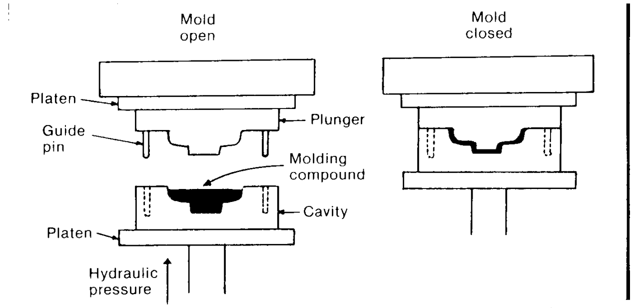
1. Definition of Plastics

- Thermoplastics
  - ***Polymers that are converted into shapes by processes involving flow of liquid (molten) polymer before solidification***
    - Must melt at a reasonable temperature
    - Must be flowable when molten
    - Must be easily shaped or fabricated

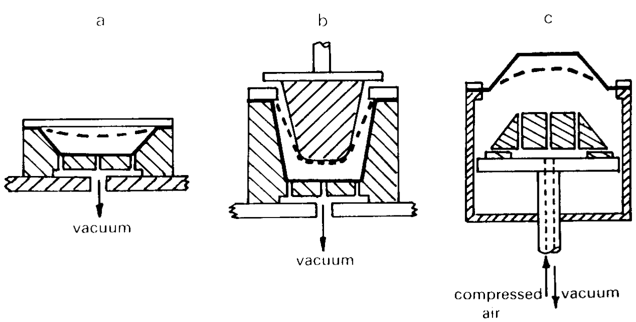
2. Plastics Fabrication

- Compression molding – also used for thermosets
  - Polymer powder or monomers placed in one half of mold
  - Application of pressure and heating melts polymer (or causes monomers to react) to form shape of mold
  - Cross-linking can occur, especially for thermosets



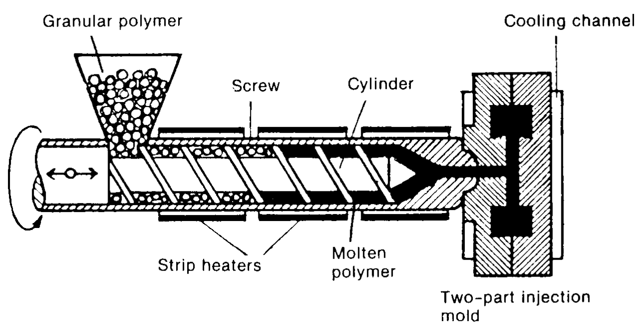
3. Plastics Fabrication

- Vacuum molding
  - Hot polymer sheet placed over top of mold
  - Vacuum pulls polymer to walls of chilled mold



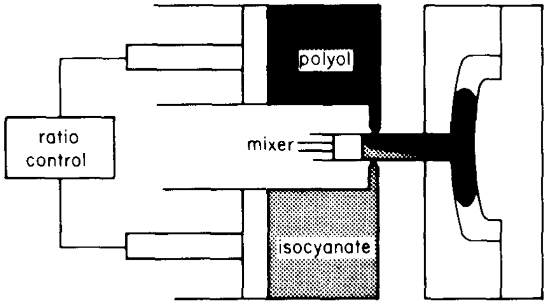
4. Plastics Fabrication

- Injection molding of thermoplastics
  - Granular polymer melted in heated screw
  - Forced through an opening directly into cooled mold



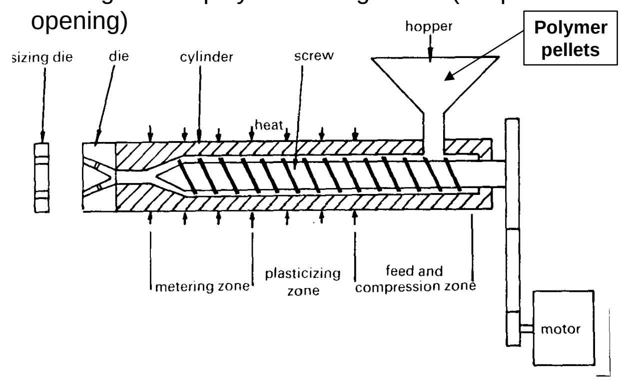
5. Plastics Fabrication

- Injection molding of polyurethane (thermoset) resins (reaction injection molding or RIM)
  - Separate compartments for polyol and isocyanate
  - Fed into the mold where polymerization takes place



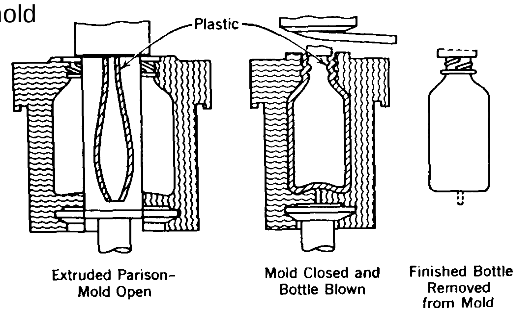
6. Plastics Fabrication

- Extrusion
  - Forcing molten polymer through a die (shaped opening)



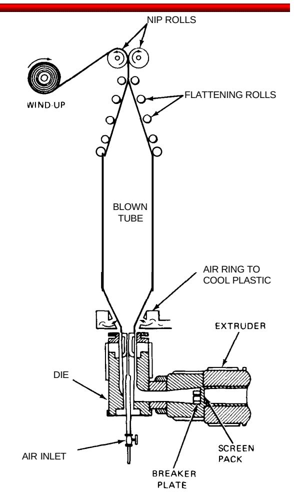
7. Plastics Fabrication

- Blow molding
  - Molten polymer extruded through circular die to form bubble or **parison**
  - Air injected, forcing polymer to walls of the cooled mold



