2.008 Design & Manufacturing II

Spring 2004

Polymer Processing I
-What is polymer?
-Polymer Science

Plastics

- $120 Billion shipments, 1999 US
- One of the greatest inventions of the millennium – Newsweek
  - Music LPs, CDs
  - No-sticking TEFLON
  - Stre-e-e-tching SPANDEX
- Applications
  Name it

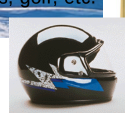
Plastic Intensive Vehicles

Automotive Plastics and Composites Use

- Exterior
  - doors
  - hoods
  - fenders
  - bumper covers (most cars have soft fascia)
- Interior
  - instrument panels, door trim, seats, consoles
- Engine
  - valve covers, intake manifolds, fluid containers, etc.

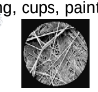
Recreational Plastics and Composites Use

- Snow Equipment
  - skis, snow boards, snow mobiles, etc.
- Water Sports Equipment
  - water skis, water crafts, snorkel equipment, fishing gear
  - diving equipment and clothes
- Land Sports Equipment
  - shoes, roller blades, skate boards, tennis, golf, etc.



Commercial Plastics Usage

- Packaging
  - Wrapping, bags, bottles, foams, shrink wrap.
- Textiles
  - Clothing, carpets, fabrics, diapers, netting for sports
- Furniture, Appliances, House wares
  - Telephones and other communication equipment, computer housings and cabinets, luggage, seating, components for washers, dryers, etc.
  - Musical instruments, CDs, VCRs, TVs, cases
- Construction
  - Moldings, counter tops, sinks, flooring, cups, paints, etc.
  - Tyvek

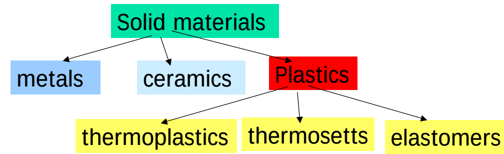
Medical Plastics and Composites Use

- Containers
  - Bottles, bags
- Drug delivery
  - IV bags, syringes
  - tubing and tools for surgery
- Implants, artificial skins

- The use of plastic materials in the medical field, about 4 billion dollars in 2000 (US).

excerpt from Prof. J. Greene, CSU

Materials

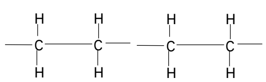


Plastic: Greek, *plastikos*, means to form or mold

Plastics, Polymers, Macromolecules

- Poly (many) + mer (structural unit)

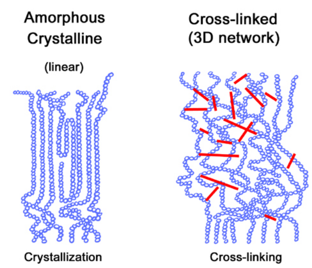
  $-[C_2H_4]_n-$,poly[ethylene]



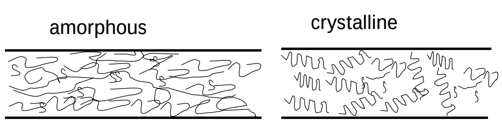
spaghetti

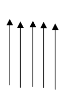
- Metal: single atoms, metallic bond
- Ceramic: metallic oxides, ionic bond or dipole interactions, van der Waals bonds

Thermoplastic vs. Thermoset

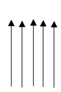


Thermoplastics



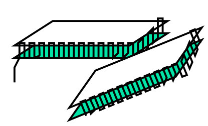


Transparent
Translucent
Opaque

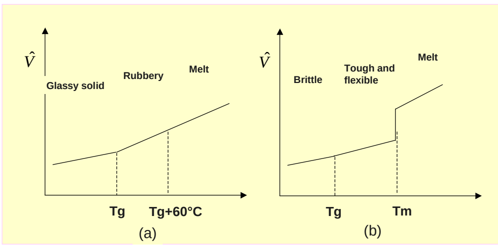


Crystalline vs. amorphous

- Crystals, lamella structure
- Degree of crystallinity
- Translucent/opaque



Amorphous vs. Semi crystalline Polymers



Early Plastics

- Phenolics (named Bakelite by Leo Bakeland)
  - Resin could be shaped and hardened with heat
  - Phenol and formaldehyde reaction after heat
  - Replacement for shellac, natural plastic (1907)
- Nylon66
  - W. H. Carothers of DuPont (1920's)
- PVC
  - W. Semon of B.F. Goodrich (1929)

