Polymer Structure-Properties Relationship

Processing → Structure → Properties & Mwt → Performance → Application

At the end of this lecture, you should be able to:

- Understand Crystallization, Melting, and Glass-Transition Phenomena in Polymers.
- Understand the Mechanical Behavior of Polymers.
- Understand the Effect of Temperature on Mechanical Behavior of Polymers
- Understand the polymer Viscoelastic Behavior.
- Understand the Pre-deformation by Drawing

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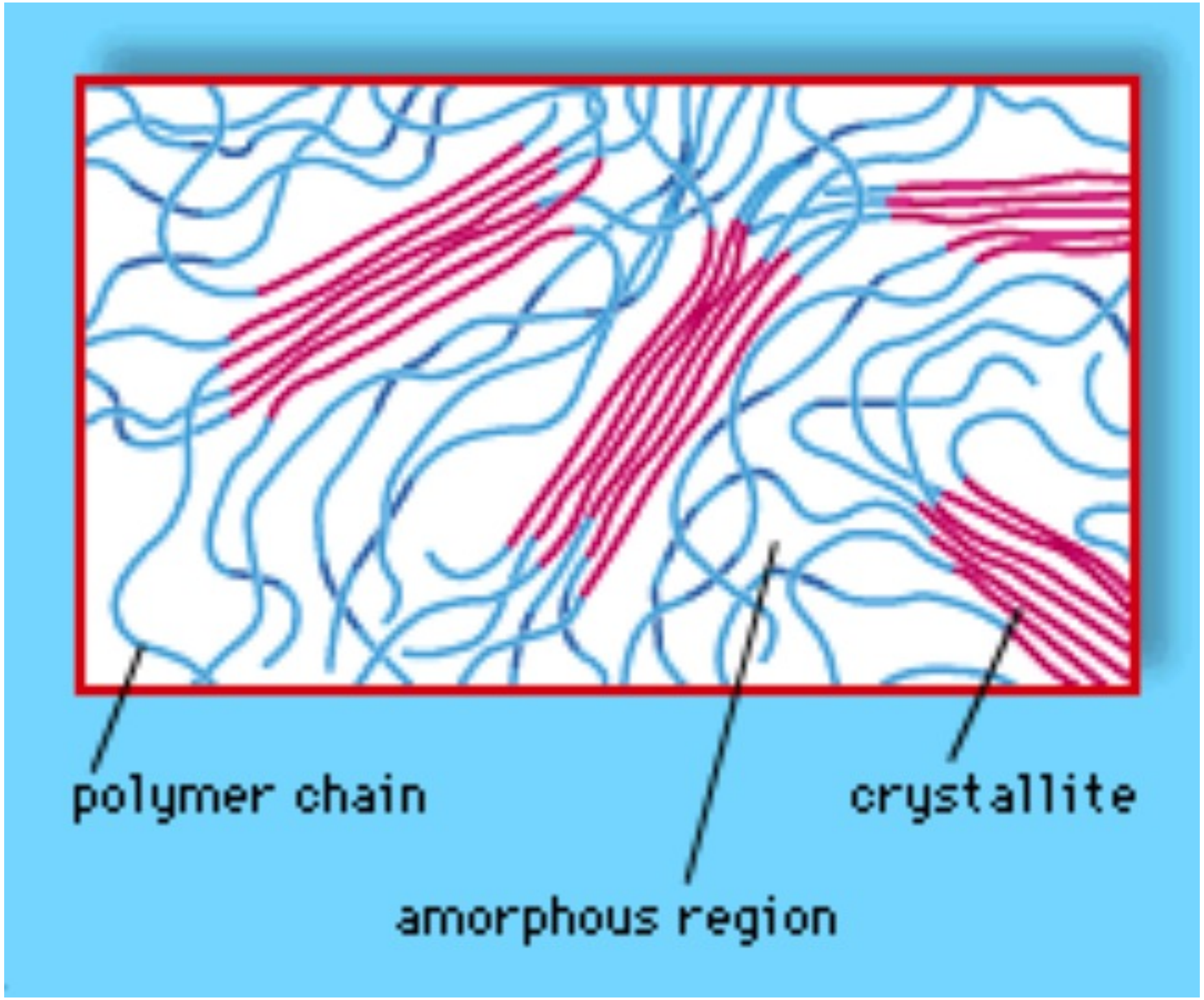
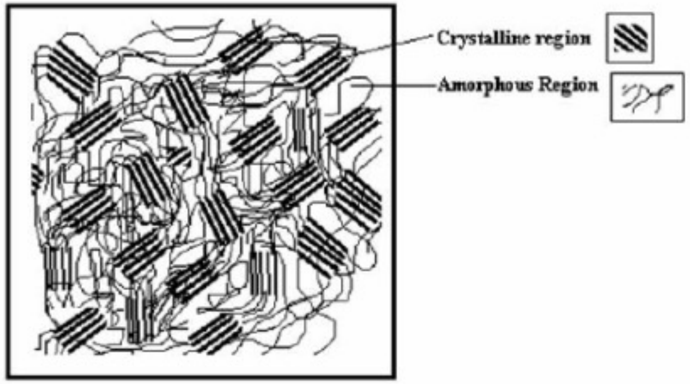
NOV. 2024

QUESTION: Are polymers , in general, considered as crystalline or amorphous materials ?



2) Based on Polymer Microstructure (Amorphous or Crystalline)



The degree of crystallinity: it is fraction of the total polymer in the crystalline regions, may vary from a few percentage points to about 90% depending on the crystallization conditions.

(a) ***Crystalline*** **(crystallinity, ≥ 50%)**	Polyethylene (HDPE and LDPE), polypropylene (isotactic), stretched nylon polyamides, polyoxymethylene etc. cellulose (cotton) fibre.
(b) ***Semi – crystalline*** **(crystallinity, 30 – 50%)**	Polybutene, cellulosics (cellulose esters (rayons) particularly if stretched), Gutta percha (1, 4 trans polyisoprene) etc.
(c) ***Amorphous or non- crystalline*** **(crystallinity < 25%)**	Natural rubber and most synthetic rubbers,N-alkylated(>15% alkylation) nylon polyamides, poly (methacry-lates and acrylates) poly (vinyl acetate), polystyrene etc.

This is taken from Lecture No.1

Crystallization, Melting, and Glass-Transition Phenomena in Polymers

Three phenomena that are important with respect to the design and processing of polymeric materials are crystallization, melting, and the glass transition. **Crystallization** is the process in which an ordered solid phase (i.e., crystalline) is produced by cooling a liquid melt having a highly random molecular structure. **The melting transformation** is the reverse process that occurs when a polymer is heated. **The glass-transition phenomenon** occurs when a liquid melt of amorphous (noncrystallizable) polymers become solids by cooling, keeping the disordered molecular structure that is characteristic of the liquid state.

Of course, alterations of physical and mechanical properties of polymers are related to crystallization, melting and the glass transition. Furthermore, for semicrystalline polymers, crystalline regions will experience melting (and crystallization), whereas noncrystalline areas pass through the glass transition.