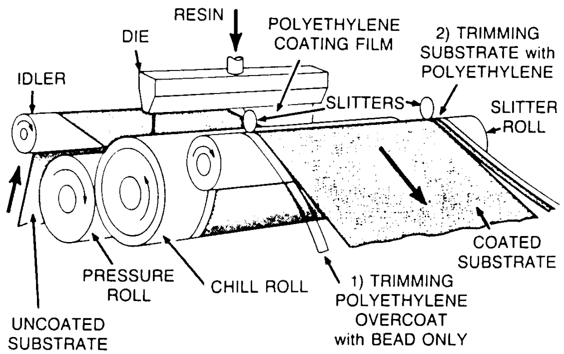
8. Plastics Fabrication

- Blown film
  - Molten polymer forced through circular die
  - Air flow forms bubble, shape controlled by cooling ring
  - Bubble can be 7 ft in diameter and > 30 ft tall
  - Bubble collapsed via rollers to form wide sheets (films)
  - Sheets rolled up for further cutting and sizing



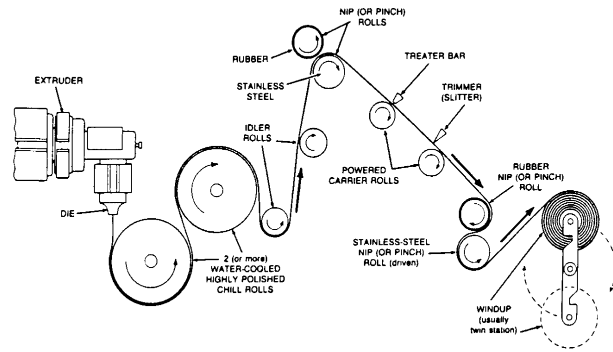
9. Plastics Fabrication

- Extrusion coating
  - Molten polymer extruded onto cooled substrate
  - Forms solid film instantly upon contact with substrate



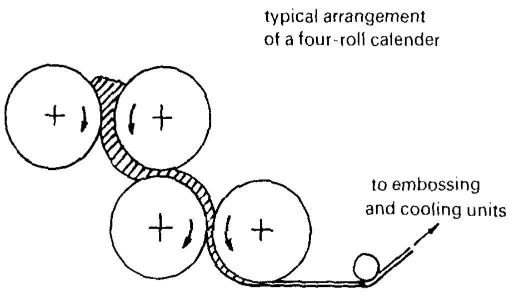
10. Plastics Fabrication

- Cast film formation
  - Molten polymer extruded onto chilled roll
  - Forms solid film instantly upon contact with roll



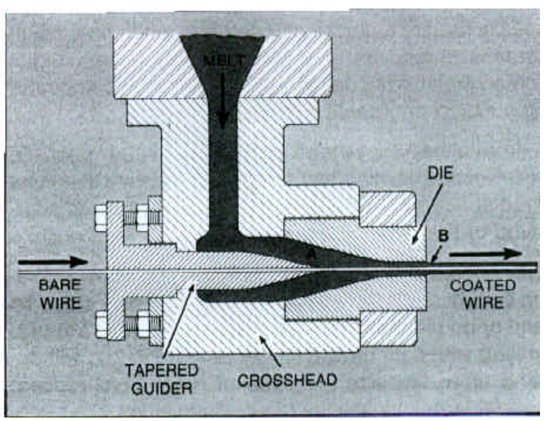
11. Plastics Fabrication

- Calendering
  - Molten polymer pressed into thin film by passing through rollers with increasingly more narrow gaps



12. Plastics Fabrication

- Wire and cable coating



13. General Plastics Uses

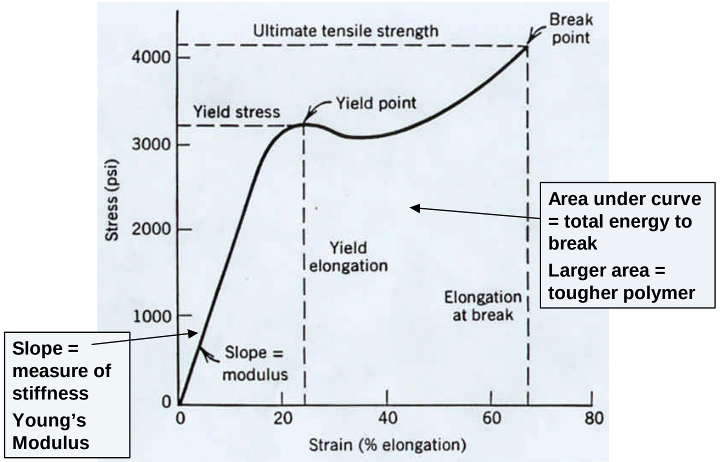
Uses of Thermoplastics		
Packaging	32%	← Containers, lids, film
Building and construction	14	← Piping, siding, fittings
Consumer products	13	
Electrical equipment	6	
Furniture	5	
Transportation equipment	4	
Miscellaneous	26	

Uses of Thermosets		
Building and construction	69%	← Piping, siding, fittings; ← Plywood adhesives
Transportation equipment	8	
Adhesives, coatings	4	← Plywood adhesives
Consumer products	4	
Electrical equipment	4	
Miscellaneous	11	