Polymers

- PE (Polyethylene)-Crystalline
- PVC (Polyvinyl chloride)-Amorphous
- PP (Polypropylene)-C
- PS (Polystyrene)-A
- PU (Polyurethane)-Thermoset
- PET (Polyethyleneterephthalate)-C
- PPO (Polyphenyleneoxide)_A
- PMMA (Polymethylmethacrylate) -A
- PEEK (Polyether-ether-ketone)-C
- Acetal, TEFLON -C

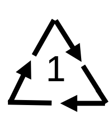
Major Plastic Materials (1995)

LDPE ($0.38/lb)	6.4 M metric tons (1000 kg)
HDPE ($0.29/lb)	5.3 M metric tons
PVC ($0.26/lb)	5.1 M metric tons
PP ($0.28/lb)	4.4 M metric tons
PS ($0.38/lb)	2.7 M metric tons
PU ($0.94/lb)	1.7 M metric tons
PET ($0.53/lb)	1.6 M metric tons
Phenolic ($0.75/lb)	1.5 M metric tons
Total	28.6 M metric tons (82% of market)
Nylon ($1.40/lb)	0.4 M metric tons
PTFE ($6.50/lb)	<0.1 M metric tons
PEEK ($36.00/lb)	<0.05 M metric tons

excerpt from Prof. J. Greene, CSU

Recycling of Plastics

- State and Federal Regulation
- Codes for plastics
  - 1 PET
  - 2 HDPE
  - 3 Vinyl/PVC
  - 4 LDPE
  - 5 PP
  - 6 PS
  - 7 Other



Polyethylene

- Ethylene is produced by cracking higher hydrocarbons of natural gas or petroleum
- LDPE commercialized in 1939
  - Density of 0.910 - 0.925 g/cc
  - Properties include good flex life, low warpage, and improved stress-crack resistance
  - Disposable gloves, shrink packages, vacuum cleaner hoses, hose, bottles, shrink wrap, diaper film liners, and other health care products, films for ice, trash, garment, and product bags
- HDPE commercialized in 1957
  - Density of 0.941 - 0.959 g/cc
  - MW from 200K to 500 K
  - Densities are 0.941 or greater-Ultra HDPE
  - Properties include improved toughness, chemical resistance, impact strength, and high abrasion resistance, high viscosities
  - Trash bags, grocery bags, industrial pipe, gas tanks, and shipping containers, chairs, tables

Polypropylene

- PP invented in 1955 by Italian Scientist F.J. Natta.
- Advantages
  - Low Cost, Excellent flexural strength, good impact strength
  - Processable by all thermoplastic equipment
  - Low coefficient of friction, excellent electrical insulation
  - Good fatigue resistance, excellent moisture resistance
  - Service Temperature to 160 C, very good chemical resistance
- Disadvantages
  - High thermal expansion, UV degradation
  - Poor weathering resistance
  - Subject to attack by chlorinated solvents and aromatics
  - Difficulty to bond or paint
  - Oxidizes readily
  - Flammable

PVC

- Polyvinyls were invented in 1835 by French chemist V. Semon. PVC was patented in 1933 by BF Goodrich Company in a process that combined a plasticizer which makes it easily moldable and processed.
- Rigid-PVC
  - Pipe for water drain, sewage
  - Pipe for structural yard and garden structures
- Plasticizer-PVC or Vinyl
  - Latex gloves
  - Latex clothing
  - Paints and Sealers
  - Signs