MELTING AND GLASS TRANSITION TEMPERATURES

Melting and glass transition temperatures (*Tm* and *Tg)* are important parameters relative to in-service applications of polymers. They are considered , respectively, the upper and lower temperature limits for numerous applications, especially for semicrystalline polymers. The glass transition temperature may also define the upper use temperature for glassy amorphous materials. Furthermore, *Tm* and *Tg* also influence the fabrication and processing procedures for polymers and polymer-matrix composites.

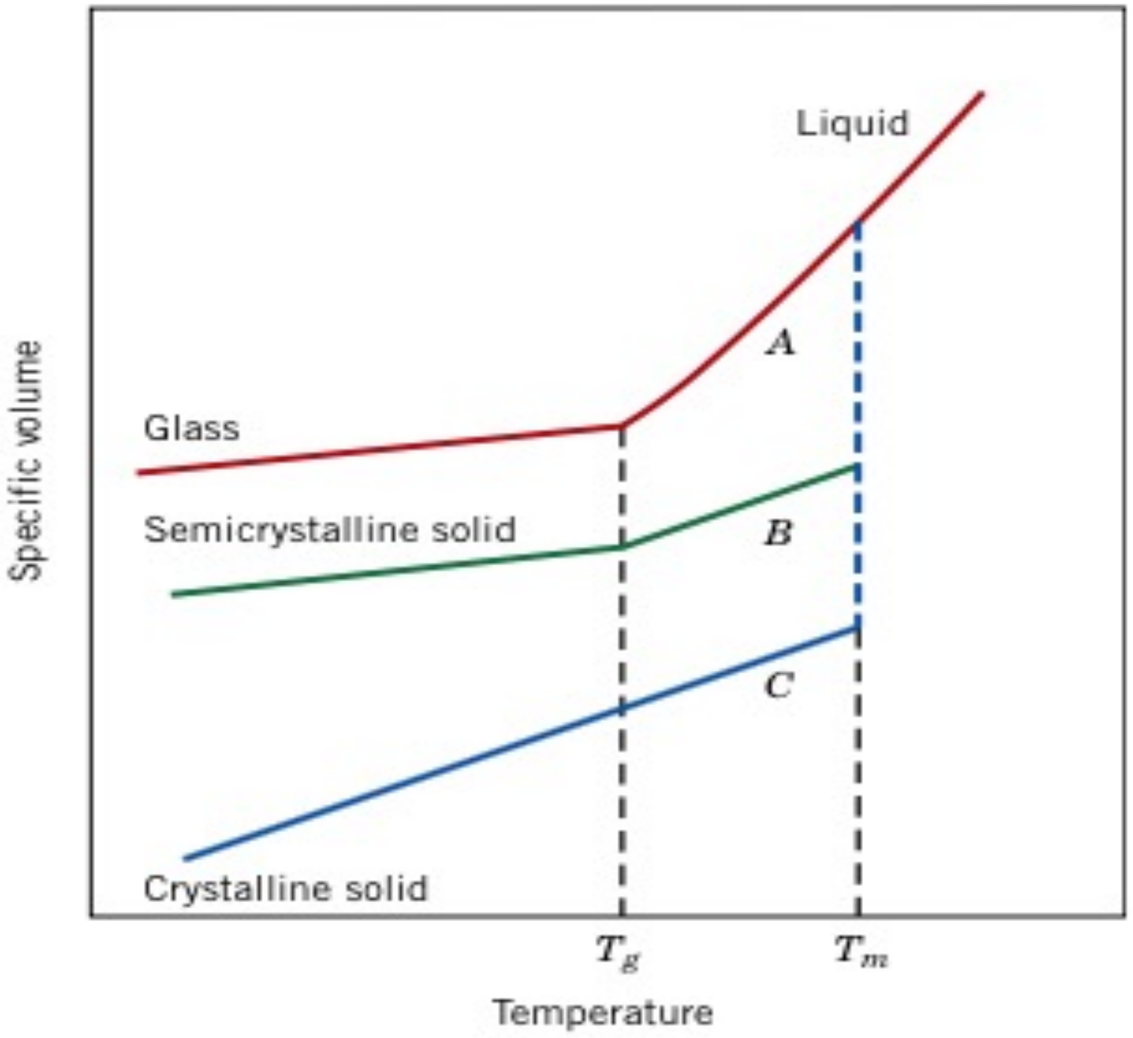
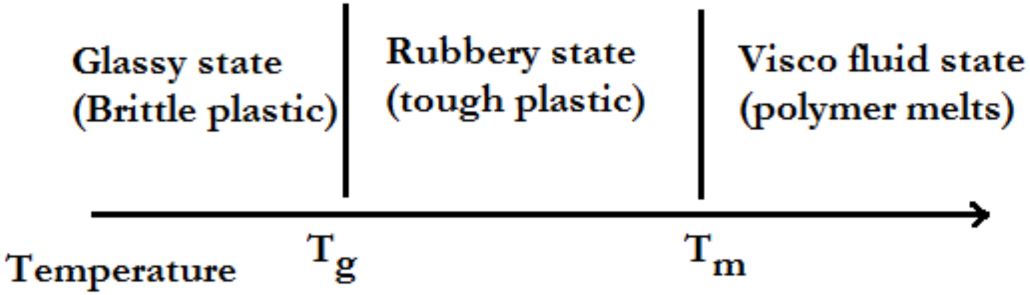


Figure 1 Specific volume versus temperature, upon cooling from the liquid melt, for totally amorphous (curve *A*), semicrystalline (curve *B*), and crystalline (curve *C*) polymers.

Material	*Glass Transition Temperature [°C (°F)]*	*Melting Temperature [°C (°F)]*
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Poly(ethylene terephthalate) (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)



Glassy state (Brittle plastic)

Rubbery state (tough plastic)

Visco fluid state (polymer melts)

Temperature **T_g** **T_m**

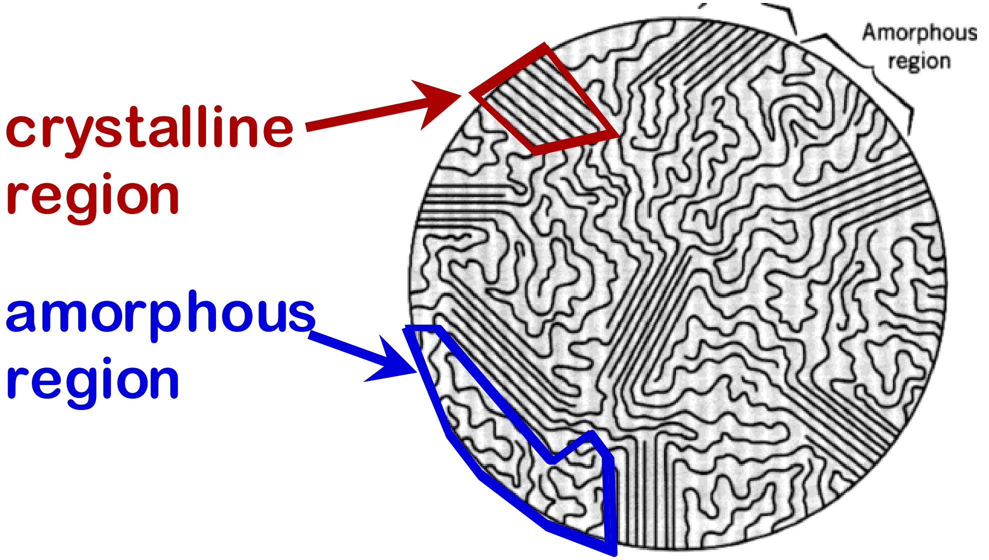
Some polymers are used below their Tg (in glassy state) like polystyrene and poly(methyl methacrylate).

