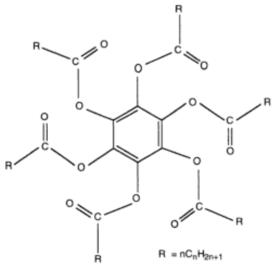
090109   Quiz 1   Introduction to Polymers

In class we discussed the definition of a polymer first by comparing polymers with metals and ceramics and then by noting certain properties of polymers that distinguish commercial polymers from low-molecular weight materials particularly pertaining to rheology.

1) Long-chain molecules crystallize in asymmetric crystals that mimic the asymmetry of the molecule.
   a) Describe the crystal shape of a moderate molecular weight alkane (wax/parafin) crystal such as dodecane. Show how the chain fits into the crystal.
   b) Sketch a plot of crystal size versus number of alkane units from butane (4) to polyethylene (1000). Explain the behavior.
   c) What determines the crystalline size for polyethylene?
   d) While alkanes display rod-like structure in the crystals you described in 1a, benzene-hexa-n-alknoate, shown below, is a macromolecule with discoidal structure. What shape crystal do you expect from such a 2 dimensional molecule?

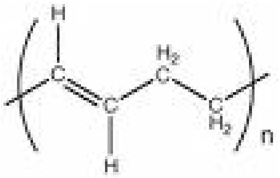


$$\text{Crystal} \xrightarrow{81.2°\text{C}} \text{Columnar hexagonal phase} \xrightarrow{87°\text{C}} \text{Isotropic liquid}$$

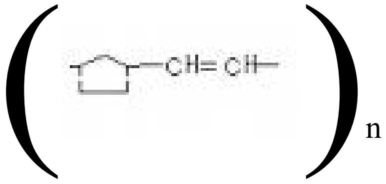
Fig. A.III.12 Homologous series of BHn (benzene-hexa-n-alkanoates). It is to this series that the first columnar phase belongs, discovered in 1977. The phase sequence presented is that of BH7 (from ref. [7]).

2) The mechanical properties of materials are usually described relative to two linear constitutive equations, Hooke's Law for linear elastic materials and Newton's Law for linearly viscous materials.
   a) Give two equations that describe a linear elastic and a linearly viscous material.
   b) A linear elastic material is characterized by the Young's modulus, E, measured in a tensile measurement. Sketch a tensile measurement defining the tensile stress and tensile strain
   c) A linearly viscous material is characterized by the melt viscosity, η, measured in a shear viscometer. Define the shear stress, rate of strain and velocity gradient in a sketch of simple shear flow.
   d) Show a plot of log of viscosity versus log of the velocity gradient for a typical high molecular weight polymer. Indicate where the fluid is Newtonian and where it displays power-law fluid behavior.
   e) Show a plot of log of the zero shear rate viscosity versus log of the molecular weight for oligomers (low-molecular weight) and polymers (high molecular weight). Indicate the slopes.

3) In class we froze a rubber ball using liquid nitrogen and observed changes in the mechanical properties as the ball warmed up to room temperature. We also observed differences in behavior between a polybutadiene (happy) and a polynorbornene (sad) rubber ball.



polybutadiene



polynorbornene

a) Plot the ratio of the viscous or loss (heat) to the elastic or storage (bounce) response of the rubber ball as it warms up.

b) Explain why there is a peak in this plot, that is, why is the ratio low at low temperature, low at high temperature and high at an intermediate temperature?

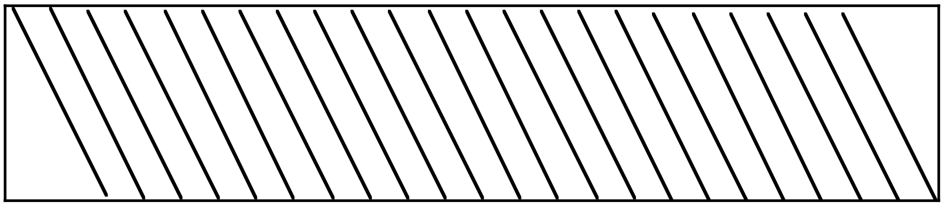
c) Explain why the happy ball is happy and why the sad ball is sad.

d) How does frequency effect this behavior and why.

