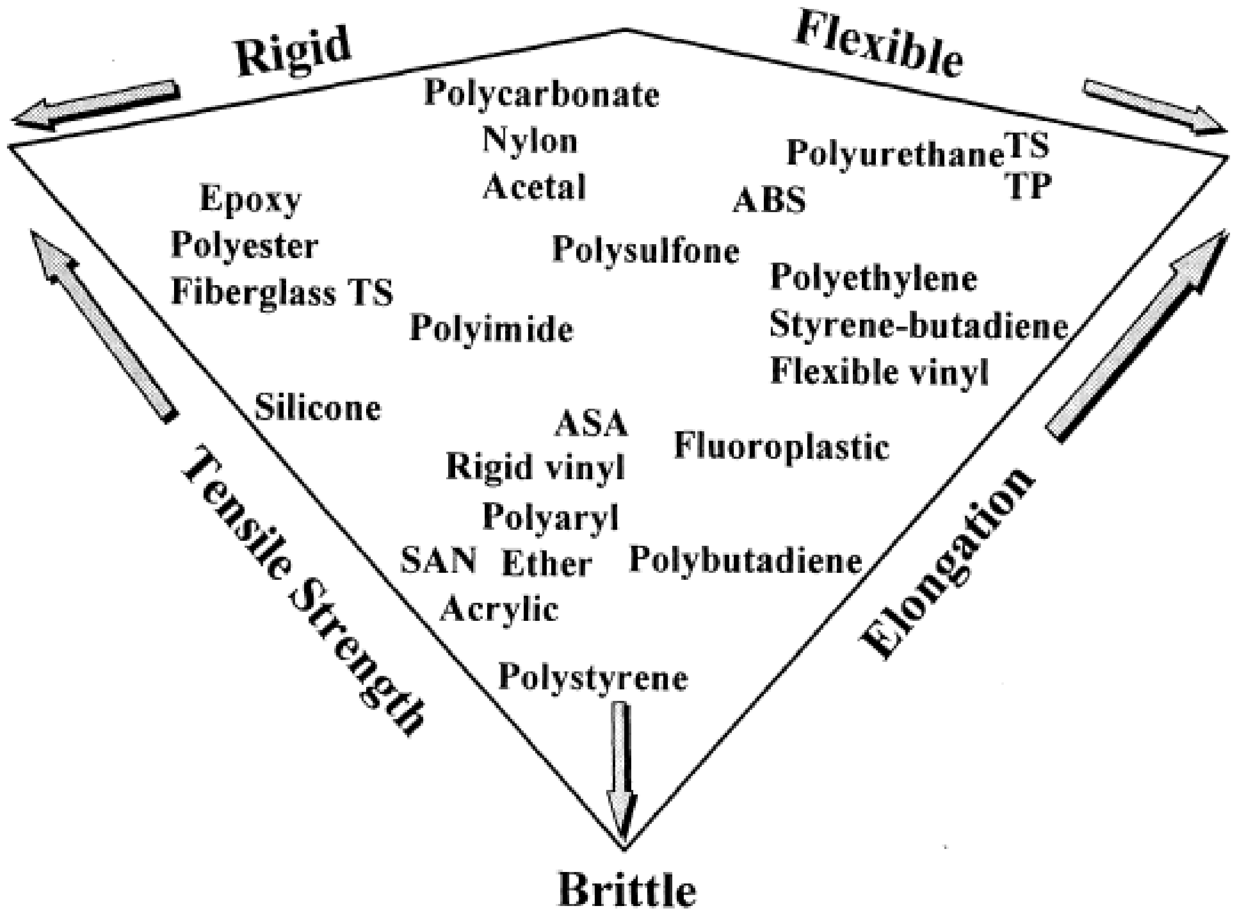


TENSILE STRESS-STRAIN RELATIONSHIPS





MECHANICAL PROPERTIES OF POLYMERS



GLASS FIBERS

“E” glass fibers: high electrical insulating properties
low susceptibility to moisture
high mechanical properties
“S” glass: higher strength, heat resistance and modulus
AR glass (alkali resistant): improved chemical resistance

Glass fibers offer many advantages such as:

- **Low cost**
- **High tensile strength**
- **High chemical resistance**
- **Relatively higher fatigue resistance**
- **Excellent insulating properties**

The limitations of glass fibers are:

- **Low tensile modulus**
- **Relatively high specific gravity**
- **Sensitivity to abrasion with handling**
- **High hardness**

CARBON FIBERS

PAN based fibers offer good strength and modulus up to 85-90 Msi. They also offer excellent compression strength, to 1 Msi.

Pitch fibers have extremely high moduli (up to 140 Msi) and favorable coefficient of thermal expansion.