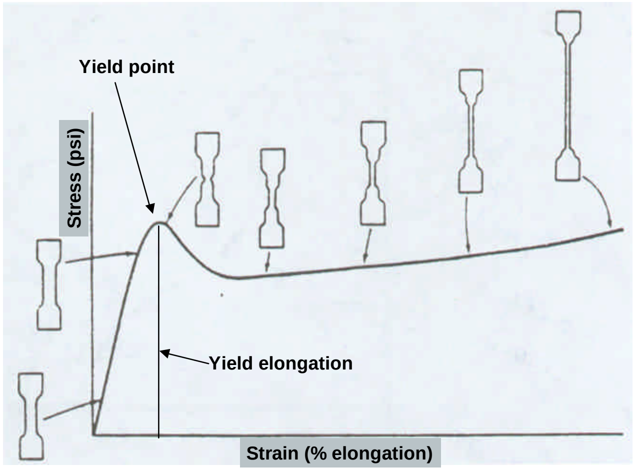
14. Definition and Classes

- Plastic
  - *Polymers that are converted into shapes by processes involving flow of liquid (molten) polymer before solidification*
- Plastics can be identified and characterized by the shape of their **stress-strain curves**
  - *Hard-tough*
  - *Hard-strong*
  - *Hard-brittle*
  - *Soft-tough*
  - *Soft-weak*

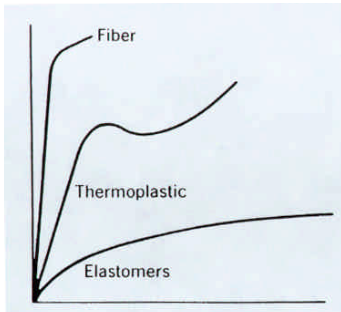
15. Stress-Strain Curve



16. Stress-Strain Curve



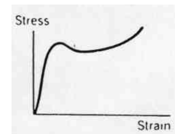
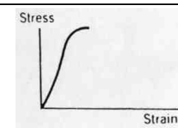
17. Stress-Strain Curve



	Elastomers	Plastics	Fibers
Modulus (psi)	15 - 150	1,500 - 200,000	150,000 - 1,500,000
Percent Elongation	100 - 1000	20 - 100	< 10
Crystallinity	Low	Moderate	High
Polymer example	Natural rubber	Polyethylene	Nylon

18. Definition and Classes

- **Hard** = high modulus (steep slope)
- **Tough** = high elongation
- **Strong** = moderate elongation and high modulus

Class of Plastic		Modulus	Yield Stress	Ultimate Tensile Strength	Elongation at Break	Examples
Hard and tough		High	High	High	High	**High density polyethylene** Cellulosics Polyamides (Nylon) **Polyesters** **Polypropylene** Engineering plastics Polyacetal, polycarbonate Polyimide, polyphenylene sulfide, polyphenylene oxide Polysulfone
Hard and strong		High	High	High	Moderate	**Poly(vinyl chloride) PVC** Impact polystyrene Styrene-acrylonitrile

19. Important Plastics

- ***Hard and tough***

$—(CH_2—CH_2)_n—$

- High density polyethylene, HDPE
  - Manufacture ?
  - Properties
    - Little branching (< 7 per 1000 C atoms)
    - High crystallinity (T_m = 135 ºC, T_g = -70 to – 20ºC)
    - Relatively opaque
    - Relatively stiff, hard with high tensile strength
    - Density > 0.94 g/cc

20. Important Plastics

- ***Hard and tough***

$—(CH_2—CH_2)_n—$

- High density polyethylene, HDPE

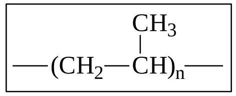
Uses of HDPE

Blow molding	35%	← **Bottles, gas tanks**
Injection molding	22	← **Crates, pails, toys**
Film	17	← **Packaging**
Pipe and conduit	14	← **Water and sewer, low pressure gas distribution**
Sheet	6	
Wire and cable	1	
Miscellaneous	5	

- Economics
  - 12.5 billion pounds produced in 2001
  - Currently about $0.48 per pound
  - Commercial value = $6.0 billion
  - Recent growth rate: 5 – 6% per year, except for 2001
  - Heavily recycled

21. Important Plastics

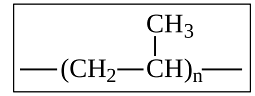
- ***Hard and tough***
- Polypropylene, PP



  - Manufacture ?
    - **What does isotactic mean?**
  - Properties
    - Stiffer, harder, higher tensile strength than HDPE
    - T_m = 170 ºC, T_g = -10 ºC (brittle at low temperatures)
    - **More degradable by heat, light and O_2 than HDPE due to ?**
    - Stabilizers and antioxidants are required
    - Density = 0.91 g/cc

22. Important Plastics

- ***Hard and tough***
- Polypropylene, PP



Uses of PP	
Injection molding	31%
Fibers and filaments	30
Distributors and compounders	23
Film and sheet	11
Blow molding	2
Miscellaneous	3

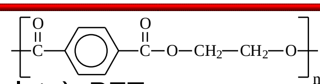
Containers, toys, furniture (→ Injection molding)

Carpet backing, carpet fibers, ropes (→ Fibers and filaments)

- Economics
  - 16 billion pounds produced in 2001
  - Currently about $0.34 per pound
  - Commercial value = $5.4 billion
  - Recent growth rate: 6.5 % per year
  - Recycling may become important

