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# INTRODUCTION TO POLYMERS (RESINS)

**By**
**Ruifeng (Ray) Liang, Ph.D.**
**Constructed Facilities Center**
**rliang@mail.wvu.edu**

West Virginia University
Where Greatness is Learned

# ACKNOWLEDGMENTS

**This presentation is based on the material included in the "Tutorial on Polymer Composite Molding" developed by Prof. Giuseppe R. Palmese, Center for Composite Materials, University of Delaware through the Michigan State University Intelligent Systems Lab under the NSF Technology Reinvestment Program in 1999.**

**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

- Role of resins in FRP composites
- Thermosets vs. thermoplastics
  - Advantage & limitations
- Polymer chemistry
  - Chain & step polymerization
    - Catalysts, inhibitors, accelerators
  - Chain crosslinking/ curing
  - Typical thermoset resin systems
- Polymer processing
- Polymer physics
  - Glass transition
  - Stress-strain curve
- Summary

# ROLE OF RESINS IN FRP COMPOSITES

**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 - compatibility**

**Fiber:**

- **Load-bearing component.**

**Resin:**

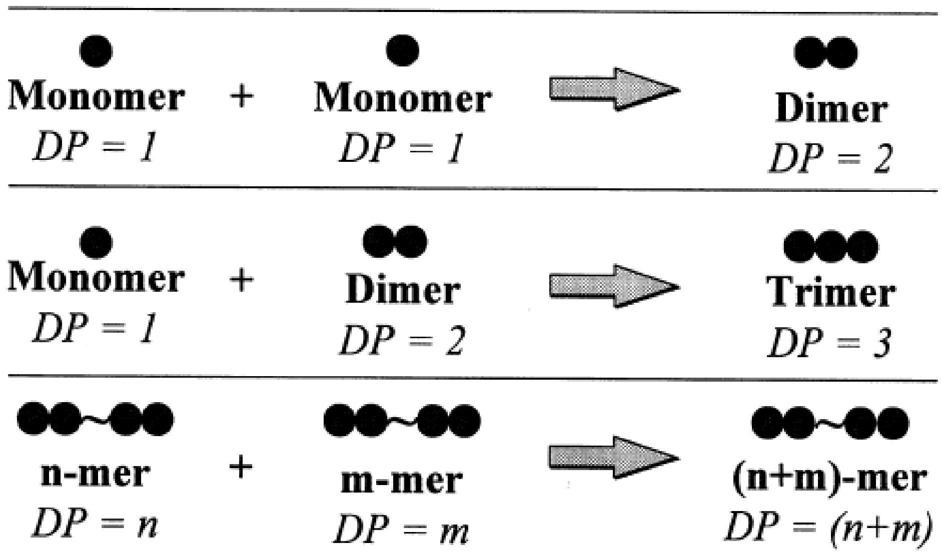
- **Dissipate loads to the fiber network**
- **Maintain fiber orientation**
- **Protect the fiber network from damaging environmental conditions such as humidity and high temperature**
- **Dictates the process and processing conditions**

# POLYMER

**Polymers are made up of a number of monomer repeat units, noting the number of repeat units as the degree of polymerization of a polymer , DP**

