

POLYMERS

- Fundamentals of Polymer Technology
- Thermoplastic Polymers
- Thermosetting Polymers
- Elastomers
- Guide to the Processing of Polymers

POLYMERS

- Polymers are generally characterized by:
 - Low density.
 - Low strength and stiffness.
 - Low electrical and thermal conductivity.
 - Good resistance to chemicals.
 - High coefficient of thermal expansion.

POLYMERS

- Many colors and transparencies
- Minimal surface-operations needed (advantage over metals)
- Can be easily machined, cast, formed, and joined
- Low in cost
- Complex shapes possible



Polymer

A compound consisting of long-chain molecules, each molecule made up of repeating units connected together

- There may be thousands, even millions of units in a single polymer molecule
- The word *polymer* is derived from the Greek words *poly*, meaning many, and *meros* (reduced to *mer*), meaning part
- Most polymers are based on carbon and are therefore considered organic chemicals

Types of Polymers

- Polymers can be separated into *plastics* and *rubbers*
- As engineering materials, it is appropriate to divide them into the following three categories:
 1. *Thermoplastic* polymers
 2. *Thermosetting* polymers
 3. *Elastomers*where (1) and (2) are plastics and (3) are rubbers

Thermoplastic Polymers - Thermoplastics (TP)

- Solid materials at room temperature but viscous liquids when heated to temperatures of only a few hundred degrees
- This characteristic allows them to be easily and economically shaped into products
- They can be subjected to heating and cooling cycles repeatedly without significant degradation

Thermosetting Polymers - Thermosets (TS)

- Cannot tolerate repeated heating cycles as thermoplastics can
 - When initially heated, they soften and flow for molding
 - But elevated temperatures also produce a chemical reaction that hardens the material into an infusible solid
 - If reheated, thermosets degrade and char rather than soften

Elastomers

Polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress

- Also known as rubber
- Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape
- Although their properties are quite different from thermosets, they share a similar molecular structure that is different from the thermoplastics

Market Shares

- Thermoplastics are commercially the most important of the three types, constituting around 70% of the tonnage of all synthetic polymers produced
- Thermosets and elastomers share the remaining 30% about evenly, with a slight edge for the former
- On a volumetric basis, current annual usage of polymers exceeds that of metals

Examples of Polymers

- Thermoplastics:
 - Polyethylene, polyvinylchloride, polypropylene, polystyrene, and nylon
- Thermosets:
 - Phenolics, epoxies, and certain polyesters
- Elastomers:
 - Natural rubber (vulcanized)
 - Synthetic rubbers, which exceed the tonnage of natural rubber

Reasons Why Polymers are Important:

- Plastics can be formed by molding into intricate part shapes, usually with no further processing required
 - Very compatible with *net shape* processing
- On a volumetric basis, polymers:
 - Cost competitive with metals
 - Generally require less energy to produce than metals
- Certain plastics are translucent and/or transparent, which makes them competitive with glass in some applications

General Properties of Polymers

- Low density relative to metals and ceramics
- Good strength-to-weight ratios for certain (but not all) polymers
- High corrosion resistance
- Low electrical and thermal conductivity

Limitations of Polymers as Engineering Materials

- Low strength relative to metals and ceramics
- Low modulus of elasticity (stiffness)
- Service temperatures are limited to only a few hundred degrees
- Viscoelastic properties, which can be a distinct limitation in load bearing applications
- Some polymers degrade when subjected to sunlight and other forms of radiation

Synthesis of Polymers

- Nearly all polymers used in engineering are synthetic
 - They are made by chemical processing
- Polymers are synthesized by joining many small molecules together into very large molecules, called *macromolecules*, that possess a chain-like structure
- The small units, called *monomers*, are generally simple unsaturated organic molecules such as ethylene C_2H_4

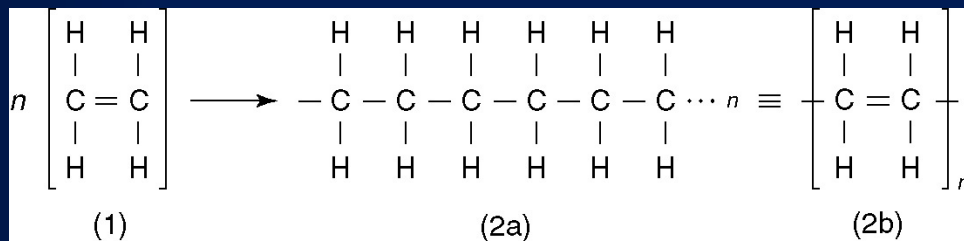


Figure 8.1 - Synthesis of polyethylene from ethylene monomers:
 (1) n ethylene monomers yields (2a) polyethylene of chain length n ; (2b) concise notation for depicting the polymer structure of chain length n