23. Important Plastics

- ***Hard and tough***



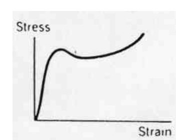
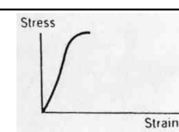
- Poly(ethylene terephthalate), PET
  - Manufacture ?
  - Properties
    - T_m = 250 – 265 ºC, T_g = 70 ºC

Uses of PET	
Soft drink bottles	60%
Other containers	30
Amorphous and crystallized	10

  - Economics
    - As a plastic, 10 – 15 % growth rate per year
    - Currently about $0.55 per pound
    - High recycling rate

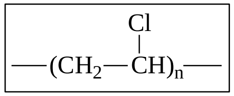
23. Definition and Classes

- **Hard** = high modulus (steep slope)
- **Tough** = high elongation
- **Strong** = moderate elongation and high modulus

Class of Plastic		Modulus	Yield Stress	Ultimate Tensile Strength	Elongation at Break	Examples
Hard and tough		High	High	High	High	**High density polyethylene** Cellulosics Polyamides (Nylon) **Polyesters** **Polypropylene** Engineering plastics Polyacetal, polycarbonate Polyimide, polyphenylene sulfide, polyphenylene oxide Polysulfone
Hard and strong		High	High	High	Moderate	**Poly(vinyl chloride) PVC** Impact polystyrene Styrene-acrylonitrile

25. Important Plastics

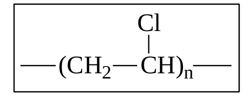
- ***Hard and strong***
- Poly(vinyl chloride), PVC



  - Manufacture ?
  - Properties
    - T_m = 140 ºC, T_g = 70 – 85 ºC
    - Low crystallinity
    - Good chemical resistance
    - Degraded by heat and light (**Why?**)
    - **Expected to be brittle or pliable at 0 ºC?**
    - Becomes soft, tough polymer with 1-2 wt % plasticizer
      - Plasticizer = dioctyl phthalate
      - **Plasticized PVC**

26. Important Plastics

- ***Hard and strong***
- Poly(vinyl chloride), PVC



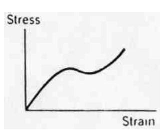
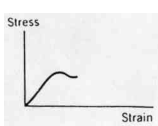
Uses of PVC

Construction	76%	← **Siding, roofing, gutters, water pipes, flooring**
Consumer goods	6	
Electrical fittings, wire and cable	4	
Home furnishings	2	
Miscellaneous	4	← **Credit cards**

- Plasticized PVC used in medical bags and tubing
- Economics
  - About 14 billion pounds produced in 2001
  - Currently about $0.36 per pound
  - Commercial value = $5.0 billion
  - Good growth rate in recent years (6.4 % per year) except 2000-2001
  - Economics tied to which industry?

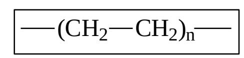
27. Definition and Classes

- **Soft** = low modulus (shallow slope)
- **Tough** = high elongation
- **Weak** = moderate elongation

Class of Plastic		Modulus	Yield Stress	Ultimate Tensile Strength	Elongation at Break	Examples
Soft and tough		Low	Low yield	Low	High	**Low density polyethylene** **Linear low density PE** Plasticized PVC Ionomer
Soft and weak		Low	Low	Low	Moderate	Polyethylene waxes

28. Important Plastics

- ***Soft and Tough***



- Low-Density Polyethylene, LDPE
  - Manufacture ?
  - Properties
    - High degree of branching
      - 60 branches per 1000 carbons – How are these formed?
    - T_m = 115 ºC, lower than HDPE and LLDPE
    - Low crystallinity ⇒ high clarity for films
    - Greater permeability to gases than HDPE
    - Density between 0.90 and 0.94 g/cc
    - Readily processed (flows well when molten)

29. Important Plastics

- ***Soft and Tough***

$—(CH_2—CH_2)_n—$

- Low-Density Polyethylene, LDPE

Uses of LDPE		
Film	59%	← **Packaging, trash bags**
Extrusion	17	← **Paper coatings**
Injection molding	6	← **Squeeze bottles, toys**
Wire and cable	4	
Adhesives and sealants	4	
Miscellaneous	10	

- Economics
  - 6.9 billion pounds produced in 2001
  - Currently about $0.49 per pound
  - Commercial value = $3.4 billion
  - Flat consumption due to competition from (substitution by) LLDPE

30. Important Plastics

- ***Soft and Tough***
- Linear Low-Density Polyethylene, LLDPE
  - Manufacture ?
  - Properties
    - Moderate degree of branching due to occasional insertion of comonomer
    - Higher melting, lower clarity than LDPE
      - More or less crystalline???
    - Higher tensile strength (stronger) than LDPE
    - Density between 0.91 and 0.94 g/cc

31. Important Plastics

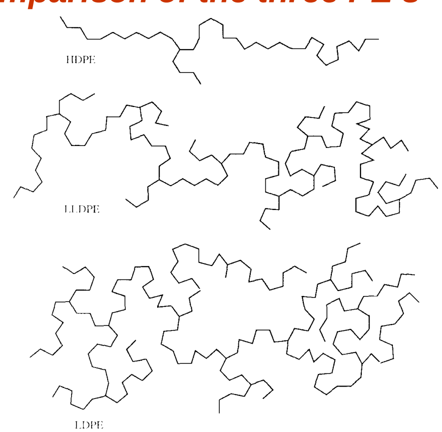
- ***Soft and Tough***
- Linear Low-Density Polyethylene, LLDPE