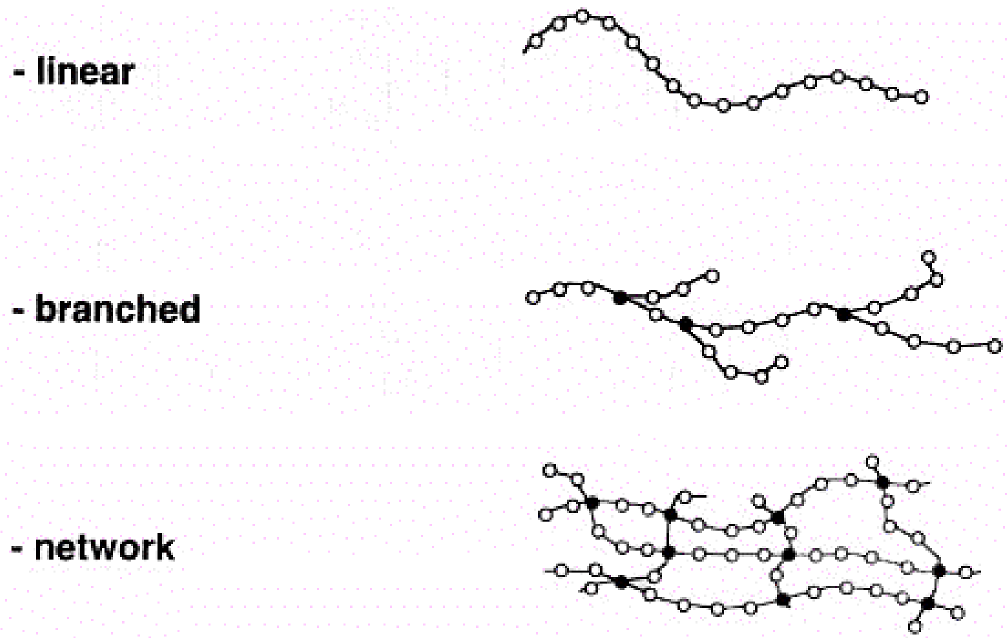
## Polymer Basics

- **poly = many**
  **mer = parts**
- **degree of polymerization = DP**

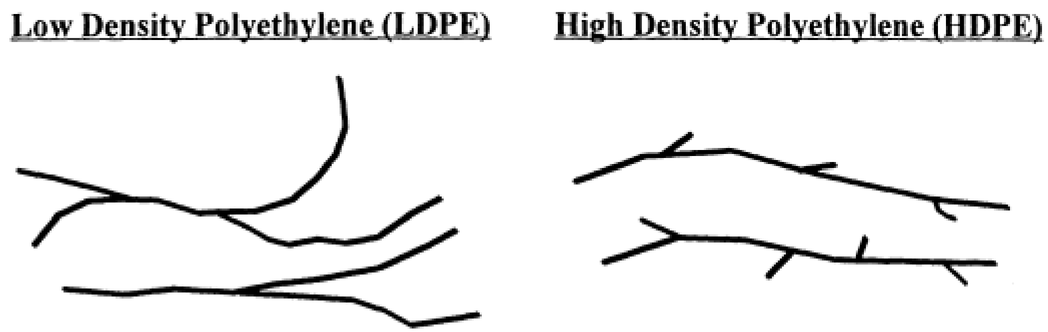


# POLYMER CONFIGURATIONS

**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**



# EFFECT OF MOLECULAR STRUCTURE ON END PERFORMANCE

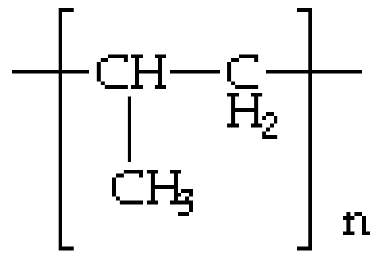



| Property | LDPE | HDPE |
|---|---|---|
| Melting Point (C) | 190-220 | 210-240 |
| Crystallinity (%) | 50 | 80 |
| Density (g/cm3) | 0.92 | 0.96 |
| Ultimate Tensile Strength (psi) | 2000 | 4500 |
| Applications | plastic bags, films, cables, containers | pipe, fittings, bottles, structural parts |

# THERMOPLASTIC POLYMERS

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

**PP**




## Characteristics:

- **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)

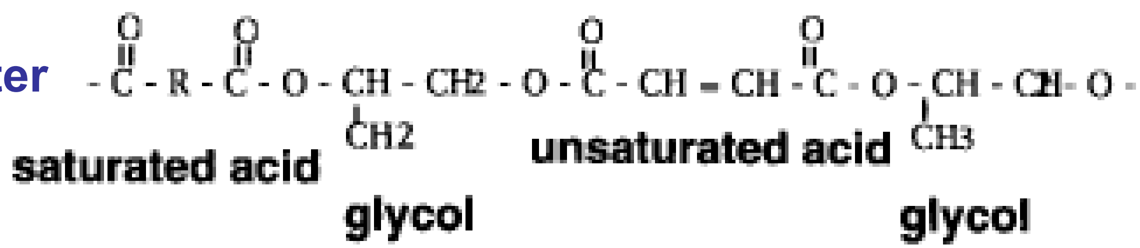
# THERMOSET POLYMERS

**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**
- **Cured 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**

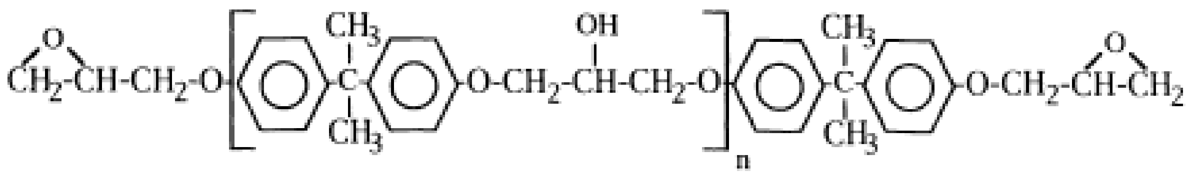


# THERMOSET POLYMERS (cont'd)

**Advantages:**

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

**Epoxy**



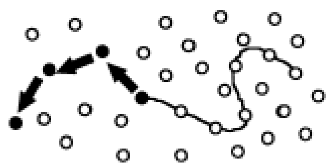
**Disadvantages:**

- **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**

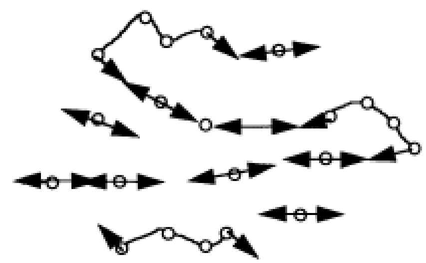
# POLYMER REACTIONS

**There are two fundamental polymerization reactions:**

Chain Polymerization



Step Polymerization



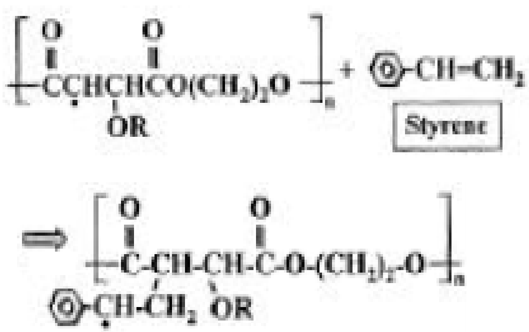
**This classification is of particular importance to thermosetting systems because the polymerization reactions between thermosets and thermoplastics are distinct in that:**

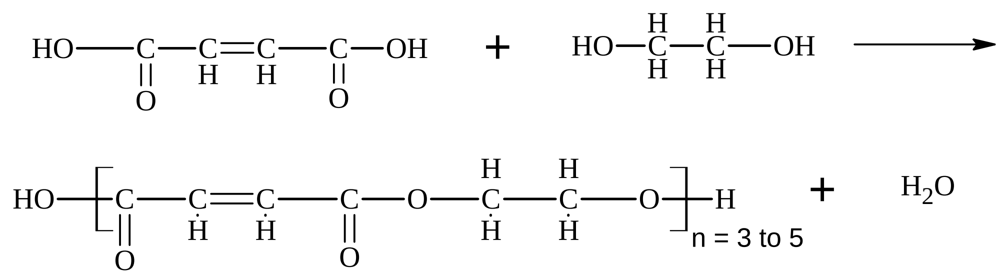
**Thermoplastics: polymerized prior to molding the final part**

