- 1. Same exam format and protocol as the previous three
- 2. If your score for any of the previous exams needs to be updated in the school records (entered wrong SID, left SID blank, entered SSN, score change approved by Dr. Ryba, took Exam 3 late etc.), please send me an e-mail with your name and SID

► Functional groups:

► Carboxylic Acid



► Functional groups:

► Ester



Functional groups:

► Alcohol



- ► Functional groups:
 - ► Amine



Polymers - Review

► Functional groups:

► Epoxide



► Functional groups:

► Amide



► Functional groups:

► Carbonate

Structures:

▶ Polydimethylsiloxane (Silicone)





▶ Polypropylene







Structures:

Polycarbonate



- ► Structures:
 - ► Polyethylene



► Aramid (Kevlar)

$$\begin{array}{c} O & O H & H \\ I & I & I \\ -C - O & -C - N - O & -N - I_n \end{array}$$



▶ Nylon 6,6

$$\begin{array}{c} \left(N \cdot (CH_2)_6 \cdot N \cdot \overset{O}{\underset{c}{\overset{} \leftarrow}} \cdot \begin{pmatrix} O & O \\ \vdots & \vdots & \vdots \\ H & \underbrace{ & -G \\ & 6 \\ \end{array} \right)_n \\ \end{array}$$

Polymer Crystallinity

 Polymer crystallinity is the packing of molecular chains so as to produce an ordered atomic array.



► Because of their size and complexity, polymer molecules are often only partly crystalline:

$$\% \ crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

► A slower cooling rate and a simpler structure mean a higher degree of crystallinity.

Due to this semi-crystalline nature, polymers melt over a range of temperatures.

Polymer $\sigma - \epsilon$ behavior



▶ There are three types of polymers:

- 1. Brittle Polymers: Failure occurs during elastic deformation.
- 2. Plastic Polymers: $\sigma \epsilon$ behavior similar to metals—elastic deformation, yielding, plastic deformation, failure. Moreover over a small temperature range, transition from elastic to plastic can occur.
- 3. Elastomeric Polymers (Elastomers): The deformation is totally elastic, but for small stresses the deformation is large and recoverable.

Semicrystalline Polymers

Many semicrystalline polymers in bulk form have a spherulitic structure, wherein each spherulite contains numerous chain folded ribbons or lamallae radiating outward from the center and surrounded by amorphous material. Tie chains passing through these amorphous regions connect adjacent lamallae. When subjected to a tensile stress:



- 1. The chains first elongate in the stress direction by the breaking and stretching of covalent bonds. This deformation is elastic.
- 2. The tie chains in the amorphous regions become extended and aligned in the tensile direction.
- 3. The lamallae tilt so that the chain folds align along the tensile axis.
- 4. The lamallae divide into crystalline block segments.
- 5. The blocks and tie chains align in the tensile direction.

Amorphous Polymers



Amorphous polymers will exist as a glass at low temperatures, a rubbery solid above T_g and a viscous liquid at still higher temperatures. The rubbery solid state is also called viscoelastic state.

Viscoelastic Polymers

- ▶ The viscoelastic behavior of a polymer is quantified in two ways:
 - 1. Relaxation Modulus: The specimen is instantly subjected to a certain (low) strain level and the instantaneous stress required to maintain this strain level is measured at a constant temperature. The stress level is found to decrease with time due to molecular relaxation.

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0}$$

E_r(t_a) is found to decrease with (increasing) temperature.
Creep Modulus: The instantaneous strain is measured after subjecting the specimen to an instant constant stress.

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)}$$

 $E_c(t_a)$ decreases with (increasing) temperature and increases with the degree of crystallinity.

▶ Importance of molecular weight: As the MW increases,

- rotational motion will be restricted
- strength increases
- melt viscosity increases
 - ▶ if too high, difficult to process.
 - ▶ if too low, the material will not hold together until solidification.