Uses of LLDPE		
Film	72%	← **Shrink wrap, packaging, heavy duty trash bags**
Injection molding	9	
Rotational molding	6	
Wire and cable	3	
Miscellaneous	10	

- Economics
  - 7.6 billion pounds produced in 2001
  - Currently about $0.39 per pound
  - Commercial value = $3.0 billion
  - High growth rate (7.4 % per year, except for 2000-2001), mainly by replacing LDPE

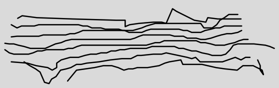
32. The Three PE's

- ***Comparison of the three PE's***



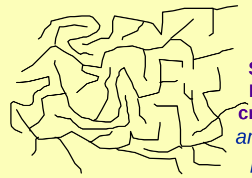
33. The Three PE's

highly crystalline polymer

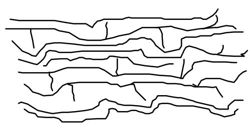


HDPE

Few short chain branches (SCB)



LDPE
SCB: YES
LCB: YES
cross-links
amorphous polymer



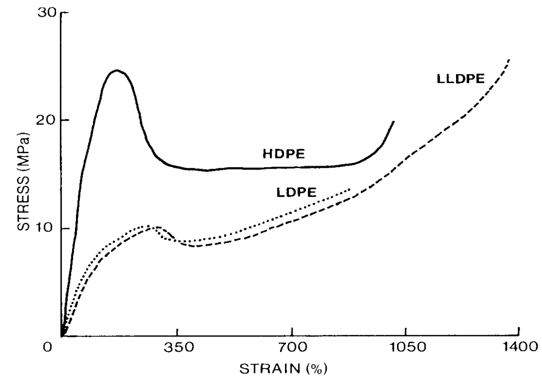
LLDPE
SCB : YES
semi-crystalline

Note the way the polymer strands pack together

Which polymer is most flexible? Why?

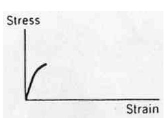
34. The Three PE's

- ***Stress-strain curves – Which is which?***



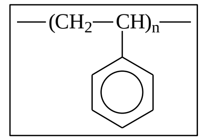
35. Definition and Classes

- **Hard** = high modulus (steep slope)
- **Brittle** = low elongation

Class of Plastic		Modulus	Yield Stress	Ultimate Tensile Strength	Elongation at Break	Examples
Hard and brittle		High	No well-defined yield	High	Low	Phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins **Polystyrene** Poly(methyl methacrylate) Unsaturated polyester resins Epoxy resins

36. Important Plastics

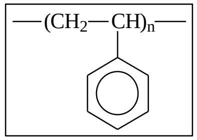
- ***Hard and brittle***
- Polystyrene, PS
  - Manufacture



  - Properties
    - T_m = 227 ºC, T_g = 94 ºC
    - Amorphous, low crystallinity
    - Flammable
    - Yellows in light – requires UV stabilization
    - **Why is this polymer unstable to light?**

37. Important Plastics

- ***Hard and brittle***
- Polystyrene, PS



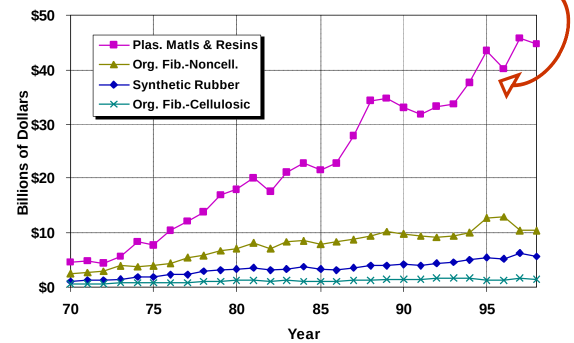
Uses of PS	
Packaging and one-time use	48%
Electrical and electronics	17
Construction	13
Consumer products	9
Medical products	7
Miscellaneous	6

Clear clam shells

- Economics
  - 2.5 % growth rate from 1990 – 2000, -11% from 2000-2001
  - About 6.1 billion pounds produced in 2001
  - Currently about $0.52 per pound
  - Commercial value = $3.2 billion

38. Plastics Economics

- Plastics Material and Resin Manufacturing
  - 11 % of total for all of Chemical Manufacturing
- High growth rate relative to other polymers



39. Plastics Economics

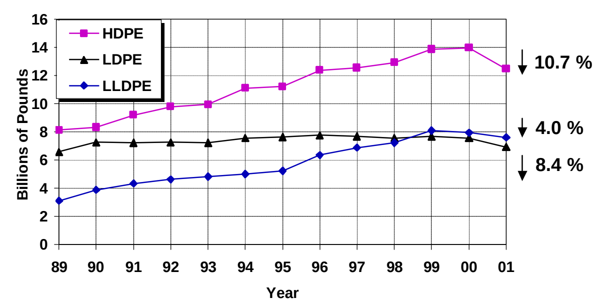
- Recent growth rates

Polymer	2000 Billion lb	Annual Change 1999-00	2001 Billion lb	Annual Change 2000-01	Annual Change 1990-00
Plastics					
Polyethylene					
Low density	7.575	-1.6%	6.94	-8.4%	0.5%
Linear low density	7.951	-1.9	7.63	-4.0	7.4
High density	13.968	0.8	12.479	-10.7	5.3
Polypropylene	15.739	1.6	15.837	0.6	6.5
Styrene Polymers					
Polystyrene	6.844	5.8	6.106	-10.8	2.5
Styrene-acrylonitrile	0.128	4.1	0.127	-0.8	-0.5
Acrylonitrile-butadiene-styrene & other	3.120	0.7	2.725	-12.7	2.9
Polyamide	1.281	-5.5	1.039	-18.9	8.6
Polyvinyl chloride & copolymers	14.442	-3.2	14.257	-1.3	4.7
Epoxy	0.693	7.5	0.610	-12.0	3.5
Total	**71.741**	**-0.05%**	**67.75**	**-5.6%**	**4.60%**

