

CME 300 Properties of Materials

Homework 8 November 17, 2011

Repeat Problems from Homework 6: 9), 10), 14-12) and from Homework 7: 11), 12), 13), and 14) and do the following 7 problems.

1) Describe the molecular difference, difference in synthesis method and different uses for high density polyethylene, low density polyethylene, linear low density polyethylene, metallocene polyethylene, compression molded ultra-high molecular weight polyethylene, gel spun ultrahigh molecular weight polyethylene (Google the latter two).

HDPE: HDPE is made up of long chains of polyethylene with a few long branches so that the branches are indistinguishable from the chain. The synthesis is by Ziegler-Natta heterogeneous polymerization in a pressurized reactor so the ethylene gas is compressed to a liquid during the polymerization. HDPE is used for low cost structural items such as child climbing toys, for packaging, milk jugs and bleach bottles and for some tubing and pipes, wire coating. It is versatile but not usually used for films (garbage bags).

LDPE: LDPE is made by free radical polymerization in an autoclave. The chain structure is highly branched with a random mixture of long and short chain branches. The branching structure makes LDPE has a high melt strength so that it is useful for production of films and other applications and processes where melt strength is needed. LDPE and HDPE are not miscible so blends of these two are not used. LDPE has a lower degree of crystallinity so it is more flexible and weaker than HDPE. It is used for plastic wrap, coating on paper for juice boxes, six-pack rings, coatings, some low cost fibers.

LLDPE: LLDPE is made by Ziegler-Natta heterogeneous catalysts (solid catalyst particles) or by the Philips process (another heterogeneous system). The chain is linear but has frequent short chain branches that disrupt crystallization. The short branches are made by introducing a comonomer: butene, hexane or octane. These comonomers cannot fit into the PE crystal so the distribution of comonomers decides the crystal thickness and melting point following the Gibbs Thompson (Hoffman Lauritzen) rule. LLDPE is an engineered polymer in that the comonomer content and reaction conditions decides the degree of crystallinity and the strength. LLDPE, in theory, does not have long chain branches, only the copolymer with short branches.

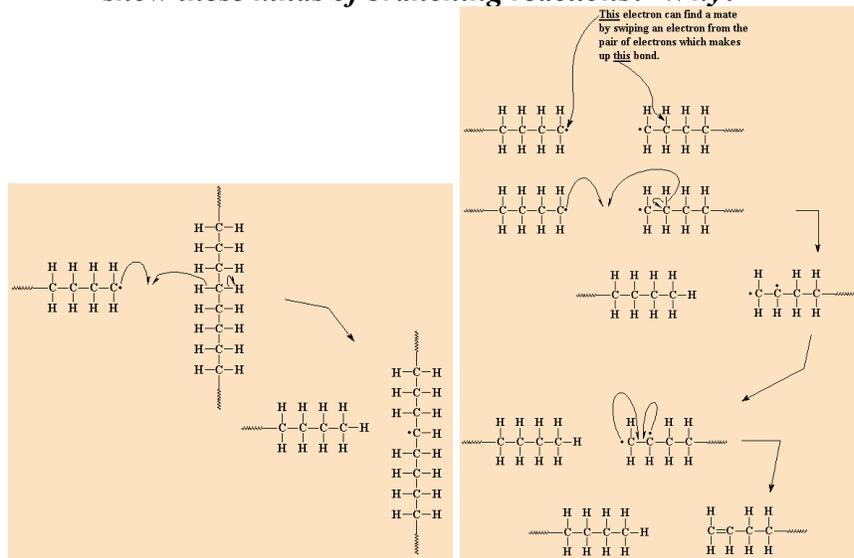
MPE: Metallocene PE is produced with homogeneous catalysts (organic molecules miscible in solvent or monomer). The catalyst has a controlled reaction site and can be designed to make copolymers with specific monomer arrangements so that the fine tuning of degree of crystallinity becomes an art form with highly engineered molecular structures. The degree of crystallinity can be adjusted to any value between 0 and 85% in these polymers. The low crystallinity polymers are elastomers and the high are tuned high density polymers. MPE is useful to make extremely inexpensive elastomers for a wide variety of applications, however, the lowered melting point can be a problem. Melt processing of

MPE's has been a problem from the get go in the late 1990's so they are usually blended with other PE's such as LLDPE to enhance the processing. MPE are used for a wide range of applications from stretch wrap to rubber facemasks for medical gas inhalation.