**Thermosets: being polymerized via a polymerization reaction during the molding process**

# POLYMER CLASSIFICATION VIA REACTION TYPE

| 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

**Chain polymerization is characterized by the presence of a few active sites which react and propagate through a sea of monomers, e.g. vinyl monomers**

**Initiators /Catalysts** **to initiate a free radical chain polymerization**:

**Benzoyl peroxide (BPO)**
**Dicumyl peroxide (DCP)**
**Methyl ethyl ketone peroxide (MEKP), Cumene hydroperoxide (CHP)**

**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** **to suppress polymerization in order to improve processability and extend gel time/ shelf life**

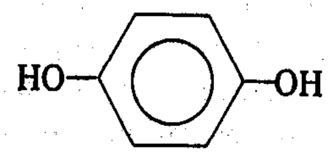
**Inhibitors and retarders differ in their effect on the conversion profile with time:**

**Inhibitors stop all radical polymerization until consumed.**
**Retarders stop only a portion of the radicals from propagating.**

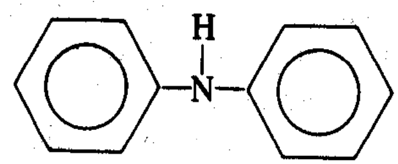
# CHAIN (OR ADDITION) POLYMERIZATION

**Examples of inhibitors and retarders used in free radical systems:**

- **Benzoquinone**
- **Hydroquinone**
- **Chloranil**
- **Diphenyl amine**
- **2,4 Pentanedione (acetylacetone)**




Hydroquinone




Diphenylamine

**Promoters and Accelerators to help initiate cure at room temperature:**
**Cobalt naphthenate (CoNap) 0-0.3%--in combination with MEKP**
**Dimethyl aniline (DMA) 0-0.3%--in combination with BPO and MEKP**

**Gel time for a given resin depends on initiator level, promoter level, second promoter level, and temperature.**

**For example, with Derakane 411 VE**
**MEKP 1%, CoNap 0.25%, 2.4-P 0, gel time 21min @ 25C**
**MEKP 1%, CoNap 0.25%, 2.4-P 0.2%, gel time 180min @ 25C**

**Note: Additives (fillers) may affect resin cure kinetics.**

# FREE RADICAL CHAIN POLYMERIZATION

**There are three important steps in free radical polymerizations:**

**Initiation:**

$$ROOR \xrightarrow{kd} 2RO\bullet$$

$$RO\bullet + M \xrightarrow{ki} M1\bullet$$

**Propagation:**

$$M1\bullet + M \xrightarrow{kp} M2\bullet$$

$$M2\bullet + M \xrightarrow{kp} M3\bullet$$

**Termination:**

$$Mi\bullet + Mj\bullet \xrightarrow{ktc} MiMj$$

$$Mi\bullet + Mj\bullet \xrightarrow{ktd} Mi + Mj$$

**Upon heating, the initiator (BPO, MEKP, DCP) dissociates to form two radicals which can attack the monomer double bonds and add to them. This forms a reactive radical center which can propagate to form polymer. Then radicals are terminated by combination or disproportionation.**

# 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.**

**Example: Polyester formation - The acid groups in diacids react with the alcohol groups in diols to form ester linkages.**
**Amide links - Amine groups react with carboxylic acids**

## 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**

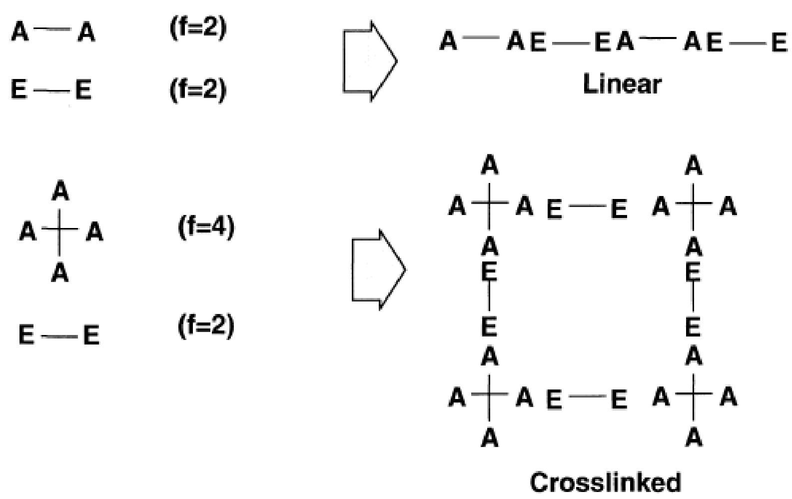
**Examples of curing agents for epoxies:**
**aliphatic amine (DETA, AEP), aromatic amine (MPDA, MDA), cyclic anhydrides (NMA, PA)**

# CHARACTERISTICS OF CHAIN AND STEP POLYMERIZATION REACTIONS

| Step Polymerization | Chain Polymerization |
|---|---|
| Any two molecular species present can react | Reaction occurs only at active centers by adding repeating units one at a time to the chain |
| Monomer disappears early in the reaction | Monomer concentration decreases steadily throughout the reaction |
| Polymer molecular weight rises steadily throughout the reaction | High polymer is formed at once--polymer molecular weight changes little throughout the reaction |
| Long reaction times are essential to obtain high molecular weights | Long reaction times give high yields but have little effect on molecular weight |
| At any stage all molecular species are present in a calculable distribution | Reaction mixture contains only monomer, high polymer, and a minuscule number of growing chains |