PS (Polystyrene)

- PS Homopolymer (crystal):
  - Clear and colorless with excellent optical properties and high stiffness.
  - Brittle.
  - Impact polystyrene (IPS): Graft copolymer or blend with elastomers
  - Properties are dependent upon the elastomer content, medium impact high impact and super-high impact
  - Copolymers include SAN (poly styrene-acrylonitrile), SBS (butadiene), ABS.
  - Expandable PS (EPS) is very popular for cups and insulation foam.
    - EPS is made with blowing agents, such as pentane and isopentane.
    - cell size and distribution

ABS

- ABS was invented during WWII as a replacement for rubber
- ABS is a terpolymer: acrylonitrile (chemical resistance), butadiene (impact resistance), and styrene (rigidity and easy processing)
- Graft polymerization techniques are used to produce ABS
- Family of materials that vary from high glossy to textured finish, and from low to high impact resistance.
- Additives enable ABS grades that are flame retardant, transparent, high heat-resistance, foamable, or UV-stabilized.
- Office machines

ABS: terpolymer
= acronitrile+butadiene+styrene

Polyamide (Nylon)

- PA is considered the first engineering thermoplastic.
- PA invented in 1934 by Wallace Carothers, DuPont. First commercial nylon in 1938.
- Nylons are described by a numbering system which indicates the number of carbon atoms in the monomer chains; nylon 6, nylon 6,6 or nylon 6,10
- Water absorption
- Fiber applications
  - 50% into tire cords (nylon 6 and nylon 6,6)
  - rope, thread, cord, belts, and filter cloths.
  - Filaments- brushes, bristles (nylon 6,10)
- Plastics applications
  - bearings, gears, cams
  - rollers, slides, door latches, thread guides
  - clothing, light tents, shower curtains, umbrellas

Polyester

- Polyesters is used for films and fibers.
- Blow molded bottles (PET bottles)
- Fiber applications
  - Tire cords, rope, thread, cord, belts, and filter cloths.
  - Monofilaments- brushes, clothing, carpet, bristles
- Film and sheets
  - photographic and x-ray films; biaxially oriented sheet for food packages
  - Transparencies (Mylar)
- Molded applications- Reinforced PET (Valox™)
  - luggage racks, grille-opening panels, functional housings
  - sensors, lamp sockets, relays, switches, ballasts, terminal blocks
- Appliances and furniture
  - oven and appliance handles, and panels
    -- pedestal bases, seat pans, chair arms, and casters

PC (Polycarbonate)

- PC was invented in 1898 by F. Bayer in Germany
- A special family of Polyester
- Amorphous, engineering thermoplastic that is known for toughness, clarity, and high-heat resistance.
- Lexan™ form GE
- High impact strength, transparency, excellent creep and temperature
  - lenses, films, windshields, light fixtures, containers, appliance components and tool housings
  - hot dish handles, coffee pots, hair dryers.
  - pump impellers, safety helmets, trays, traffic signs
  - aircraft parts, films, cameras, packaging
- High processing temp, UV degradation, poor resistance to alkalines and subject to solvent cracking

PMMA, Acrylics

- Optical applications, outdoor advertising signs, aircraft windshields, cockpit covers
- Plexiglas ™ for windows, tubs, counters, vanities
- Optical clarity, weatherability, electrical properties, rigid, high glossy
- Poor solvent resistance, stress cracking, combustibility, Use below Tg.
- Lenses for cameras

Acetal or Polyoxymethylene (POM)