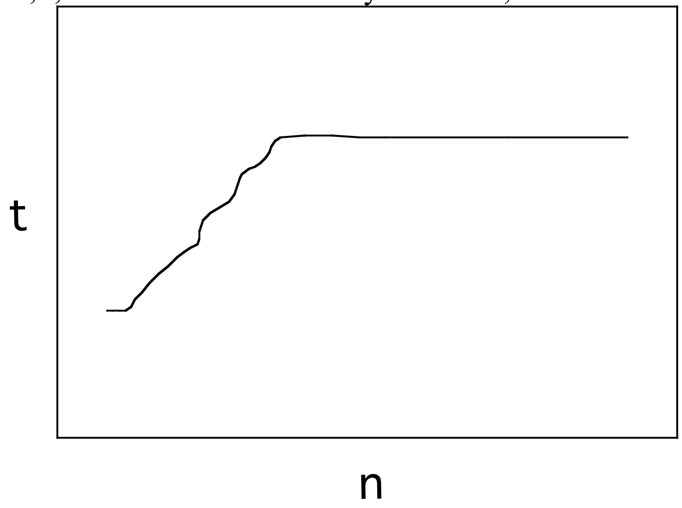
e) Tires have a maximum safe velocity and a minimum use temperature. Explain why tires might have a miximum velocity and minimum use temperature while other components of a car such as the springs or axle do not.

ANSWERS: 090109 Quiz 1 Introduction to Polymers

1) a) Alkanes crystallize into sheet like crystals with the major molecular axis at a tilt (usually) to the sheet surface.



b) Crystalline thickness, t, versus number of methylene units, n.



c) The crystallization temperature, T_c, governs the crystalline thickness following the Hoffman Lauritzen Equation (Gibbs Thompson Equation).

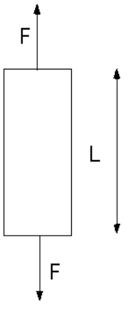
$$t = \frac{2\gamma T_\infty}{\Delta H(T_\infty - T_c)}$$

where γ is the surface energy ΔH is the enthalpy of crystallization, T_∞ is the equilibrium melting temperature.

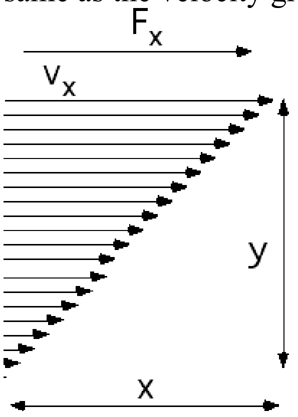
d) 1-d molecules form 2d crystals, 2d molecules form 1 crystals. Benzene-hexa-n-alknoate forms columnar crystals (liquid crystals).

2) a) Linear elastic: tensile stress is proportional to tensile strain with the Young's Modulus as the scaling coefficient $\sigma = E\varepsilon$. Linearly viscous: shear stress is proportional to the shear strain rate with the viscosity as the scaling coefficient $\tau = \eta\dot{\gamma}$.

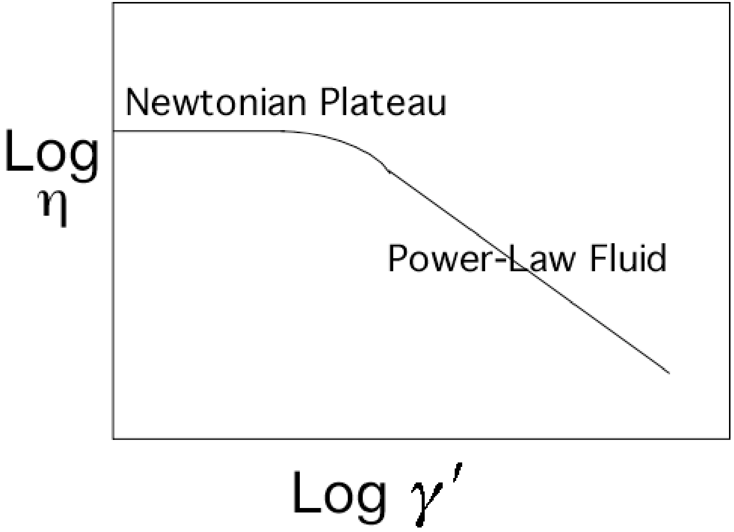
b) A force is applied to the surface normal to the force. The length changes in the same direction as the force. $\sigma = F/A$ and $\varepsilon = \Delta L/L$