# 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**

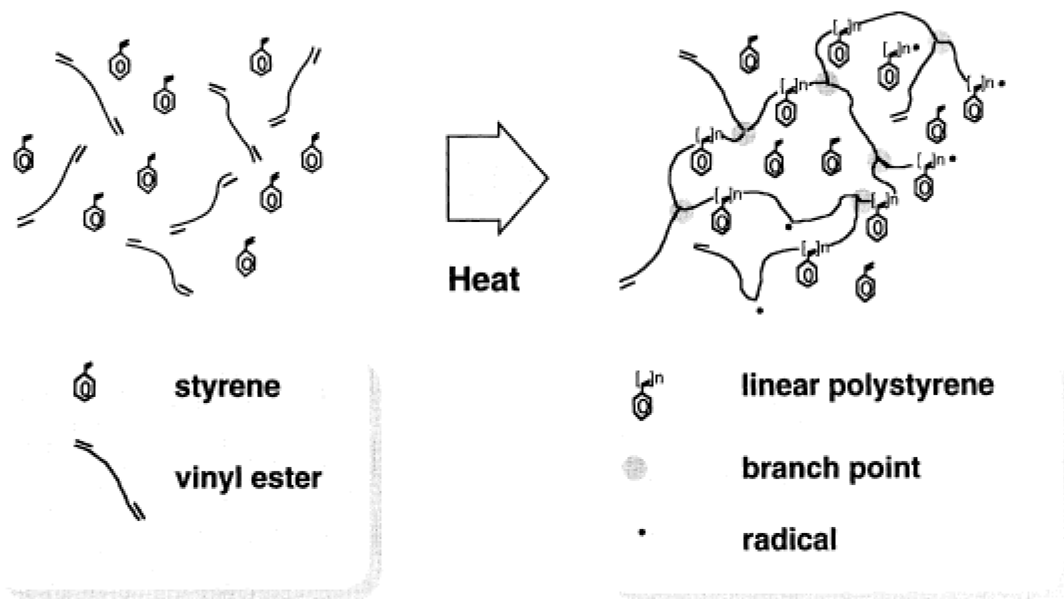
**Thermosets cured via this process include**

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

# CROSSLINKING IN CHAIN POLYMERIZATION

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

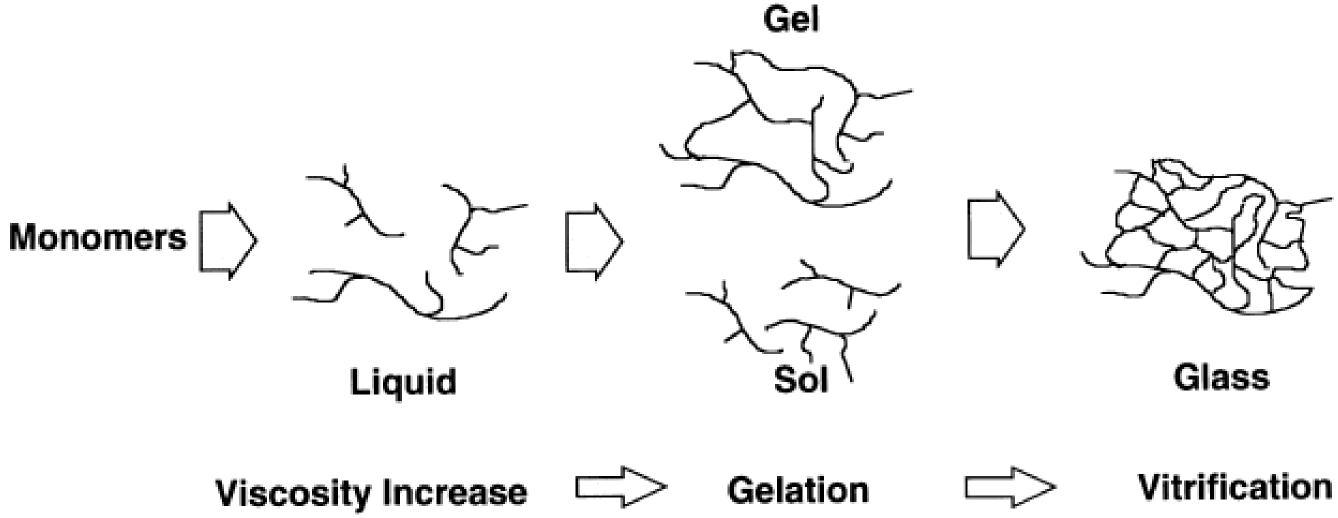
Examples of this type of systems: unsaturated polyesters, vinyl esters




- 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

Cure for thermosetting resins is defined as a process for changing the properties of a resin via chemical reaction with evolution of heat & any volatiles, increase in viscosity, gelation, and hardening.




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.

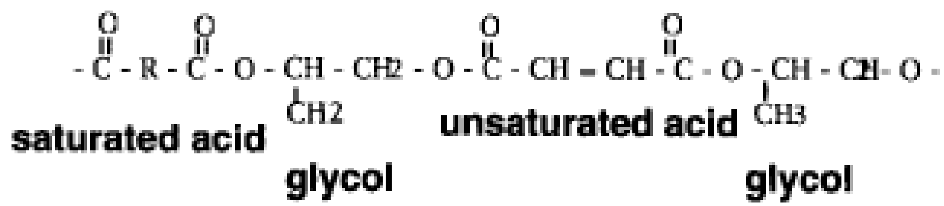
# POLYESTER AND VINYL ESTER RESINS

**Resin/ pre-polymer/ oligomer- 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%**

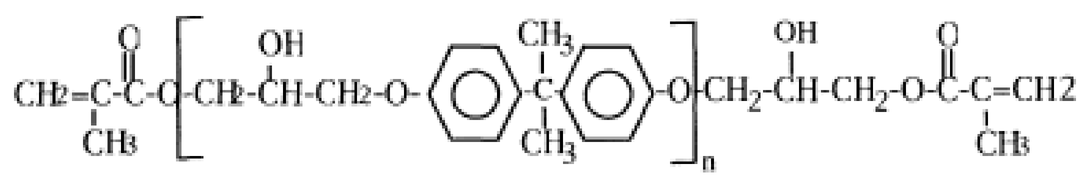
- **Peroxide necessary to begin chemical reaction**