Compression Molded UHMWPE: Ultra High Molecular Weight Polyethylene can be made by anionic polymerization. Molecular weights in the millions of Da are possible. At extremely high molecular weights PE cannot be extruded so processing options are limited, however, due to the unique properties of UHMWPE it is widely used. The material has extremely high abrasion resistance and is very low cost so it is used for coal shuttles, truck bed liners, hip implant materials (the contact points), and other applications requiring low creep over long times such as replacement window sashes etc. Since it cannot be extruded, a powder of UHMWPE is compression molded, meaning it is poured into a mold and pressed into shape, and held for a relatively long period at temperature until the particles meld.

Gel Spun UHMWPE: UHMWPE, when mixed with a solvent, makes a gel. If the gel can be made dilute enough, it is possible to extrude a fiber from this solution. These gel spun fibers have a special molecular property that the PE chains are aligned almost perfectly with few imperfections. Then the strength of the C-C covalent bond is almost attained in a gel spun UHMWPE fiber. This process was developed in the 1970's and 1980's by DSM in the Netherlands (now part of SABIC the Saudi Oil company that bought most of the high-end US polymer firms such as GE plastics). Gel spun fibers are so strong that they have been mentioned for use as space tethers and are commonly used to make bullet proof vests, armor and sails for America's Cub Yachts. Gel spun UHMWPE shows the wide range of properties that can be achieved in polymer processing from a common inexpensive material, PE.

2) Which termination routes for polyethylene can lead to branching? Show a reaction scheme for these routes including the branching reaction. Do you expect polypropylene to show these kinds of branching reactions? Why?



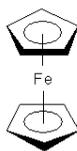
Hydrogen Abstraction

Disproportionation

Both hydrogen abstraction and disproportionation can lead to a long chain branched polymer. Polypropylene can not show this type of branching since the alpha proton is stabilized by the methyl group. It is similar to the reason that polypropylene cannot be synthesized by free radical mechanisms, the free radical shows resonance states that stabilize it and prevent propagation.

3) *Ferrocene is the least expensive and prototypical metallocene molecule consisting of two cyclopentane rings and a Fe^{+2} iron ion. In 1973 Fischer and Wilkinson shared a Nobel Prize for their work elucidating the structure of Ferrocene and for development of other metallocene molecules. In the late 1990s and early 21'st century Dow Chemical, ExxonMobil and Dupont competed to develop polyolefin catalysts based on metallocenes that lead to the current metallocene catalyst systems in industrial use. Ferrocene is so inexpensive that is used as a diesel fuel additive to reduced soot emissions and can be used in the synthesis of carbon nanotubes, in both cases taking advantage of the organo-solubility of this iron salt. Describe how you think ferrocene might be useful in these two cases, i.e. a) how does it lead to degradation of soot and b) how could it be useful in the synthesis of nanotubes?*

In both cases Ferrocene is burned releasing Fe^{+2} . The iron ion is a catalyst for degradation of carbon to CO and CO_2 . It is also a catalyst for synthesis of carbon nanotubes from acetylene gas at high temperatures in the absence of oxygen. The structure of ferrocene is compose of two cyclopentane rings that are bridged by the iron ion.



4) Why is it impossible to synthesize polypropylene by free radical polymerization?

See question 2 above.

5) The Gaussian distribution is described by a mean value and a standard deviation. The mean is given by $\frac{\int MP(M)dM}{\int P(M)dM}$ where $P(M)$ is the number distribution of chains as a function of molecular weight, M . The standard deviation is defined as $\sqrt{\frac{\int P(M)(M - \text{mean})^2 dM}{\int P(M)dM}}$. Define the number average, weight average, z average and the polydispersity index in terms of the mean and standard deviation from the Gaussian distribution.

You need to derive this.

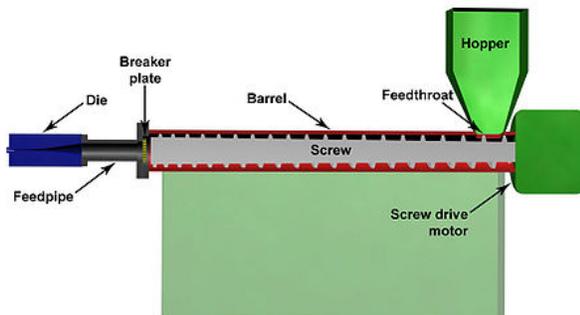
Number is the Mean.

Weight Average is $\left(\frac{\sigma^2}{\text{mean}^2} + 1\right)\text{mean}$

z-Average can not be described by the mean and standard deviation since it involves the third order moment.