Trade name: Derlin

- First commercialized in 1960 by Du Pont,
- Similar in properties to Nylon and used for plumbing fixtures, pump impellers, conveyor belts, aerosol stem valves
- Advantages
  - Easy to fabricate, has glossy molded surfaces, provide superior fatigue endurance, creep resistance, stiffness, and water resistance.
  - Among the strongest and stiffest thermoplastics.
  - Resistant to most chemicals, stains, and organic solvents
- Disadvantages
  - Poor resistance to acids and bases and difficult to bond
  - Subject to UV degradation and is flammable
  - Toxic fumes released upon degradation

PEEK

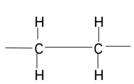
- Polyether-ether-ketone (PEEK) and Polyether ketone (PEK)
- PEEK invented by ICI in 1982. PEK introduced in 1987
- Expensive
- Advantages
  - Very high continuous use temperature (480F)
  - Outstanding chemical resistance, wear resistance
  - Excellent mechanical properties, Very low flammability and smoke generation, Resistant to high levels of gamma radiation
- Disadvantages
  - $$$, high processing temperatures
- Aerospace: replacement of Al, replacement of primary structure
- Electrical, wire coating for nuclear applications, oil wells, flammability-critical mass transit.
- Semi-conductor wafer carriers which can show better rigidity, minimum weight, and chemical resistance to fluoropolymers.
- Internal combustion engines (replacing thermosets)

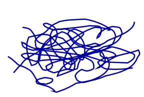
Polymers' Structure

- Poly (many) + mer (structural unit)

  -[C_2H_4]$_n$- ,poly[ethylene]

spaghetti

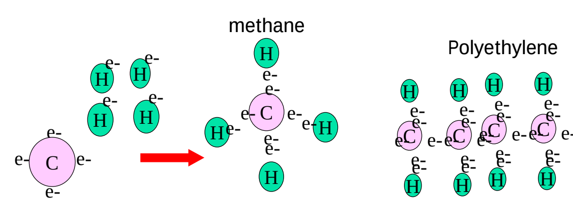




- Metal: single atoms, metallic bond
- Ceramic: metallic oxides, ionic bond or dipole interactions, van der Waals bonds

Covalent bonding

- Occurs when two nonmetal atoms are in close proximity.
- Both atoms share outer electron shells.
- Strong Bond

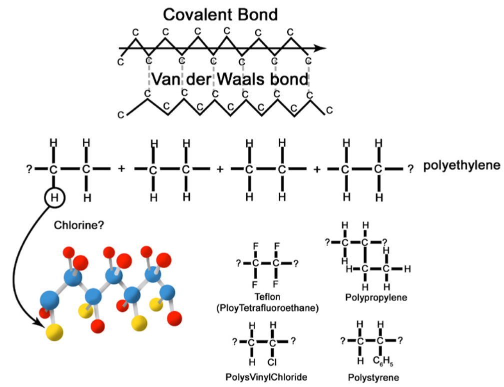


from J. Greene, CSU

Secondary bonding

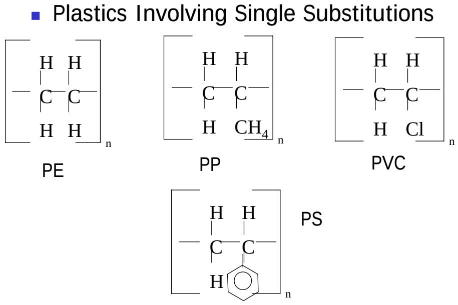
weaker than ionic, metallic, covalent

- Hydrogen bonding
  - Between the positive end of a bond and the negative end of another bond.
    Example, water
- van der Waals
  - Due to the attraction of all molecules have for each other, e.g. gravitational. Forces are weak since masses are small.