"Facts and Figures for the Chemical Industry", C&E News, June 24, 2002, p. 63-64

40. Plastics Economics

- Growth Rates, except for 2000 – 2001
  - HDPE = 5 % AAGR
  - LLDPE = 7 - 8 % AAGR – slightly higher than PP
  - LDPE = 0.5 % AAGR



41. Requirements for Fibers

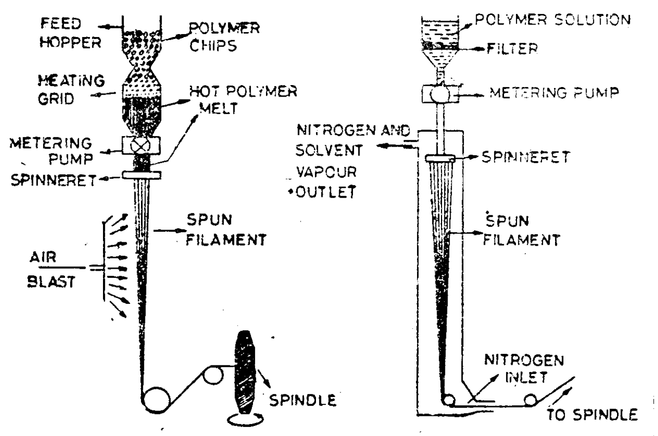
- High tensile strength (tenacity)
- Pliable but low elongation
- Abrasion resistant
- High melting point (esp. for clothing)
  - T_m > 200 ºC (iron without damage) but < 300 ºC to enable spinning from melt
  - T_g < 100 ºC so fibers soften when ironed at 150 ºC
    - Creases removed

Polymer	T_g (ºC)	T_m (ºC)
PET	70	265
Nylon 6,6	60	265
PAN	105	320
PP	-5	165

42. Requirements for Fibers

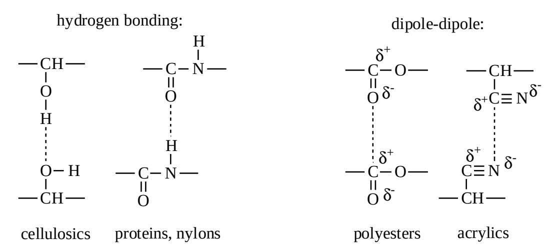
- Fibers are pulled (drawn) during spinning
  - Melt spinning
  - Wet spinning (polymer dissolved in solvent, filaments extruded into non-solvent)
  - Dry spinning (polymer dissolved in solvent, solvent evaporates)
- Drawing orients amorphous regions, stronger fibers result
- Drawing makes fibers much stronger in direction of draw than across it (anisotropic)

43. Spinning of Fibers



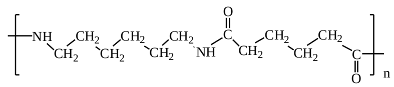
44. Requirements for Fibers

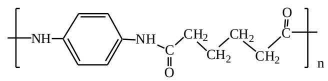
- Symmetrical, unbranched polymer
  - High crystallinity promotes linear molecular alignment – this is critical
  - High cohesive energy (intermolecular forces)
- Strong intermolecular forces promote
  - High tenacity, fiber strength, low elongation

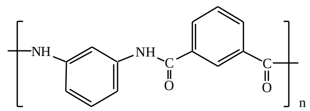


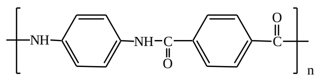
45. Requirements for Fibers

- Rigid backbone structures
  - Aramids (aromatic polyamides)
    - high stiffness
    - heat resistance
  - Compete with wire and glass fibers
  - Form rodlike polymers



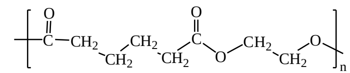


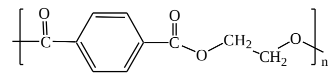


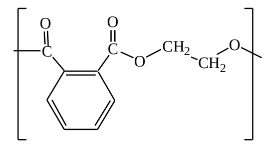


46. Requirements for Fibers

- Rank these fibers by strength

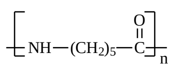




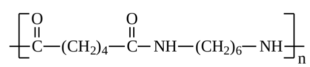


47. Important Fibers

- Nylon



nylon 6

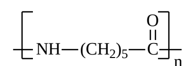


nylon 6,6

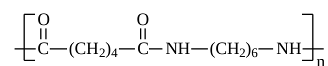
  - Manufacture
    - Nylon 6,6 formed by condensation polymerization between adipic acid and hexamethylenediamine
    - 280 – 300 ºC under vacuum
    - Acetic acid terminates chains, controls M_w
  - Properties
    - Dyeable
    - Strong, hard wearing fiber
    - Withstands high temperature
    - Hydrophobic