Polymerization

- As a chemical process, the synthesis of polymers can occur by either of two methods:
 1. Addition polymerization
 2. Step polymerization
- Production of a given polymer is generally associated with one method or the other

Addition Polymerization

- In this process, exemplified by polyethylene, the double bonds between carbon atoms in the ethylene monomers are induced to open up so that they join with other monomer molecules
- The connections occur on both ends of the expanding macromolecule, developing long chains of repeating mers
- It is initiated using a chemical catalyst (called an *initiator*) to open the carbon double bond in some of the monomers

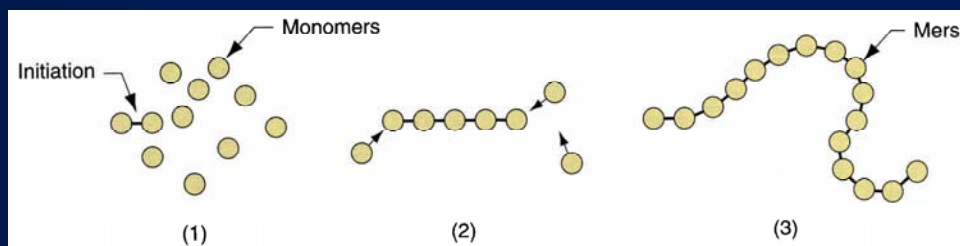


Figure 8.2 - Model of addition (chain) polymerization: (1) initiation, (2) rapid addition of monomers, and (3) resulting long chain polymer molecule with n mers at termination of reaction

Step Polymerization

- In this form of polymerization, two reacting monomers are brought together to form a new molecule of the desired compound
- As reaction continues, more reactant molecules combine with the molecules first synthesized to form polymers of length $n = 2$, then polymers of length $n = 3$, and so on
- In addition, polymers of length n_1 and n_2 also combine to form molecules of length $n = n_1 + n_2$, so that two types of reactions are proceeding simultaneously

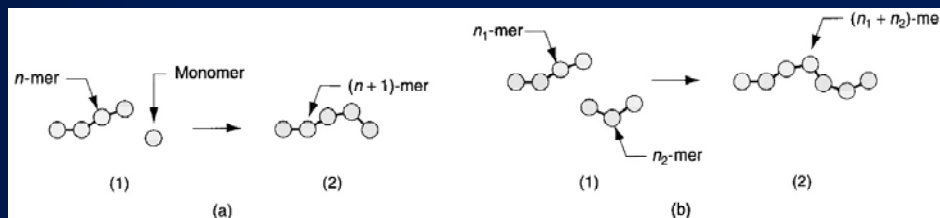


Figure 8.4 - Model of step polymerization showing the two types of reactions occurring: (a) n -mer attaching a single monomer to form a $(n+1)$ -mer; and (b) n_1 -mer combining with n_2 -mer to form a (n_1+n_2) -mer

Sequence is shown by (1) and (2)

Some Examples

- Polymers produced by *addition* polymerization:
 - Polyethylene, polypropylene, polyvinylchloride, polyisoprene
- Polymers produced by *step* polymerization:
 - Nylon, polycarbonate, phenol formaldehyde

Degree of Polymerization

- Since molecules in a given batch of polymerized material vary in length, n for the batch is an average; its statistical distribution is normal
- The mean value of n is called the *degree of polymerization* (DP) for the batch
- DP affects properties of the polymer: higher DP increases mechanical strength but also increases viscosity in the fluid state, which makes processing more difficult

Molecular Weight

- The *molecular weight* (MW) of a polymer is the sum of the molecular weights of the mers in the molecule;
 - $MW = n$ times the molecular weight of each repeating unit
 - Since n varies for different molecules in a batch, the molecule weight must be interpreted as an average

Typical Values of DP and MW for Selected Polymers

<u>Polymer</u>	<u>DP(n)</u>	<u>MW</u>
Polyethylene	10,000	300,000
Polyvinylchloride	1,500	100,000
Nylon	120	15,000
Polycarbonate	200	40,000

Linear, Branched, and Cross-linked Polymers

- *Linear* structure – chain-like structure
 - Characteristic of thermoplastic polymers
- *Branched* structure – chain-like but with side branches
 - Also found in thermoplastic polymers
- *Cross-linked* structure
 - Loosely cross-linked, as in an elastomer
 - Tightly cross-linked, as in a thermoset