Some polymers are used above their Tg (in rubbery state), for example, rubber elastomers like polyisoprene and polyisobutylene.

Polymer Crystallinity

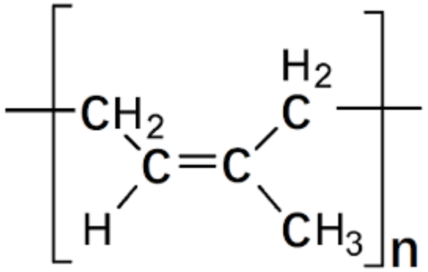
Crystalline is a state at which the molecular structure is capable of forming regular order (crystallizing) with molecules or portions of molecules regularly stacked in crystal-like fashion. The opposite of this state is known as ‘**Amorphous**’. Crystalline state may exist in polymeric materials. polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material (as shown in the figure). Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common, because twisting, kinking, and coiling of the chains prevent the strict ordering of every segment of every chain.

1. The degree of crystallinity may range from completely amorphous to almost entirely (up to about 95%) crystalline; in contrast, metal specimens are almost always entirely crystalline, whereas many ceramics are either totally crystalline or totally noncrystalline. Semicrystalline polymers are, in a sense, analogous to two-phase metal alloys.



PLEASE: REVIEW THE CLASSIFICATION Based on Polymer Microstructure (Amorphous or Crystalline)

2 ***The molecular chemistry as well as chain configuration*** also influence the ability of a polymer to crystallize. Crystallization is not favoured in polymers that are composed of chemically complex repeat units (e.g., polyisoprene). On the other hand, crystallization is not easily prevented in chemically simple polymers such as polyethylene and polytetrafluoroethylene, even for very rapid cooling rates.



polyisoprene

3. For linear polymers, crystallization is easily accomplished because there are few restrictions to prevent chain alignment. Any side branches interfere with crystallization, such that branched polymers never are highly crystalline; in fact, excessive branching may prevent any crystallization whatsoever. Most network and crosslinked polymers are almost totally amorphous because the crosslinks prevent the polymer chains from rearranging and aligning into a crystalline structure. A few crosslinked polymers are partially crystalline. With regard to the stereoisomers, **atactic** polymers are difficult to crystallize; however, **isotactic and syndiotactic** polymers crystallize much more easily because the regularity of the geometry of the side groups facilitates the process of fitting together adjacent chains. Also, the bulkier or larger the side-bonded groups of atoms, the less tendency for crystallization.

4. For copolymers, as a general rule, the more irregular and random the repeat unit arrangements, the greater the tendency for the development of noncrystallinity. For **alternating and block copolymer**s there is some likelihood of crystallization. On the other hand, **random and graft copolymers** are normally amorphous.

5. To some extent, the physical properties of polymeric materials are influenced by the degree of crystallinity. Crystalline polymers are usually ***stronger and more resistant to dissolution and softening by heat.***

Degree of Crystallinity Calculation

An example of unit cell

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

where ρ_s is the density of a specimen for which the percent crystallinity is to be determined, ρ_a is the density of the totally amorphous polymer, and ρ_c is the density of the perfectly crystalline polymer. The values of ρ_a and ρ_c must be measured by other experimental means.

Q1: Compute the following:

(a) The density of totally crystalline polyethylene, taking the the unit cell volume equals to $9.33X10^{-23}$ cm^3/unit cell and the equivalent of two ethylene repeat units is contained within each unit cell.

(b) The crystallinity percent of a branched polyethylene that has a density of 0.925 g/cm^3. The density of totally amorphous material is 0.870 g/cm^3.

Solution: The repeating unit of polyethylene is C_2H_4

(a) The density of totally crystalline polyethylene can be calculated using the following relation:

$$\rho = \frac{nMo}{Vc\ N_A} \dots\dots\dots\dots (1)$$

Where n represents the number of repeat unit within the unit cell (for polyethylene $n = 2$), and A is the repeat unit molecular weight, which for polyethylene is:

$$M_o = 2\,(12.01) + 4(1.008) = 28.05\ g/gmol$$

V_c *is* unit cell volume and equals to 9.33X10^{-23} cm^3/unit cell, N_A is Avogadro number (6.022 X 10^{23} repeat unit/mol).

Now, substituting the above parameters in Eq.1, one can find the density of totally crystalline polyethylene:

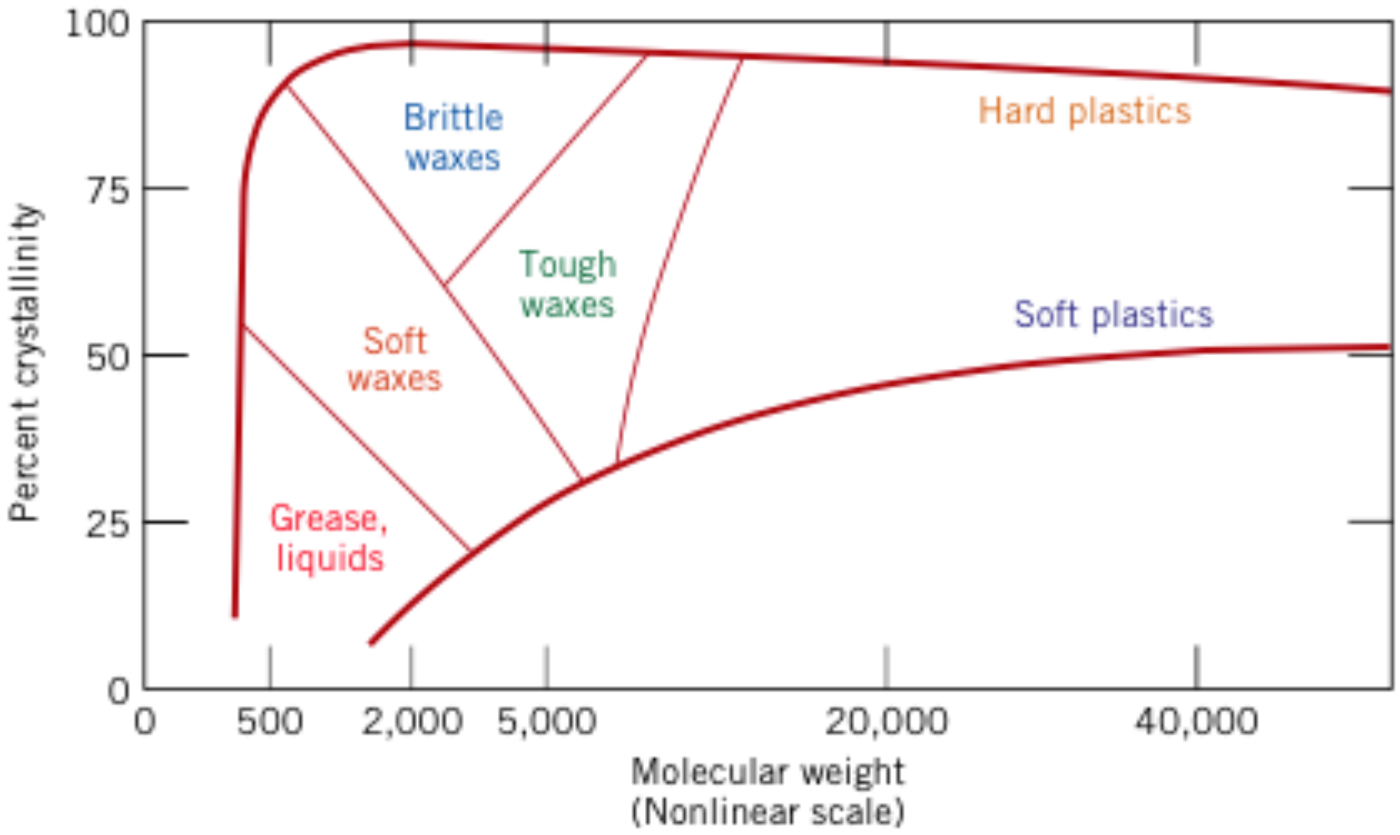
$$= \frac{(2\ \text{repeat units/unit cell})(28.05\ \text{g/mol})}{(9.33 \times 10^{-23}\ \text{cm}^3\text{/unit cell})(6.022 \times 10^{23}\ \text{repeat units/mol})}$$
$$= 0.998\ \text{g/cm}^3$$