**Promoter – 0.1 to 0.5%**

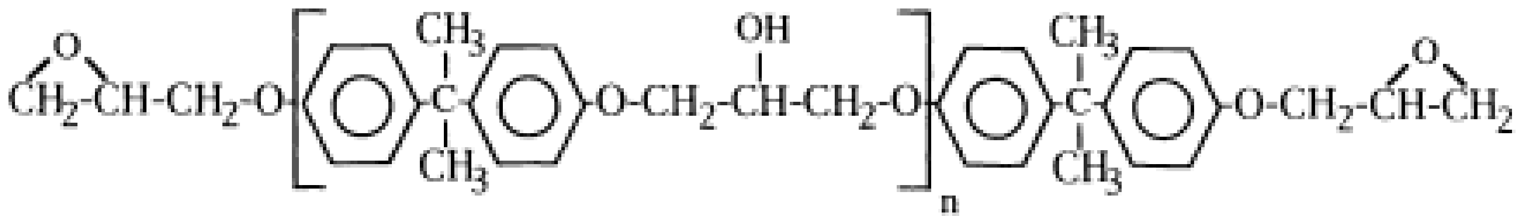
- **Speed up and enhance the cure**

**Inhibitors— 0.05 to 0.3%**

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



# EPOXY RESIN



The above most widely used epoxy resin is based on diglycidyl ethers of bisphenol A (DGEBA).

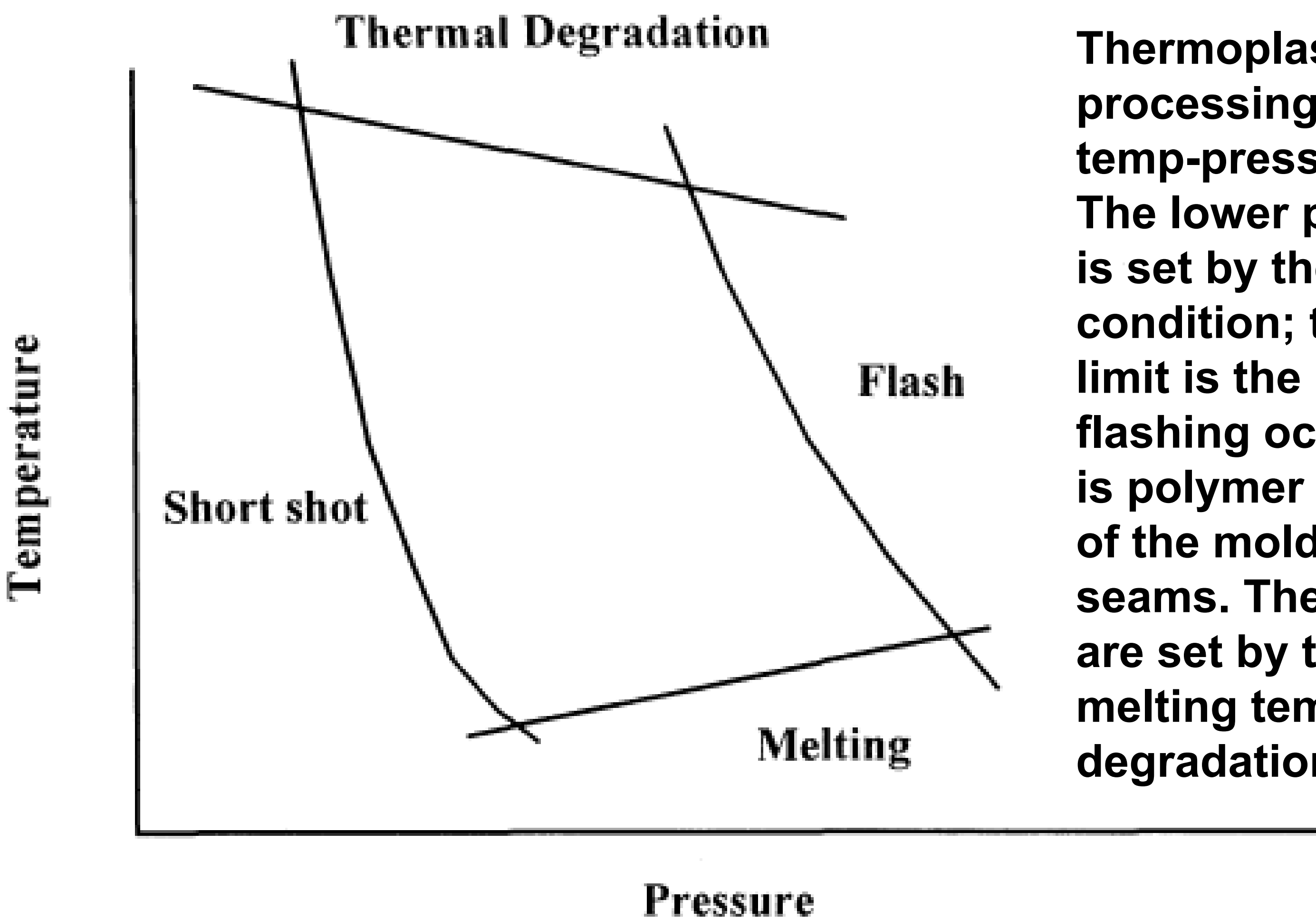
## Characteristics of epoxies

- Excellent chemical resistance
- Low shrinkage
- Two component system (for example, amine to epoxy ratio 1:2)
- Good adhesion to many substrates
- More difficult to process than polyesters and vinyl esters
- Vast selection of crosslinking agents or hardeners
- Control over final properties and processability

## Types of curing agents

**Amine: Diethylene triamine (DETA), Aminoethyl piperazine (AEP)**
**Meta-phenylenediamine (MPDA), Methylene dianilene (MDA)**
**Anhydride: Nadic methyl anhydride (NMA), Phthalic anhydride (PA)**