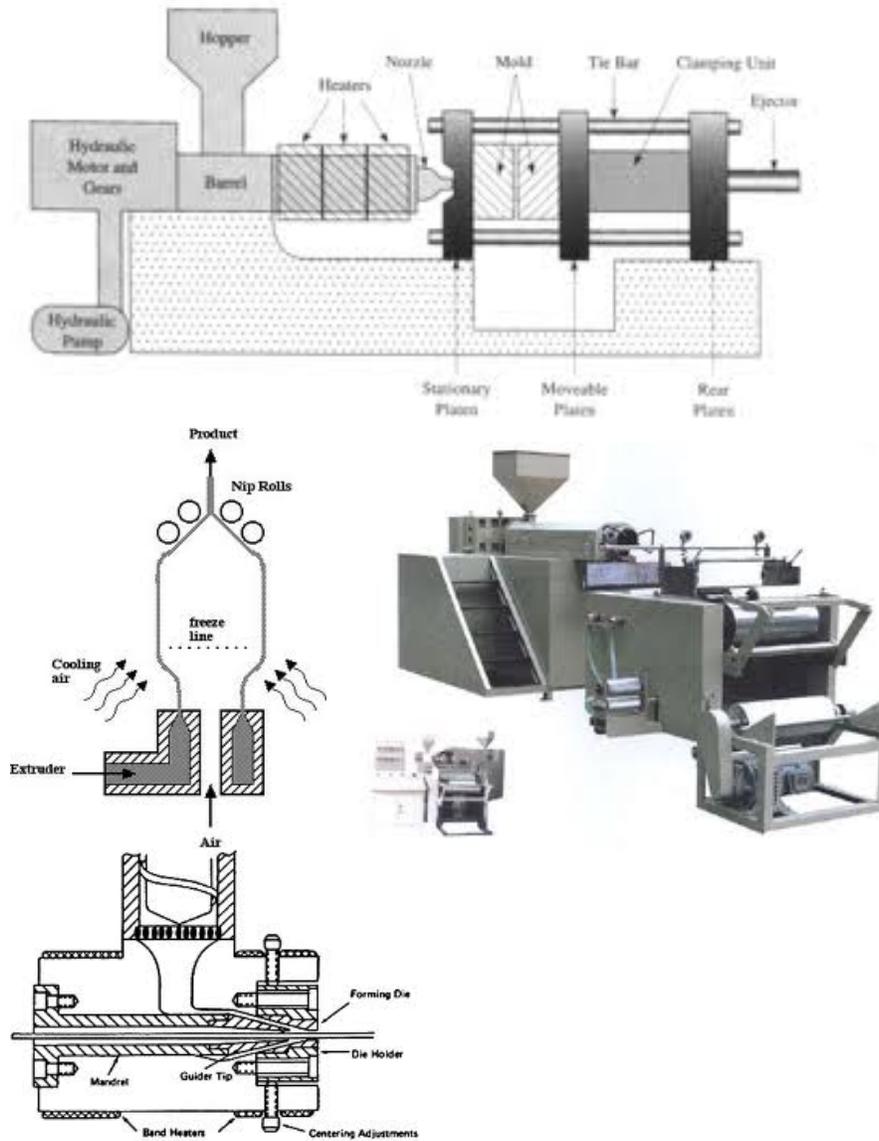
The PDI is $\left(\frac{\sigma^2}{\text{mean}^2} + 1\right)$

6) Metals are processed in the melt and cast in molds. This metal can later be rolled, drawn and annealed to form various parts. Polymers are generally processed in an extruder. Sketch an extruder showing where pellets are fed in, melting occurs, pressure is built up and extrusion occurs. Why aren't polymers processed like metals? What is the most important material property for polymer processing? How do injection molding, film blowing, film casting and wire coating rely on an extruder?



Pellets are fed at the hopper and feeder stage, melting occurs in the mid region of the barrel, pressure is built up after melting and before the die, extrusion occurs at the die. Polymer melts are much more viscous compared to metals, they have viscosities similar to silly putty while metals have viscosities like water. Also, the viscosity of a polymer drops with shear (shear

thinning) so it is important to process polymers under high shear. The viscosity is the most important material property for processing. Each of these processes involves an extruder to produce a pressurized melt.



7) What is a band gap and why is it important to semi-conducting materials.

The energy levels for isolated atoms are split and blurred into a density of energy states in dense materials such as metallic, semiconductor and insulating crystals.