48. Important Fibers

- Nylon



nylon 6



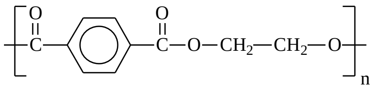
nylon 6,6

Uses of Nylon	
Carpets and rugs	74%
Industrial	16 ← **Belts, hoses, tire cords**
Apparel	10

  - Economics
    - Production relatively flat for past 15 years
    - 2.6 billion pounds produced in 2000
    - Nylon 6,6 is two-thirds of US market, nylon 6 is one-third
    - Carpet and rug markets increasing, other applications decreasing

49. Important Fibers

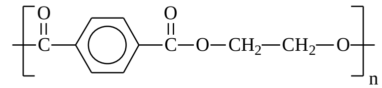
- Polyester



  - Manufacture
    - Initial formation of oligomers by:
      - Reaction of TPA and ethylene glycol
      - Reaction of DMT and ethylene glycol
    - Polymerization at 200 – 290 ºC in vacuo with SbO_3 catalyst
    - Fibers melt spun like nylon at about 260 ºC
  - Properties
    - Readily blended with other fibers (cotton)
    - Choice of phthalate can vary tensile and elongation properties
    - Hydrophobic (does not absorb water)
    - Stains easily
    - Static charge

50. Important Fibers

- Polyester

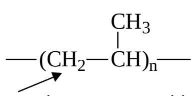


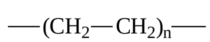
Uses of Polyester	
Clothing	50%
Home furnishings	20
Industrial	30

  - Economics
    - Largest volume fiber produced
    - 3.9 billion pounds produced in 2000
    - Large production increases in 1970's
    - Roughly same amount produced in 1980 and in 2000
      - Decreased slightly from 1980 – 1990
      - Increased slightly from 1990 – 2000

51. Important Fibers

- Polyolefin

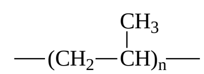


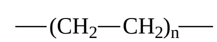


  - Manufacture
    - Isotactic polypropylene prepared by Ziegler-Natta catalyzed polymerization
    - Some HDPE (from Ziegler-Natta catalysis) for monofilaments
    - Fibers produced by melt spinning
    - Fiber strength achieved by high molecular weight
      - Only weak intermolecular forces (van der Waals)
  - Properties
    - Low density (0.91 g/cc) yield lightweight fiber
    - Chemical and abrasion resistance
    - Good insulating properties
    - Not easily dyed

52. Important Fibers

- Polyolefin

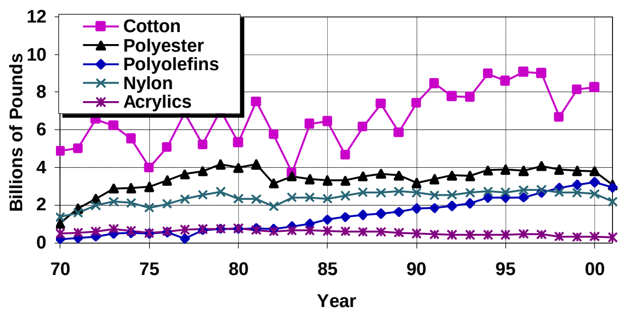




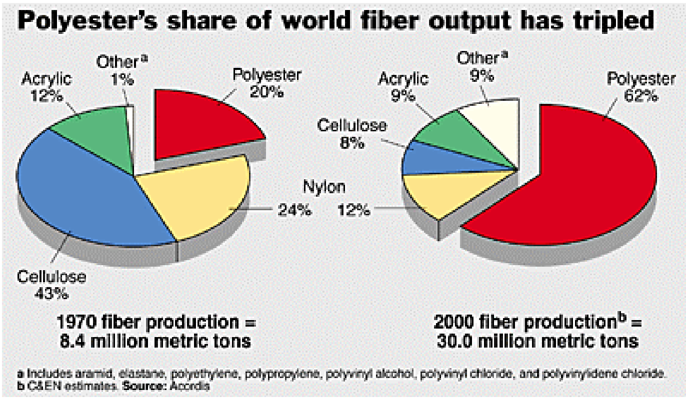
  - Uses
    - Industrial (rope, belts, carpet backing awnings)
    - Home textile (floor covering, upholstery fabric, blankets)
    - Apparel (sportswear, hosiery)
    - Diapers (nonwoven fibers)
  - Economics
    - Largest growth segment within fibers
    - Steady growth of 6 – 8 % per year since 1982
    - Surpassed nylon in 1998
    - Closing in on polyester as the highest production fiber

53. Fiber Production

- Polyester most important synthetic fiber
- Polyolefins are rising star (PP)
  - Highest growth rate – nearly 6% per year

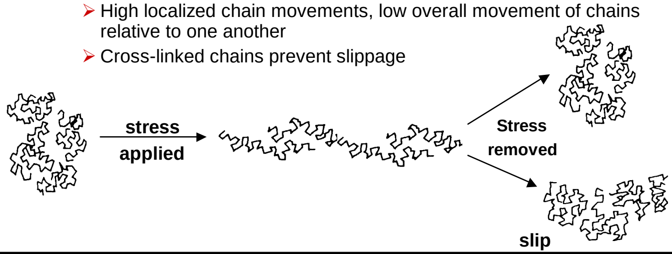


54. Important Fibers



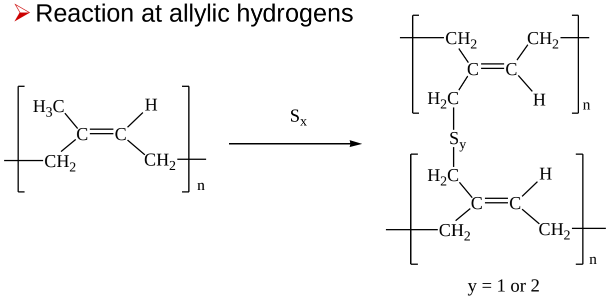
55. Properties of Elastomers

- Requirements for Elastomers
  - Completely amorphous, used above their T_g
  - Low intermolecular forces allow for flexibility
  - High modulus and strength when stretched
    - Often crystallize when stretched
  - Large reversible extensions (several hundred percent)
    - High localized chain movements, low overall movement of chains relative to one another
    - Cross-linked chains prevent slippage