# THERMOPLASTIC PROCESSING




**Thermoplastic processing window in temp-pressure chart: The lower pressure limit is set by the short shot condition; the upper limit is the point where flashing occurs, which is polymer leaking out of the mold at the seams. The temp limits are set by the polymer melting temp and the degradation temp.**

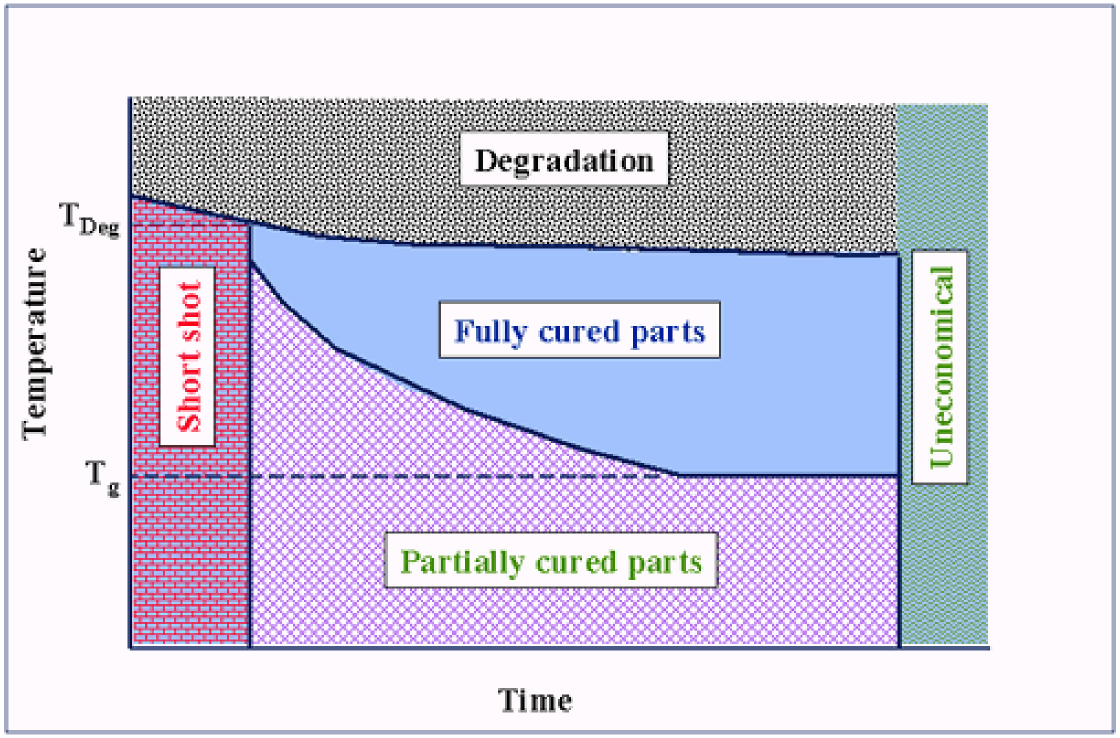
# THERMOSET PROCESSING

**Reaction kinetics control thermosetting polymer processes. For any polymer system, reaction kinetics are a function of**

- **Temperature**
- **Time**
- **Reactant concentration**

**Reaction time to highly cured system for some resin systems**

| Resins | reaction time |
|---|---|
| Epoxies | 60 min to 7 days |
| Vinyl ester | 30 min to ~1 hour |
| Polyesters | 30 min to ~1 hour |
| Urethanes | 10 to 60 seconds |



# FACTORS AFFECTING POLYMER PROCESSING

- **Material issues**
  - √ **Resin selection**
  - √ **Fiber / fabric selection and orientation**
  - √ **Resin / fiber sizing compatibility**

- **Processing Issues**
  - √ **Process selection**
    - ►**Injection molding, extrusion, compression…**
    - ►**Pultrusion, VARTM, infusion…**
  - √ **Tg or Tm < Tproc < Tdeg**
  - √ **Pressure selection (no residual tress, no flash)**
  - √ **Reaction kinetics for thermosets**
  - √ **Economical cycle times**

- **Case Study- Glass/VE, Carbon/VE or Carbon/Epoxy**
  - √ **Strength, stiffness vs. weight, cost**
  - √ **Carbon fiber sizing compatibility**
  - √ **VARTM, pultrusion, high temp infusion**