(b) Now, we can use the given information and the calculated density value of totally crystalline polyethylene to find the degree of crystallinity as follows:

$$\%\ \text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$
$$= \frac{0.998\ \text{g/cm}^3\ (0.925\ \text{g/cm}^3 - 0.870\ \text{g/cm}^3)}{0.925\ \text{g/cm}^3\ (0.998\ \text{g/cm}^3 - 0.870\ \text{g/cm}^3)} \times 100$$
$$= 46.4\%$$

Percent of Crystallinity Vs. Molecular Weight

Figure The influence of degree of crystallinity and molecular weight on the physical characteristics of polyethylene. (From R. B. Richards, "Polyethylene—Structure, Crystallinity and Properties," *J. Appl. Chem.*, **1**, 370, 1951.)



SUMMARY AND NOTES :

- The **glass transition temperature**, **T_g**, is the temperature at which the amorphous domains of a polymer take on characteristic glassy-state properties; brittleness, stiffness and rigidity (upon cooling).
- The **melting temperature, T_m**, is the melting temperature of the crystalline domains of a polymer sample
- The operating temperature of polymers is defined by transition temperatures

- Crystallinity depends on the molecular structure of polymers
- No bulk polymer is completely crystalline
- In semi-crystalline polymers, regular crystalline units are linked by un-orientated, random conformation chains that constitute amorphous regions
- Presence of crystalline structures has a significant influence on physical, thermal and mechanical properties

  Highly crystalline: polyolefins

  Totally amorphous: atactic PS and PMMA

Mechanical Behavior of Polymers

- Polymers fall within three general classifications (shown in Figure 1): brittle (curve A), plastic (curve B), and highly elastic (curve C).

- Polymers are neither as strong nor as stiff as metals. However, their high flexibilities, low densities, and resistance to corrosion make them the materials of choice for many applications.

- The mechanical properties of polymers are sensitive to changes in temperature and strain rate. With either rising temperature or decreasing strain rate, modulus of elasticity diminishes, tensile strength decreases, and ductility increases.

stress–strain behavior

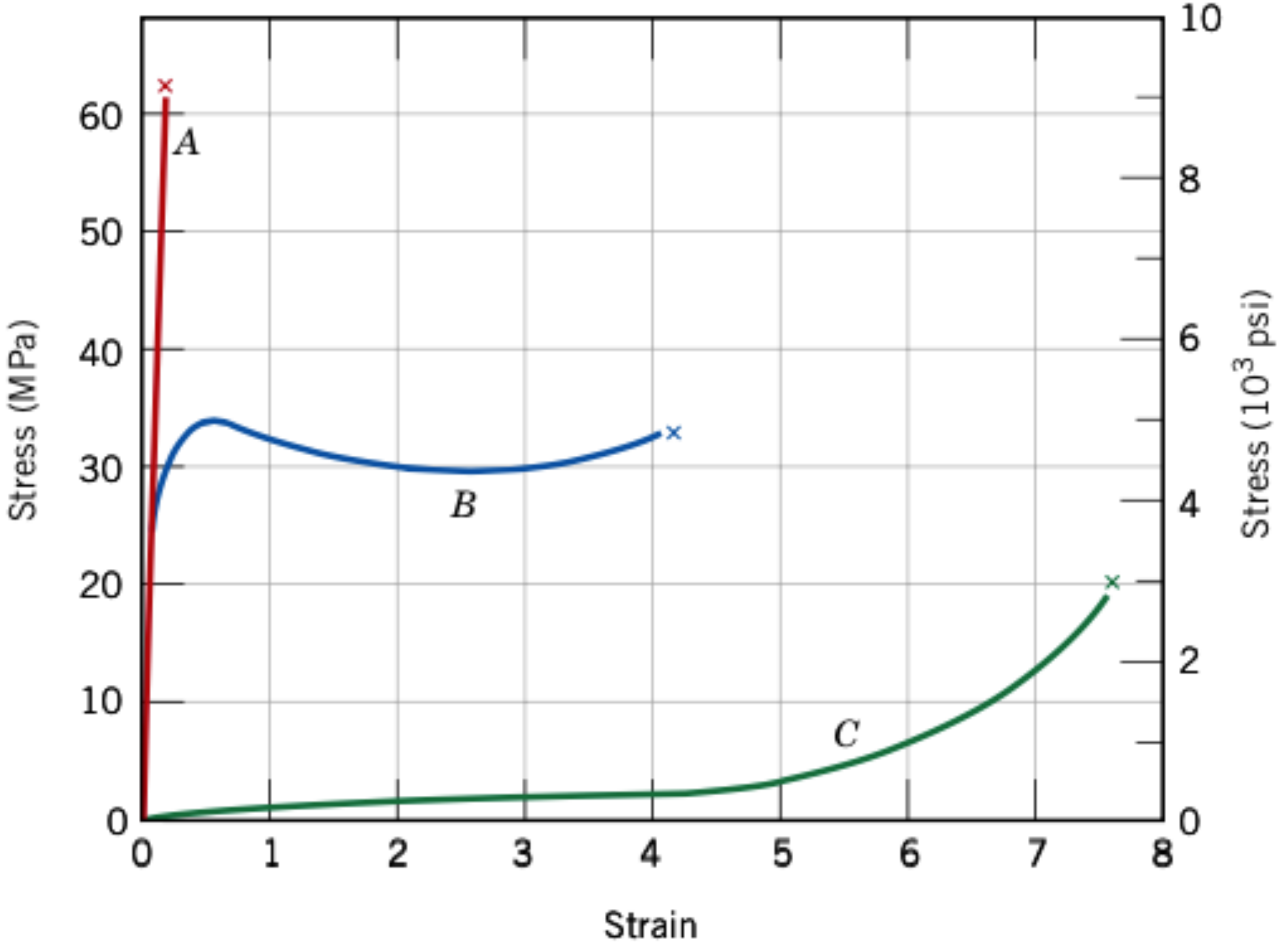


Figure 2: stress–strain behavior for brittle (curve A), plastic (curve *B*), and highly elastic (elastomeric) (curve *C*) polymers