Carbon fibers offer the following advantages:

- **High tensile strength-to-weight ratio**
- **High tensile modulus-to-weight ratio.**
- **Very low coefficient of linear thermal expansion.**
- **High fatigue strength.**

Some of the disadvantages of carbon fibers are:

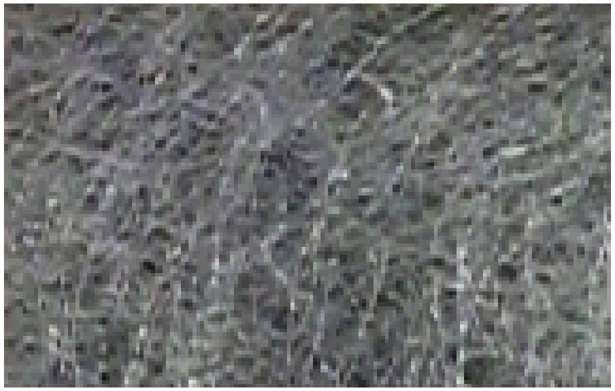
- **High cost**
- **Brittle, reducing the impact resistance**
- **Electrical conductive, which limits their application potential.**

PREFORM -RANDOM MATS

A preform is the assembly of reinforcing fibers that is preshaped and oriented by placement in a mold to its near-net configuration, prior to introduction of resin.

Advantages

- **High permeability**
- **Easy infusion**
- **Easy handling**
- **High degree of structural**
- **Good integrity**

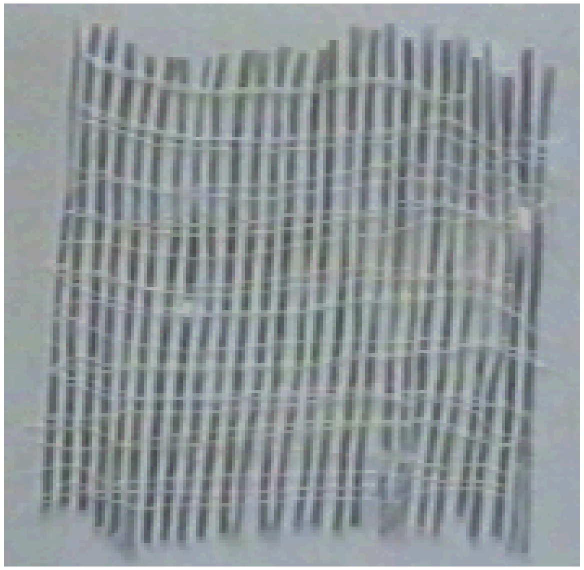


Disadvantages

- **Poor stiffness**
- **Limited strength**
- **Limited fiber volume fractions**

UNIDIRECTIONAL FABRIC

Unidirectional Fabric consists of parallel filaments held loosely in place by stitches in a plane:



Advantages

- **High stiffness and strength in filament direction**

Disadvantages

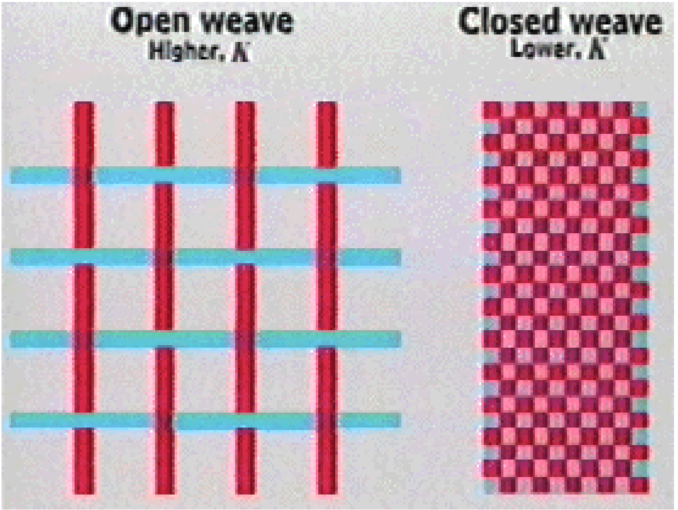
- **Poor integrity - "fiber wash" may occur**
- **Anisotropic flow and performance**

TWO-DIMENSIONAL WOVEN FABRICS

Weaves can be classified according to the spacing between the tows. Weaves with big open spaces between the tows are termed open weaves, while weaves with no space between the tows are termed closed weaves.

Advantages

- Balanced properties in the plane of fabric
- Good impact resistance
- Good conformability