Linear structure of a thermoplastic polymer

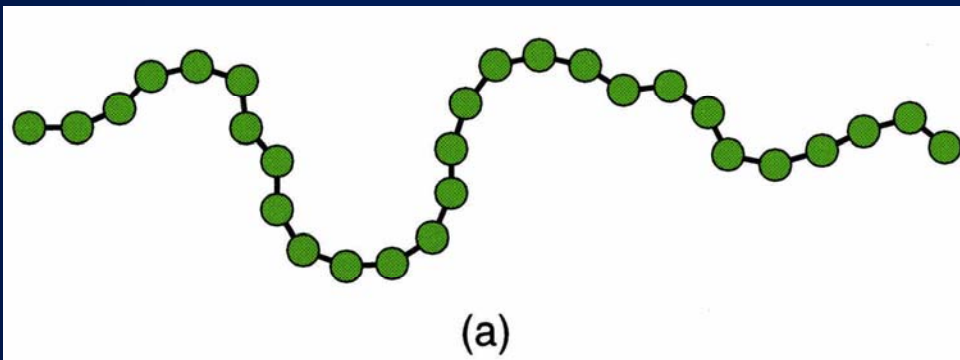


Figure 8.7 - Various structures of polymer molecules:
(a) linear, characteristic of thermoplastics

Branched structure that includes side branches along the chain

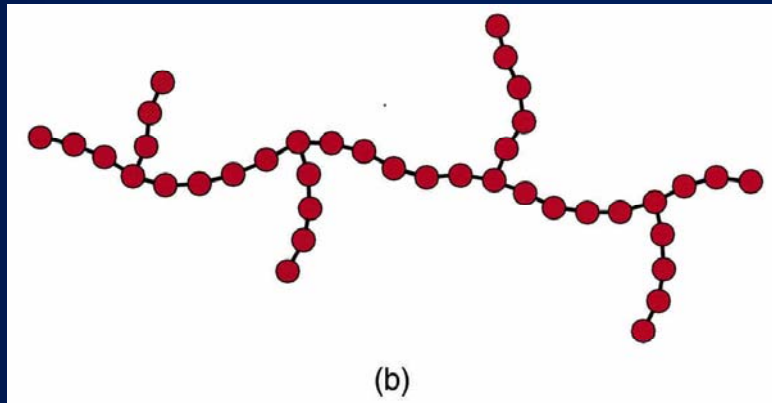


Figure 8.7 - Various structures of polymer molecules: (b) branched

Loosely cross-linked, in which primary bonding occurs between branches and other molecules at certain connection points

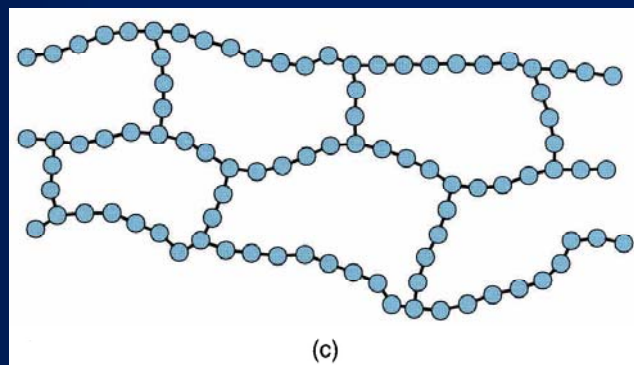


Figure 8.7 - Various structures of polymer molecules:
(c) loosely cross-linked as in an elastomer

Tightly cross-linked or *network structure* - in effect, the entire mass is one gigantic macromolecule

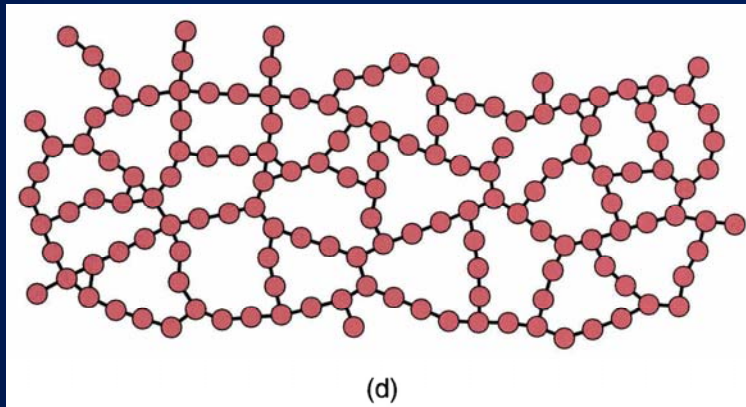


Figure 8.7 - Various structures of polymer molecules:
(d) tightly cross- linked or networked structure as in a thermoset