Effect of Temperature on Mechanical Behavior of Polymers

In addition, the mechanical characteristics of polymers are much more sensitive to temperature changes near room temperature. Consider the stress—strain behavior for poly(methyl-methacrylate)(Plexiglas) at several temperatures between 4 and 60 °C. Increasing the temperature produces (1) a decrease in elastic modulus, (2) a reduction in tensile strength, and (3) an enhancement of ductility. At 4°C Increasing the temperature produces (1) a the material is totally brittle, whereas there is considerable plastic deformation at both 50 and 60 °C.

stress–strain behavior at different temperatures

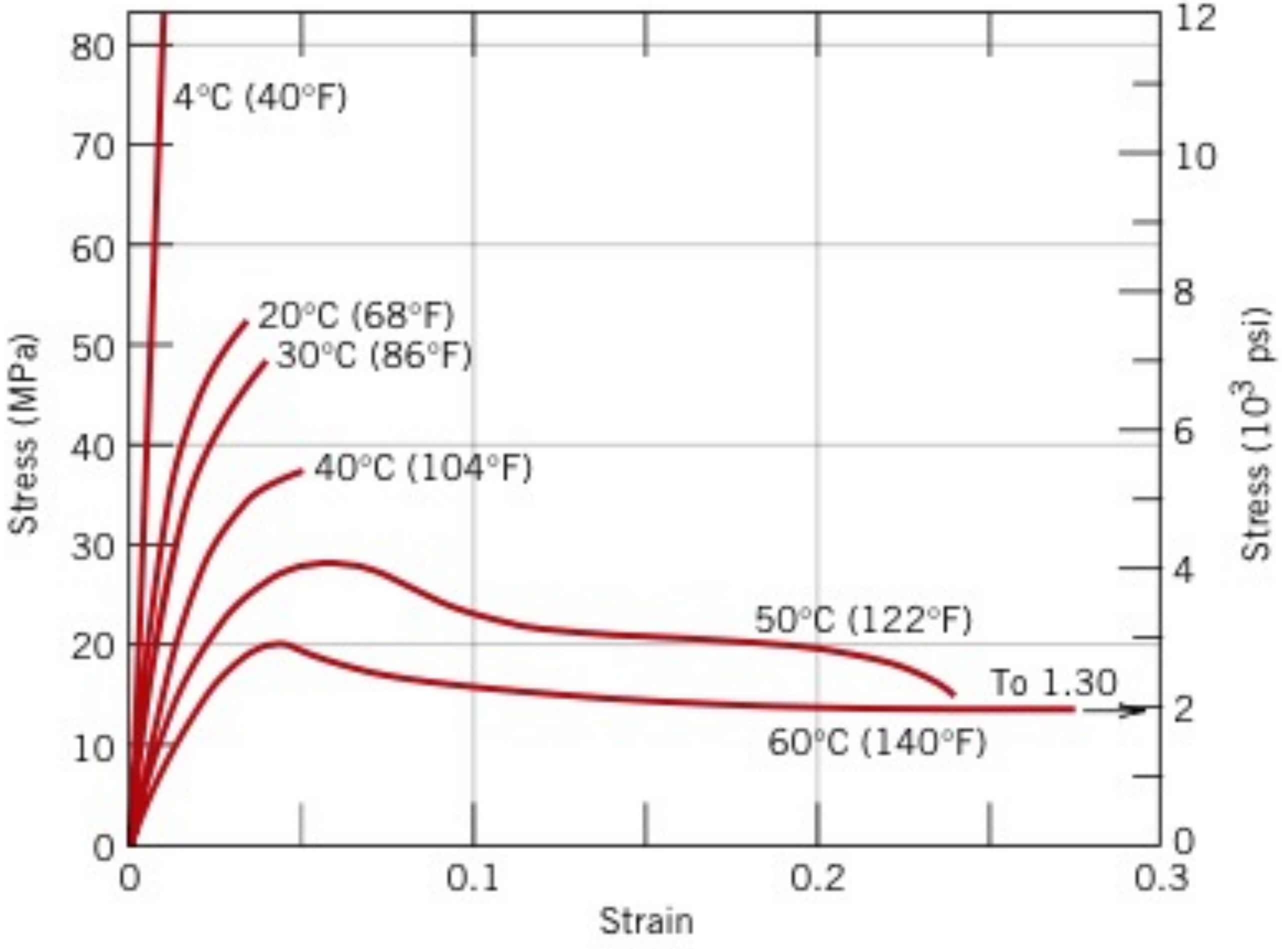
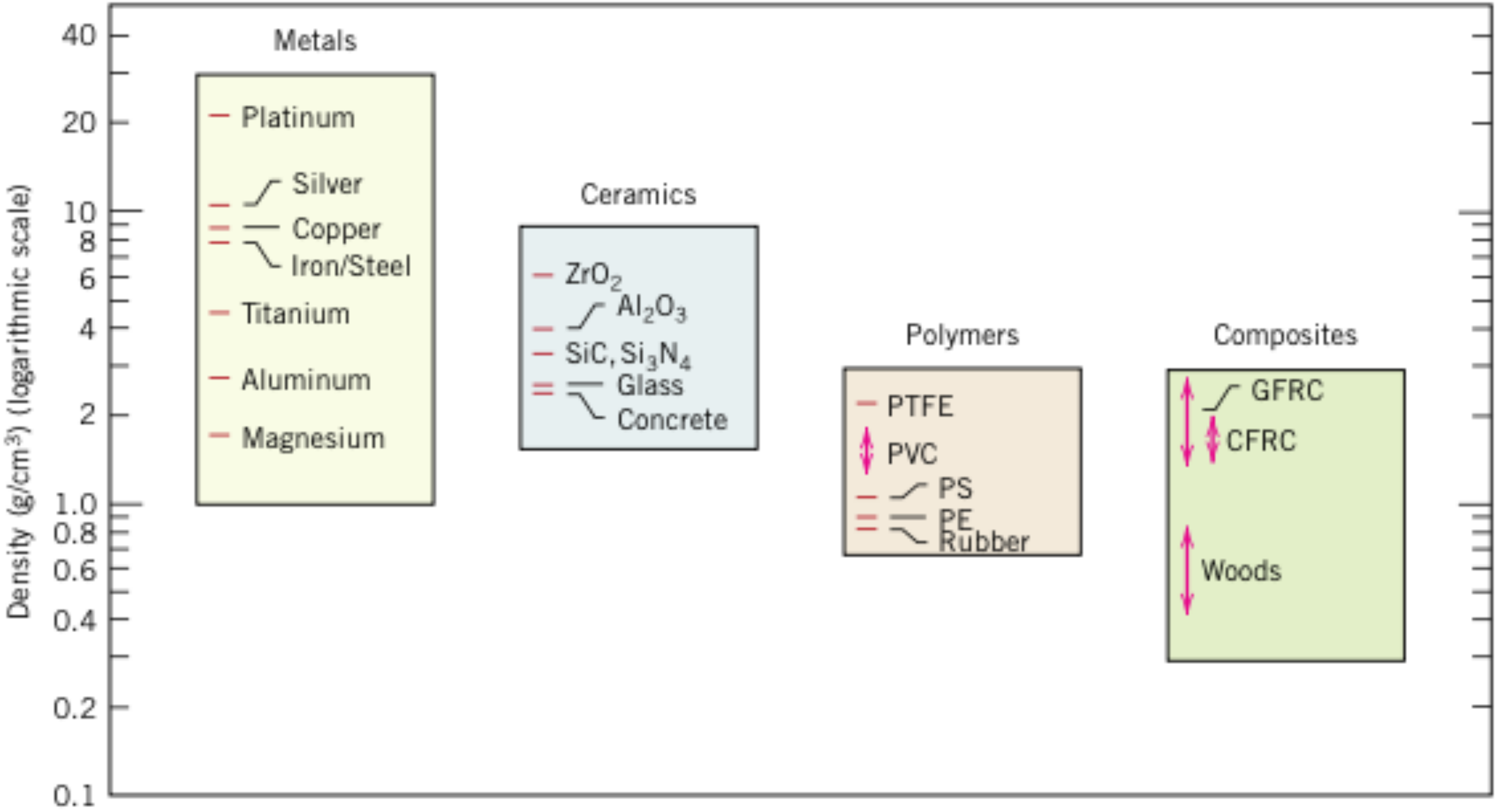