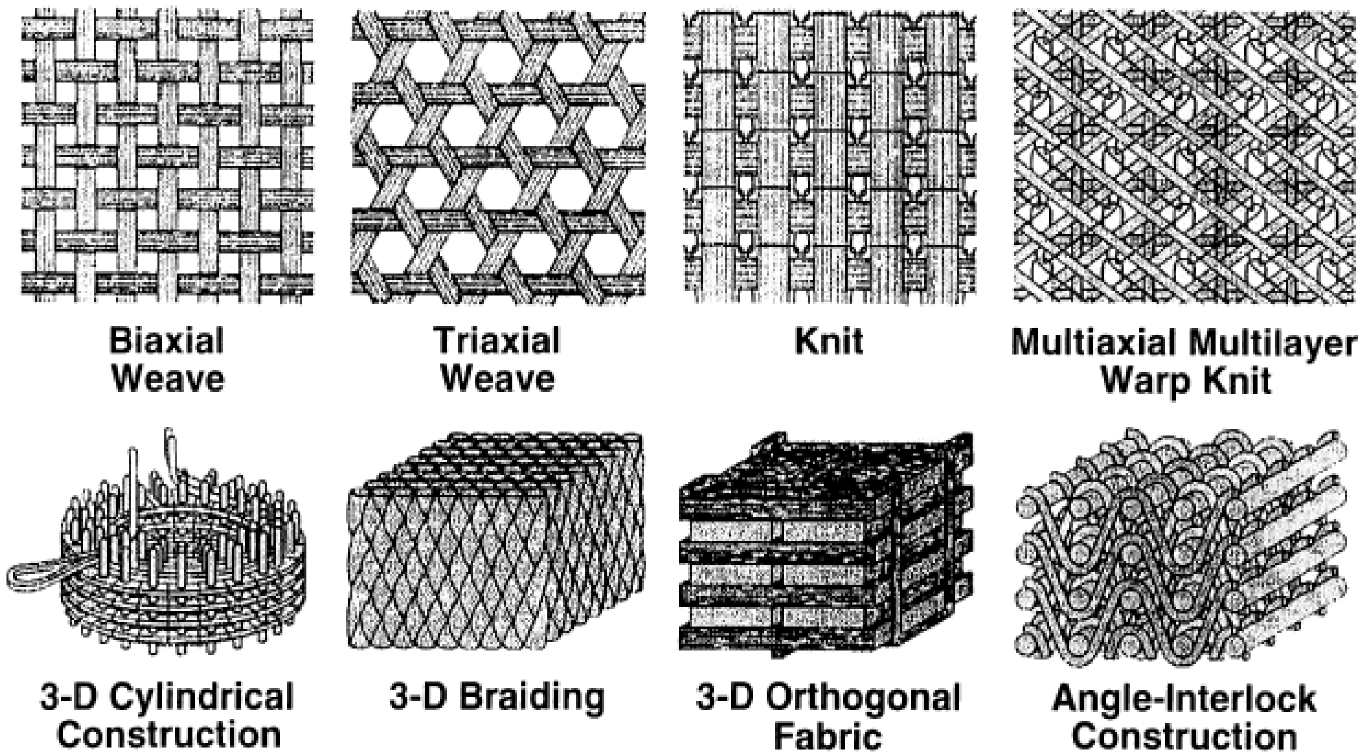


Disadvantages

- Fiber undulation
- Asymmetry
- Trimming / Handling

OTHER FABRIC ARCHITECTURES

PREFORM ARCHITECTURES



illustrations—Scientific American

FIBER ARCHITECTURE SELECTION

Processing Issues	Performance Issues
•Permeability (X,Y, Z directions) •Compressibility •Drapeability •Ease of Handling	•Moduli, strengths, etc. •Durability •Compressibility (Fiber volume fraction) •Drapeability

COMPOSITE PROPERTIES

Given the properties of the fiber and resin which comprise a composite material, it is possible to estimate the properties of the composite.

Specifically, the overall objective in estimating composite properties is to use:

- **Properties of components**
- **Volume fraction of components**
- **Reinforcing geometry**
- **Orientation of fibers**

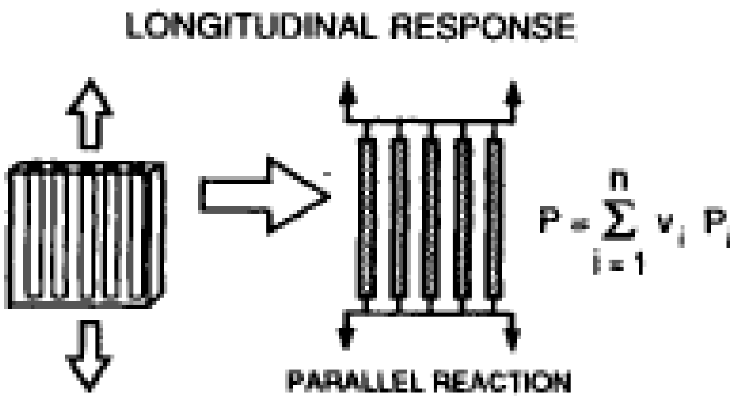
To predict:

- **Young's Modulus**
- **Shear modulus**
- **Poisson's Ratio**
- **Thermal expansion coefficient**

MODELS FOR UNIDIRECTIONAL CONTINUOUS FIBER COMPOSITES

RULE OF MIXTURES

The composite property is estimated as the sum of the responses of the composite components weighted by the component volume fractions.



The composite property is estimated as a reciprocal sum of the responses of the composite components weighted by the component volume fractions.