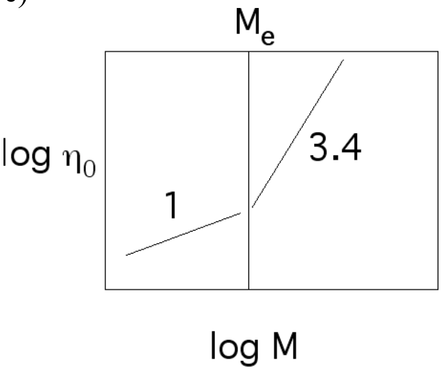
c) A force is applied to a surface whose normal is perpendicular to the direction of the force. The ratio of the stress to the area is the shear stress, τ. The length changes in the direction of the force with a gradient normal to the force. The ratio of the length change with respect to the gap or gradient distance is the shear strain, γ. We usually consider a dynamic shear process where the gradient of the x-velocity in the y-direction is the rate of shear strain. The rate of strain is the same as the velocity gradient.



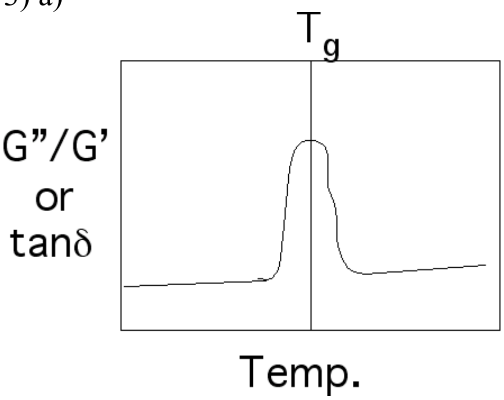
d)



e)



3) a)



b) The polymer chain has a characteristic time, τ, that is needed for it to vibrate. This time is associated with the time for coordinated bond rotation at a local level (9 mer units). There is also a characteristic energy, E_a, associated with this molecular motion. In a temperature ramp the point at which the energy associated with temperature, kT, equals the energy needed to move the polymer, E_a, we observe close to complete conversion of mechanical energy to heat, that is the loss or G” is maximum relative to the storage G’. At temperatures (or frequencies) lower than this characteristic temperature or glass transition temperature, T_g, there is insufficient energy for coordinated motion of the polymer chains. At these temperatures the material is a glass. The elastic modulus is large compared to the storage modulus. At high temperatures the chains move freely and because the chains are tethered to each other through crosslink’s in a rubber we see rubber elasticity where mechanical energy is stored in chain deformation relative to the random state. The existing motion of the chains at high temperature does not allow for much of the mechanical energy added in bouncing to be converted to heat.

c) The happy ball is happy because polybutadiene has a glass transition temperature at about -60C. The sad ball is sad because polynorbornene has a glass transition at room temperature. The difference in chemical structure leads to differences in the energy required to rotate bonds. Polynorbornene has a stiffer backbone so a higher glass transition temperature, requiring more thermal energy to cause bond rotation.

d) There is a characteristic temperature at a fixed frequency of mechanical deformation (speed of ball impact). For higher frequency the material acts as if the temperature were dropped. A rubber ball will act like a glass at sufficient speed.

e) Basically the tire rubber could approach T_g or worse the glassy state at high frequencies or at low temperatures. Near the glass transition the tires would dissipate a lot of heat and would give bad fuel efficiency. Below T_g you would get a very rough ride of the tires might exploded.