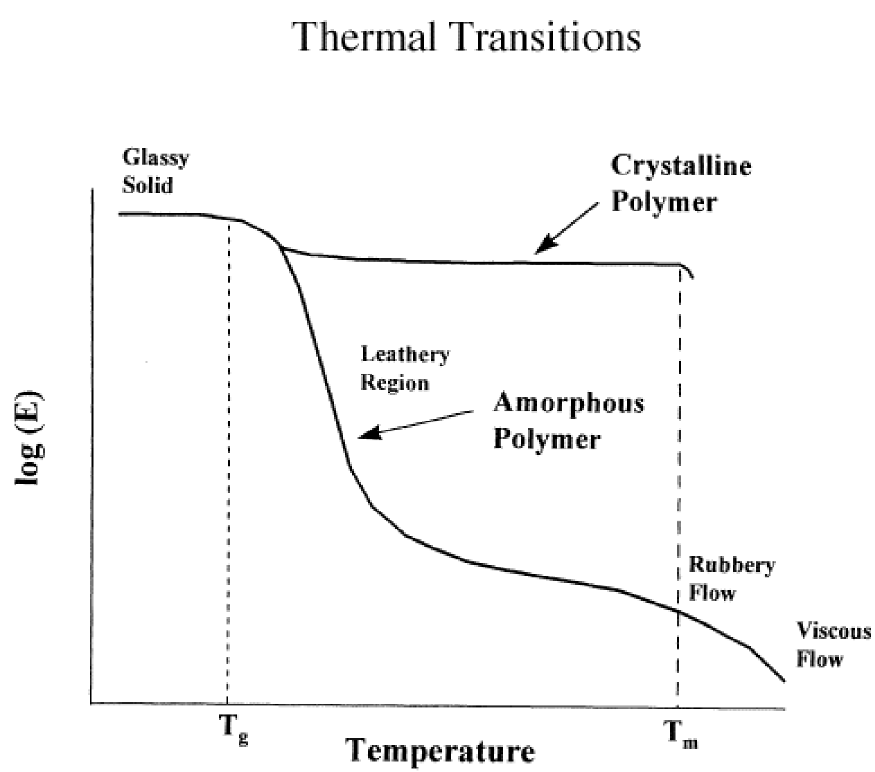
# GLASS TRANSITION TEMPERATURE

**T < Tg: Glassy state - brittleness, stiffness, and rigidity**
**T >Tg: Rubber state - softening and flow**

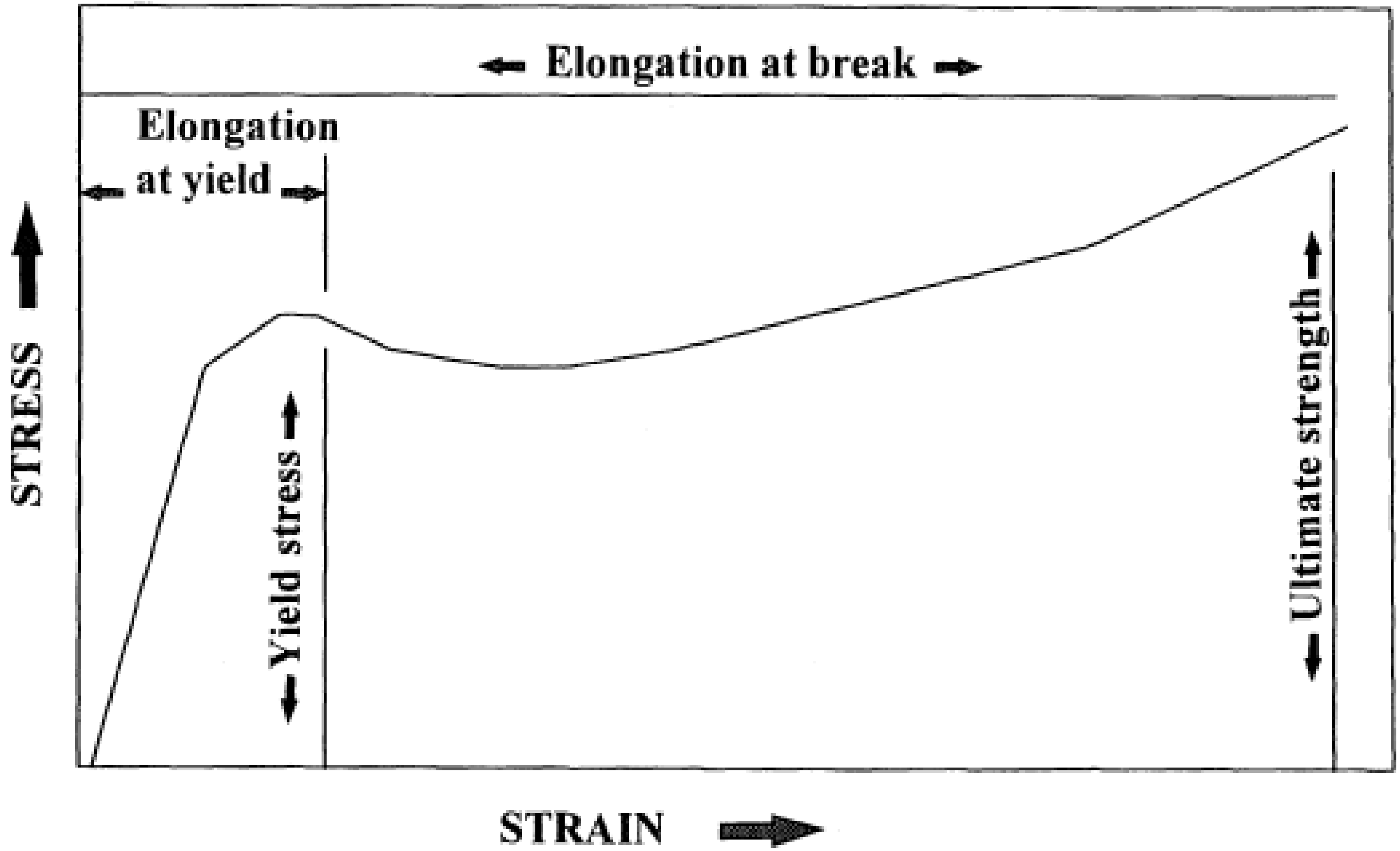
**Molecular Interpretation:**

**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**



# TENSILE STRESS-STRAIN RELATIONSHIPS



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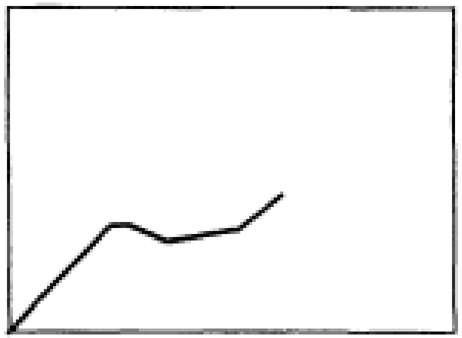
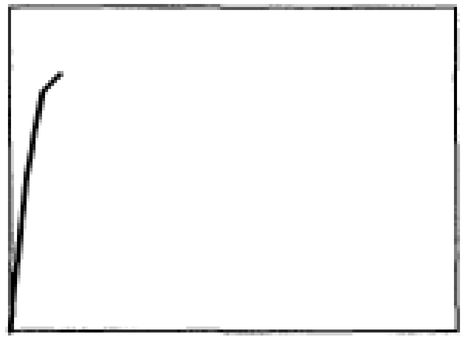
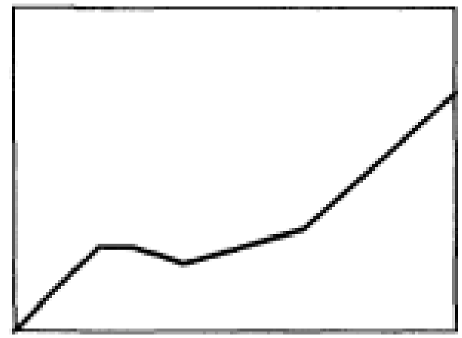