Glass Transition

- ▶ The glass transition is a gradual transformation that occurs upon cooling in amorphous or semicrystalline polymers from liquid to rubbery material to rigid solid.
- ▶ The temperature at which this transformation completes is called the glass transition temperature, T_g .
- $\blacktriangleright T_g \approx (0.5 0.8)T_m$
- ▶ T_g and T_m are determined from a specific volume-temperature plot for a polymer.
- ▶ Chain stiffness (double chain bonds or aromatic groups), molecular weight, polar side-groups and bulky side-groups $\uparrow T_m$ and T_g

- ► Thermosets generally fracture in a brittle manner. Thermoplasts can have either brittle or ductile fractures. Moreover, a ductile to brittle transition may occur depending on temperature (↓) and strain rate (↑).
- Crazing: Some glassy thermoplasts exhibit crazing before fracture; wherein regions of localized yielding form small and interconnected μ voids separated by fibrillar bridges. Crazing is indicated by whitening of the plastic. If the tensile load is high enough, the μ voids coalesce and cracks form.

Composites

- ► A composite is any multi-phase material that exhibits a significant proportion of the properties of all the constituent phases such that a better combination of properties is realized. The constituent phases must be chemically dissimilar and separated by an interface, with each constituent being artificially made.
- Most composites are composed of two phases—the matrix phase, which is continuous and surrounds the dispersed phase.
- ▶ The relative amounts of the two phases, the geometry of the dispersed phase and the individual properties of the phase determine the properties of the composite.

Composites—Classification

- 1. Particle-reinforced
 - 1.1 Large particle (Ex: concrete, cermets)
 - 1.2 Dispersion-strengthened (Ex: TD Ni, SAP)
- 2. Fiber-reinforced



I > 15 lc

- 3. Structural
 - 3.1 Laminates
 - 3.2 Sandwich panels

- 2.1 Continuous (aligned)
- 2.2 Discontinuous (short)
 - 2.2.1 Aligned2.2.2 Randomly oriented2.2.3 Partially oriented

Fiber-reinforced Composites (FRCs)

- ▶ FRCs have fibers as the dispersed phase. Their USP is their specific strength and specific modulus.
- ▶ Fiber length is important to the degree to which the matrix can transfer the load to the fiber. The minimum length for effective strengthening and stiffening is called the critical length:

$$l_c = \frac{\sigma_f^* d}{2 \tau_c}$$

▶ $l > 15 l_c \Rightarrow Continuous; l < 15 l_c \Rightarrow Discontinuous$

Fiber-reinforced Composites (FRCs)

- ▶ FRCs have fibers as the dispersed phase. Their USP is their specific strength and specific modulus.
- ▶ Fiber length is important to the degree to which the matrix can transfer the load to the fiber. The minimum length for effective strengthening and stiffening is called the critical length:

$$l_c = \frac{\sigma_f^* d}{2 \tau_c}$$

▶ $l > 15 l_c \Rightarrow Continuous; l < 15 l_c \Rightarrow Discontinuous$



Longitudinal Loading of an Aligned FRC

- ▶ The fiber is brittle and the matrix is ductile.
- ► Stage 1: Both the fiber and the matrix deform elastically (so does the composite).
- Stage 2: The matrix deforms plastically and the fiber elastically. The proportion of the load borne by the fiber increases.
- ► At the end of stage 2, the fibers start to fail, but the failure of the composite is not drastic—the shorter fractured fibers still bear some load along with the matrix as it plastically deforms.



The matrix phase may be either metal (MMC), polymer(PMC) or ceramic (CMC). Its functions are :

- 1. To bind the distributed phase and transmit load to it.
- 2. To protect the distributed phase from surface damage.
- 3. To separate fibers so that cracks may not propagate easily.

For a good matrix-reinforcement bond,

- ▶ good wetting
- chemical and mechanical bonding

Influencing factors:

- 1. Economics
- 2. Environmental
- 3. Political
- 4. Market
- 5. Aesthetics
- 6. Material properties
 - 6.1 Safety factor, N
 - 6.2 Ashby diagrams