Figure 3: The influence of temperature on the stress–strain characteristics of poly(methyl methacrylate). (From T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," *Symposium on Plastics,* American Society for Testing and Materials, Philadelphia, 1944. Copyright, ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.)

Comparison among Metals, Ceramics, polymer and Composites



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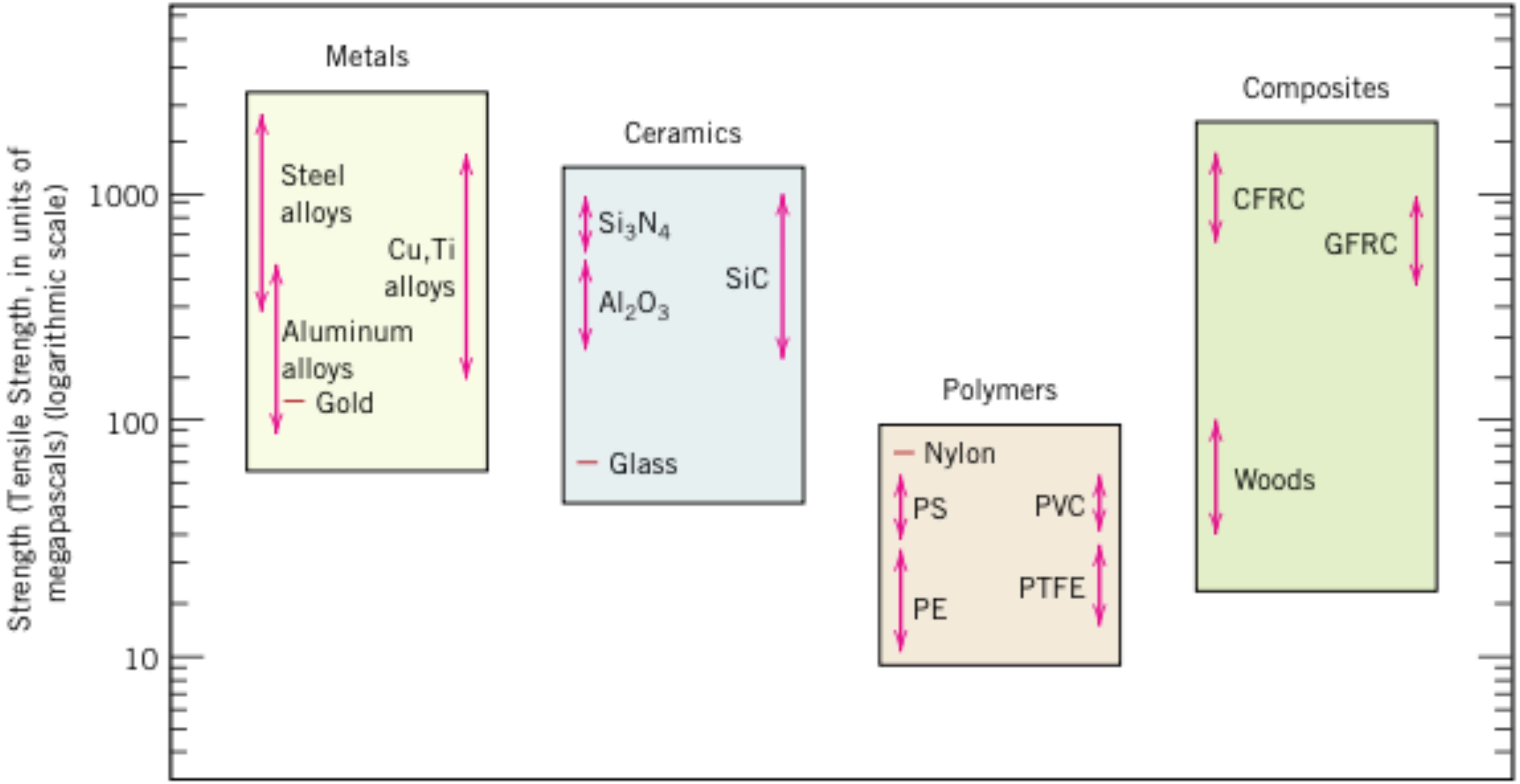