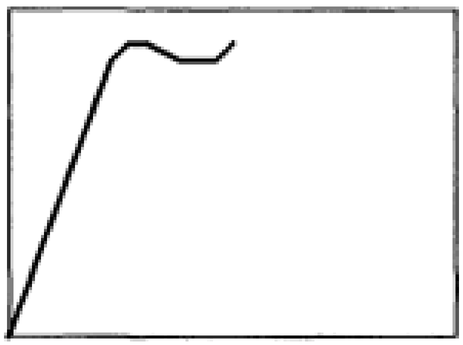
Soft and weak



Hard and brittle



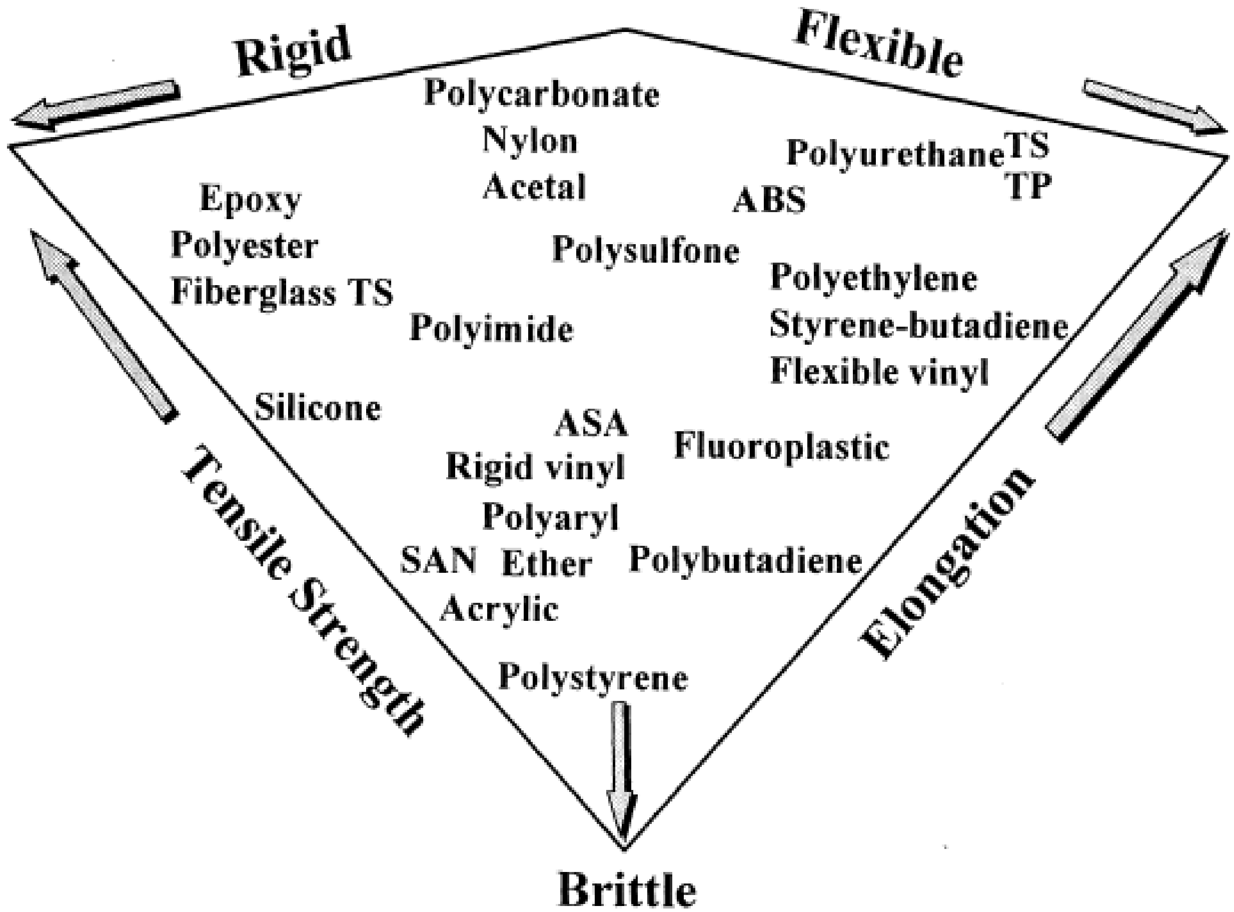
Soft and tough



Hard and strong


Hard and tough

# MECHANICAL PROPERTIES OF POLYMERS



# SUMMARY

**Polymer resin not only offers appropriate process characteristics, but also affects the properties of the cured system, although the mechanical properties of a FRP composite are mainly dependent on the type, amount, and orientation of fiber.**

**One of the great design strengths of composites is the multiple choices of both polymer types and reinforcement forms to meet the design requirements including environment.**

**In order to make effective use of these choices, product developers should be familiar with the properties, advantages and limitations of commercially available resins and fibers.**

**The ability to tailor the resin system and fiber architecture allows for optimized performance of a product that translates to weight and cost savings.**