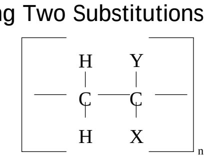
Homopolymers

- Single monomers
- Plastics Involving Single Substitutions



Homopolymers

- Plastics Involving Two Substitutions

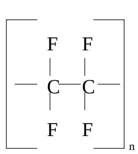


F	F	Polyvinylidene fluoride	PVDF
Cl	Cl	Polyvinyl dichloride	PVDC
CH_3 (Methyl group)	CH_3	Polyisobutylene	PB
$COOCH_3$	CH_3	Polymethyl methacrylate	PMMA

Homopolymers

- Three or more substitutions

PTFE
polytetrafluoroethylene
(Teflon)



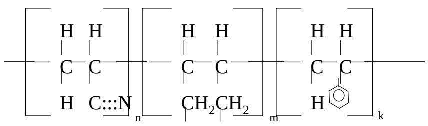
Copolymers

- Structure
  - Alternating - ABABABABABABAB
  - Random - AABBABBBAABABBBAB
  - Block copolymer- AABBBAABBBAABBBAABBB
  - Graft copolymer- AAAAAAAAAAAAAAA

    B B
    B B
    B B

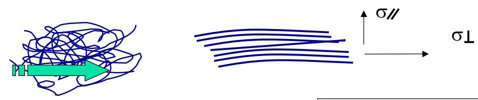
Copolymers

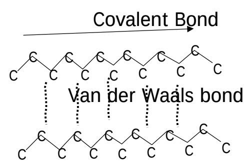
- ABS
- Three mers (terpolymer)

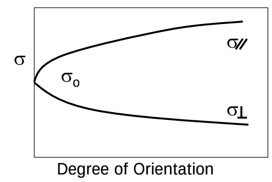


ABS (acronitrile butadiene styrene)

Molecular orientation







Birefringence

-Optical anisotropy
-Mechanical anisotropy

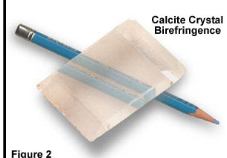


Figure 2

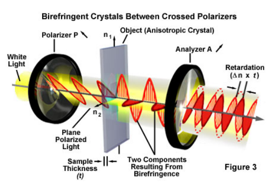
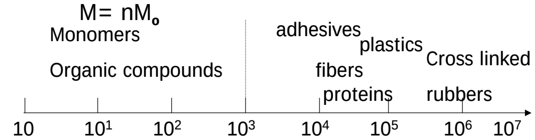


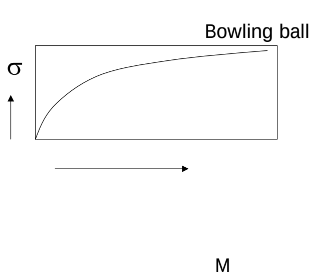
Figure 3

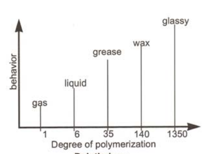
Molecular Weight

- Poly (many) + mer (structural unit)
  -$[C_2H_4]_n$- ,poly[ethylene]
- Degree of Polymerization, n
- Molecular Weight
  M= nM_o



Degree of Polymerization





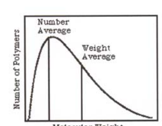
Molecular Weight

Number Averaged

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 + ...}$$

Weight Averaged

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + ...}{N_1M_1 + N_2M_2 + N_3M_3 + ...}$$



Number Average Molecular Weight, M_n

Number Average Molecular Weight gives the same weight to all polymer lengths, long and short.

- Example, What is the molecular weight of a polymer sample in which the polymers molecules are divided into 5 categories.

Group	Frequency
50,000	1
100,000	4
200,000	5
500,000	3
700,000	1

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \ldots}{N_1 + N_2 + N_3 + \ldots}$$