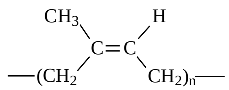
56. Properties of Elastomers

- Possess high molar mass to allow chain entanglements or are cross-linked
  - Gives dimensional stability
- Cross-linked with sulfur
  - Reaction at allylic hydrogens



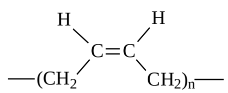
57. Important Elastomers

- Natural Rubber, NR
  - Cis-1,4-polyisoprene



Biological polymerization
Agricultural crop
T_g = -70 ºC
Primary use is auto tires
2.2 billion lb/yr – all imported

- Polybutadiene, BR



Free-radical polymerization
Primary use is auto tires
Also belts, hoses, gaskets
1.33 billion lb/yr
T_g = -110 ºC

Why is the T_g 40 ºC lower than that of natural rubber?

58. Polybutadiene

Reaction:

$nCH_2{=}CH{-}CH{=}CH_2 \longrightarrow {-}(CH_2{-}CH{=}CH{-}CH_2)_n{-}$

1,3-butadiene → polybutadiene

Mechanism:

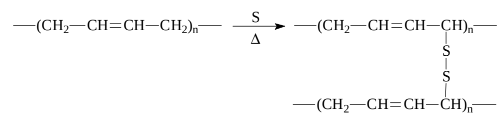
(1) $ROOR \longrightarrow 2RO\cdot$

(2) $RO\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow RO{-}CH_2{-}CH{=}CH{-}CH_2\cdot$

(3) $RO{-}CH_2{-}CH{=}CH{-}CH_2\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow RO{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2\cdot$

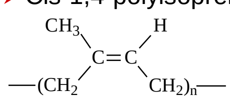
then (3), (3), (3), etc.

Vulcanization:



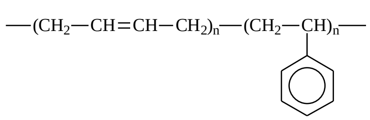
59. Important Elastomers

- Natural Rubber, NR
  - Cis-1,4-polyisoprene



Biological polymerization
Agricultural crop
T_g = -70 ºC
Primary use is auto tires
2.2 billion lb/yr – all imported

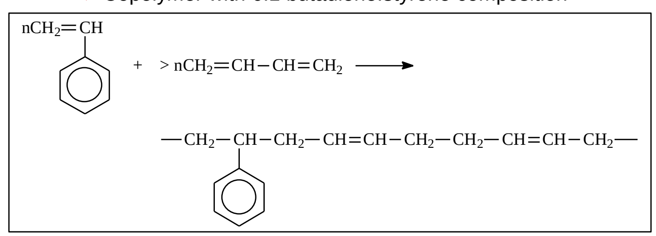
- Styrene-Butadiene Rubber, SBR



Free radical polymerization
Mechanism???
T_g = -65 ºC
Primary use is auto tires
Competes with NR
1.93 billion lb/yr

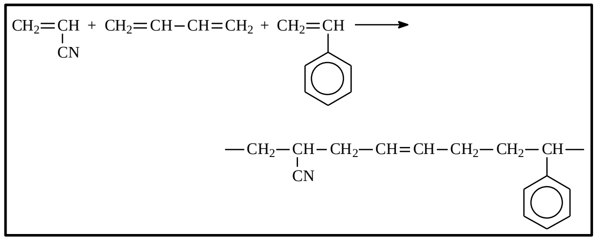
60. Copolymerization

- Many important elastomers like SBR are **random copolymers**
  - Sequence of monomer insertion is completely random
  - Random arrangement of styrene and butadiene
    - SBR (styrene-butadiene rubber)
    - Copolymer with 6:1 butadiene:styrene composition



61. Copolymerization

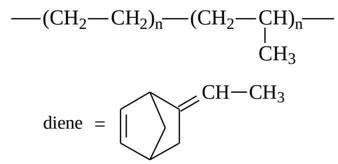
- Another important elastomer is formed by random polymerization of three monomers
  - Acrylonitrile, butadiene, and styrene
  - ABS = acrylonitrile-butadiene-styrene terpolymer



  - Three monomers need not be present in the same amount

62. Important Elastomers

- Ethylene-Propylene Diene Monomer, EPDM



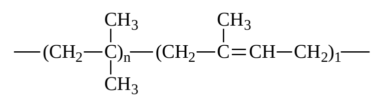
Ziegler-Natta catalyst

Random arrangement of C_2 and C_3 units creates highly flexible polymer

Diene provides reactive sites for cross-linking

0.76 billion lb/yr

- Polyisobutylene, Butyl Rubber



Cationic polymerization

Mechanism?

Isoprene used to cross-link

Primarily used for tubes and tires