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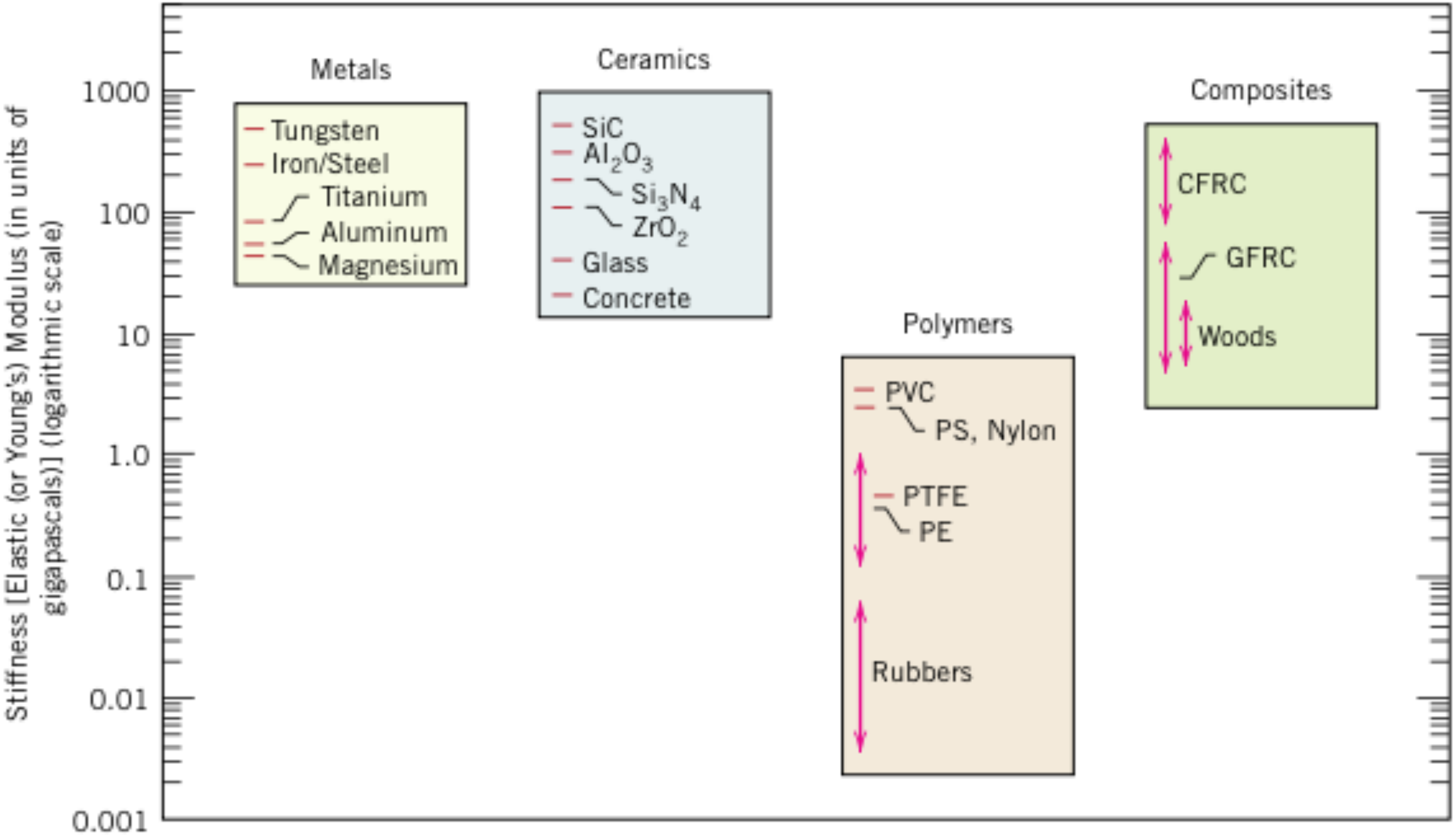

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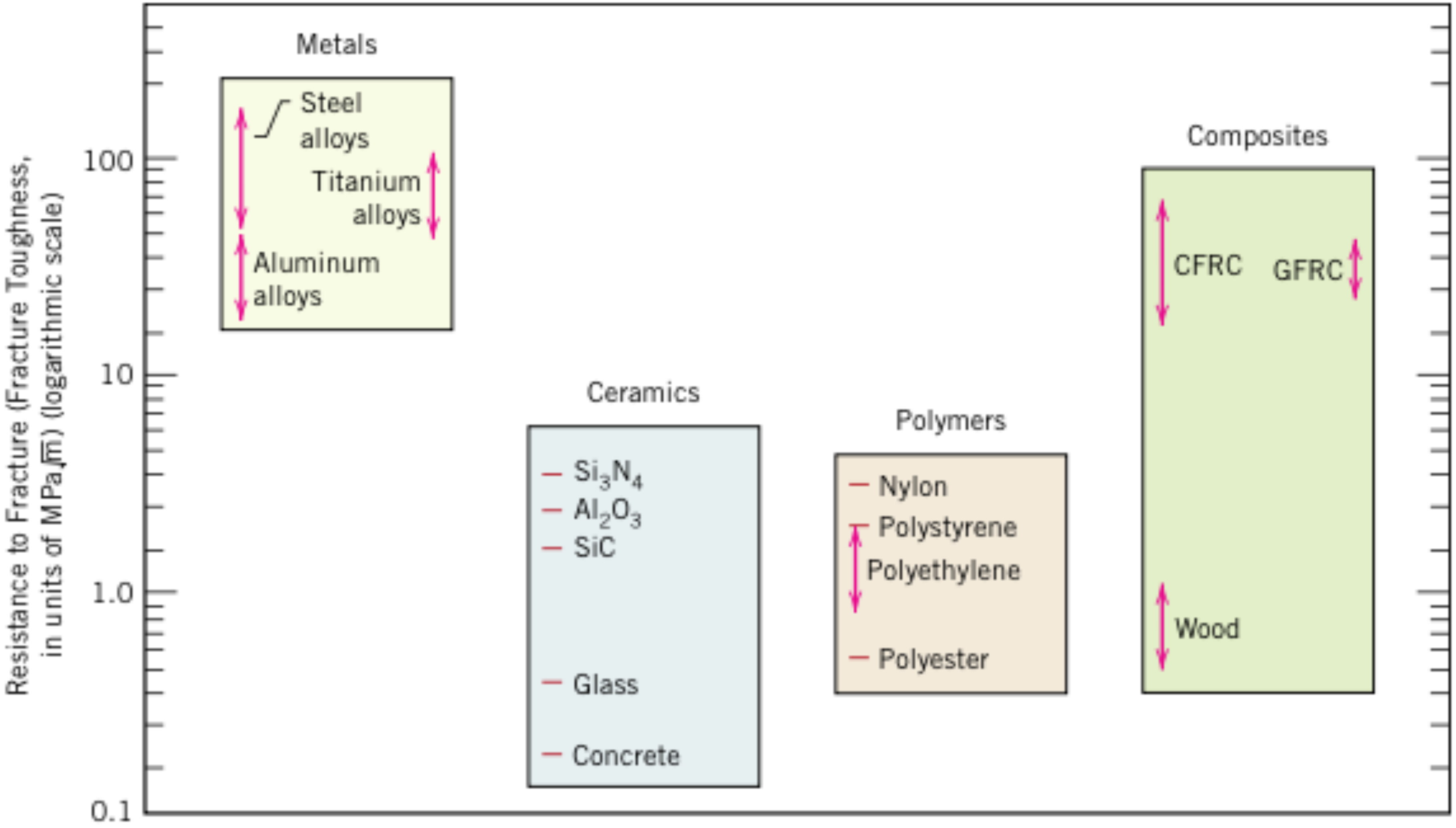
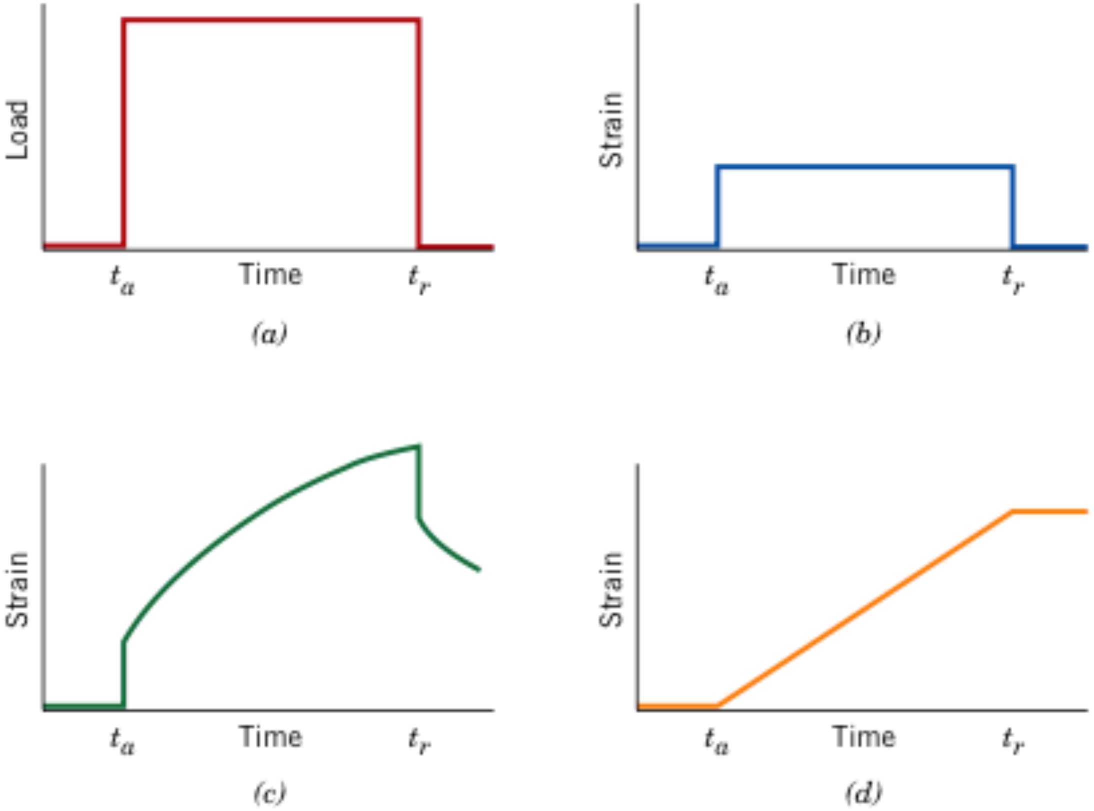