$$M_n = \frac{1(50K) + 4(100K) + 5(200K) + 3(500K) + 1(700K)}{(1+4+5+3+1)}$$

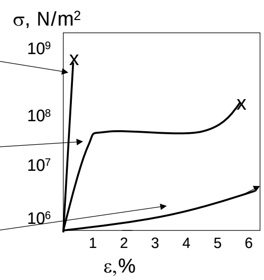
$$M_n = 260{,}000$$

Weight Average Molecular Weight, M_w

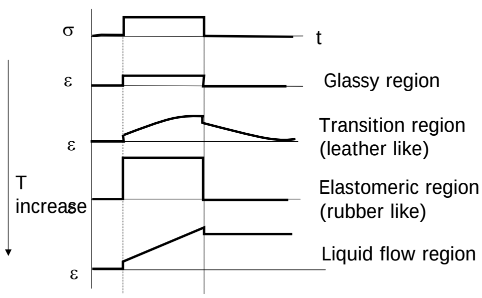
- Favors large molecules versus small ones
- Useful for understanding polymer properties that relate to the weight of the polymer, e.g., penetration through a membrane or light scattering.
- Example,
  - Same data as before would give a higher value for the Molecular Weight. Or, M_w = 420,000 g/mole

Mechanical Properties

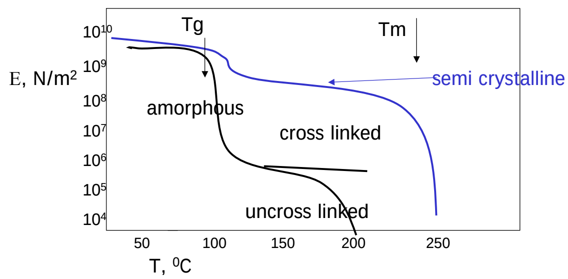
- Rigid plastic
- Flexible plastic
- Rubber

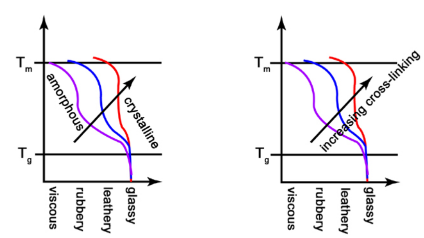


Step loading and unloading



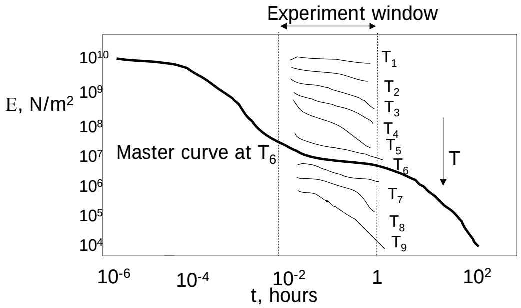
Modulus-temperature of PS





Semicrystalline **Cross-linking**

Time-Temperature Superposition



WLF equation

$$\text{Log } a(T) = \frac{-C1\ (T-To)}{C2+T-To}$$

At To=Tg, C1= 17.44, C2=51.6

Empirical equation for the shift factor a(T)

by William, Landel, and Ferry

Amorphous, glassy polymers Tg< T < Tg+100^{o}C

example

- A plastic part made of PC requires 100 years of leak proof performance at 23^{o}C. Accelerated test?

100 yrs = 3.16 x 10^9 sec
Log a(T) = 9.5

From data, log a(23) →4.8 to the master curve.
Log a(T) $_{\text{from the master curve}}$ = - 4.7
4.7 (51.6+ (T-Tg))= 17.44 (T-Tg)
T = Tg + 19^{o}C = 119^{o}C

Master Curve, PC

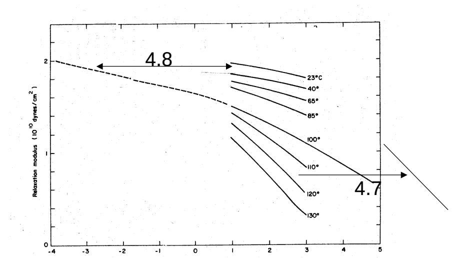


Fig. VI.20 Relaxation modulus of polycarbonate. (*From I. V. Yannas, "The Range of Validity of Linear Viscoelastic Theory," unpublished paper, March 1970.*)