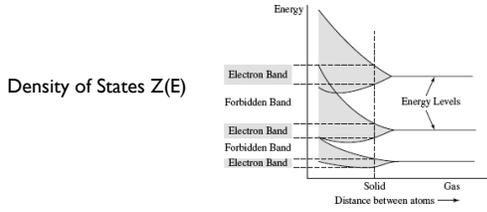


FIGURE 11.5. Schematic representation of energy levels (as for isolated atoms) and widening of these levels into energy bands with decreasing distance between atoms. Energy bands for a specific case are shown at the left of the diagram.

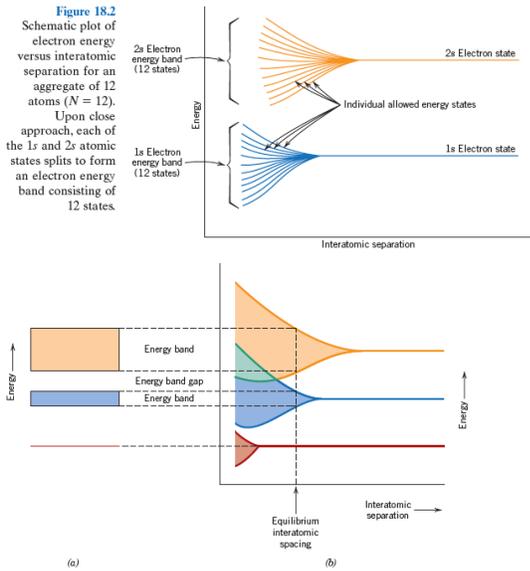


Figure 18.2 Schematic plot of electron energy versus interatomic separation for an aggregate of 12 atoms ($N = 12$). Upon close approach, each of the 1s and 2s atomic states splits to form an electron energy band consisting of 12 states.

Figure 18.3 (a) The conventional representation of the electron energy band structure for a solid material at the equilibrium interatomic separation. (b) Electron energy versus interatomic separation for an aggregate of atoms, illustrating how the energy band structure at the equilibrium separation in (a) is generated. (From Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd edition. Copyright © 1987 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

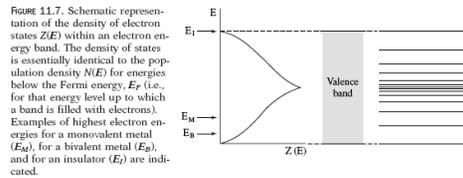


FIGURE 11.7. Schematic representation of the density of electron states $Z(E)$ within an electron energy band. The density of states is essentially identical to the population density $N(E)$ for energies below the Fermi energy, E_F (i.e., for that energy level up to which a band is filled with electrons). Examples of highest electron energies for a monovalent metal (E_M), for a bivalent metal (E_B), and for an insulator (E_I) are indicated.

For conductor metals the bands the empty electron states and lower energy filled states overlap in energy and there is no gap so that electrons can be drawn into the conduction band. For insulators a large energy gap exists between occupied orbital's and the conduction band. For semi-conductors a smaller gap exists that can be overcome if electrons of the right energy are available. Semi-conductors can switch from insulator to conductor because of the small band gap, and the size of their band gap is an important property to understand their behavior.

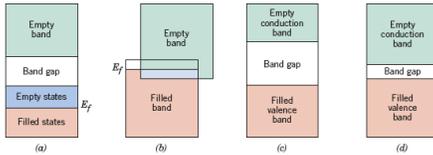
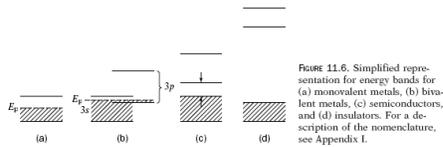


Figure 18.4 The various possible electron band structures in solids at 0 K. (a) The electron band structure found in metals such as copper, in which there are available electron states above and adjacent to filled states, in the same band. (b) The electron band structure of metals such as magnesium, wherein there is an overlap of filled and empty outer bands. (c) The electron band structure characteristic of insulators; the filled valence band is separated from the empty conduction band by a relatively large band gap (>2 eV). (d) The electron band structure found in the semiconductors, which is the same as for insulators except that the band gap is relatively narrow (<2 eV).



Fermi Energy = E_F

Figure 11.6. Simplified representation for energy bands for (a) monovalent metals, (b) bivalent metals, (c) semiconductors, and (d) insulators. For a description of the nomenclature, see Appendix I.