Viscoelastic Behavior

An amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures [above the glass transition temperature)], and a viscous liquid as the temperature is further raised. For relatively small deformations, the mechanical behavior at low temperatures may be elastic; that is, in conformity to Hooke's law. At the highest temperatures, viscous or liquid- like behavior prevails. For intermediate temperatures the polymer is a rubbery solid that exhibits the combined mechanical characteristics of these two extremes; the condition is termed **viscoelasticity.**

Figure (*a*) Load versus time, where load is applied instantaneously at time t_a and released at t_r. For the load–time cycle in (*a*), the strain-versus-time responses are for totally elastic (*b*), viscoelastic (*c*), and viscous (*d*) behaviors.



Predeformation by Drawing

On a commercial basis, one of the most important techniques used to improve mechanical strength and tensile modulus is to permanently deform the polymer in tension. This procedure is sometimes termed *drawing* and corresponds to the neck extension process. In terms of property alterations, drawing is the polymer analogue of **strain hardening in metals**. It is an important stiffening and strengthening technique that is employed in **the production of fibers and films**. During drawing the molecular chains slip past one another and become highly oriented; for semicrystalline materials the chains assume conformations similar to that represented schematically in Figure below.

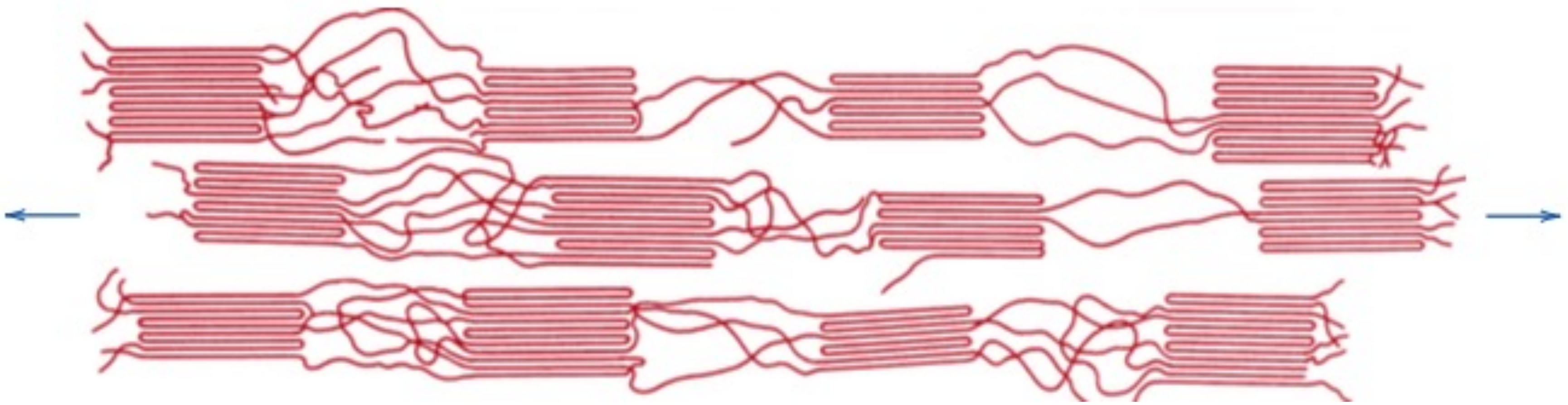


Figure: Orientation of block segments and tie chains with the tensile axis in the final plastic deformation stage

NOTES:

1. Degrees of strengthening and stiffening will depend on the extent of deformation (or extension) of the material. Furthermore, the properties of drawn polymers are highly anisotropic. For materials drawn in uniaxial tension, tensile modulus and strength values are significantly greater in the direction of deformation than in other directions. Tensile modulus in the direction of drawing may be enhanced by up to approximately a factor of three relative to the undrawn material.

2. For an amorphous polymer that is drawn at an elevated temperature, the oriented molecular structure is retained only when the material is quickly cooled to the ambient; this procedure gives rise to the strengthening and stiffening effects described in the previous paragraph. On the other hand, if, after stretching, the polymer is held at the temperature of drawing, molecular chains relax and assume random conformations characteristic of the predeformed state; as a consequence, drawing will have no effect on the mechanical characteristics of the material.