Effect of Branching on Properties

- *Thermoplastic* polymers always possess *linear* or *branched* structures, or a mixture of the two
- Branches increase entanglement among the molecules, which makes the polymer:
 - Stronger in the solid state
 - More viscous at a given temperature in the plastic or liquid state

Effect of Cross-Linking on Properties

- Thermosets possess a high degree of cross-linking, while elastomers possess a low degree of cross-linking
- Thermosets are hard and brittle, while elastomers are elastic and resilient
- Cross-linking causes the polymer to become chemically set
 - The reaction cannot be reversed
 - The polymer structure is permanently changed; if heated, it degrades or burns rather than melt

Crystallinity in Polymers

- Both amorphous and crystalline structures are possible, although the tendency to crystallize is much less than for metals or non-glass ceramics
- Not all polymers can form crystals
- For those that can, the *degree of crystallinity* (the proportion of crystallized material in the mass) is always less than 100%

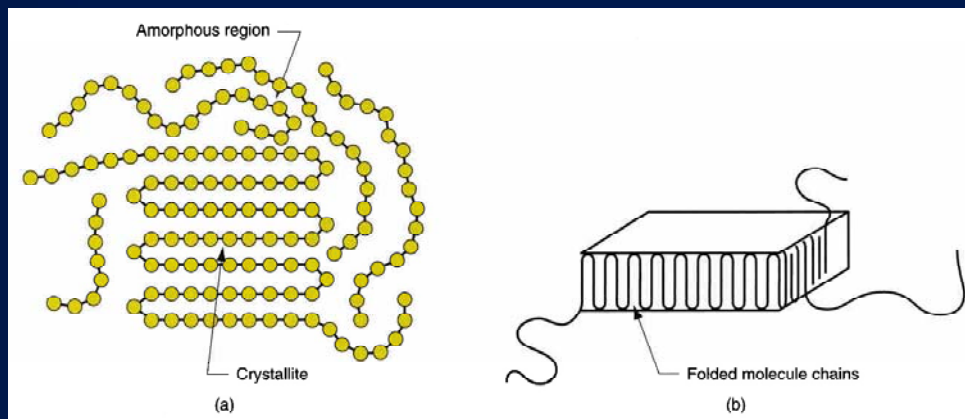


Figure 8.9 - Crystallized regions in a polymer: (a) long molecules forming crystals randomly mixed in with the amorphous material; and (b) folded chain lamella, the typical form of a crystallized region

Crystallinity and Properties

- As crystallinity is increased in a polymer:
 - Density increases
 - Stiffness, strength, and toughness increases
 - Heat resistance increases
 - If the polymer is transparent in the amorphous state, it becomes opaque when partially crystallized

Low Density vs. High Density Polyethylene

<u>Polyethylene type</u>	<u>Low density</u>	<u>High density</u>
Degree of crystallinity	55%	92%
Specific gravity	0.92	0.96
Modulus of elasticity	140 MPa (20,000 lb/in ²)	700 MPa (100,000 lb/in ²)
Melting temperature	115°C (239°F)	135°C (275°F)

Some Observations About Crystallization

- Linear polymers consist of long molecules with thousands of repeated mers
 - Crystallization involves folding back and forth of the long chains upon themselves to achieve a very regular arrangement
- The crystallized regions are called *crystallites*
- Crystallites take the form of lamellae randomly mixed in with amorphous material
 - A polymer that crystallizes is a two-phase system - crystallites interspersed throughout an amorphous matrix

Factors for Crystallization

- Slower cooling promotes crystal formation and growth
- Mechanical deformation, as in the stretching of a heated thermoplastic, tends to align the structure and increase crystallization
- Plasticizers (chemicals added to a polymer to soften it) reduce the degree of crystallinity

Additives

- Properties of a polymer can often be beneficially changed by combining it with additives
- Additives either alter the molecular structure or
- Add a second phase, in effect transforming the polymer into a composite material

Types of Additives by Function

- *Fillers* – to strengthen polymer or reduce cost
- *Plasticizers* – to soften polymer and improve flow
- *Colorants* – pigments or dyes
- *Lubricants* – to reduce friction and improve flow
- *Flame retardents* – to reduce flammability of polymer
- *Cross-linking agents* – for thermosets and elastomers
- *Ultraviolet light absorbers* – to reduce degradation from sunlight
- *Antioxidants* – to reduce oxidation damage

Thermoplastic Polymers (TP)

- A thermoplastic polymer can be heated from a solid state to a viscous liquid state and then cooled back down to solid
 - This heating and cooling cycle can be repeated multiple times without degrading the polymer
- The reason is that TP polymers consist of linear (and/or branched) macromolecules that do not cross-link upon heating
- By contrast, thermosets and elastomers change chemically when heated, which cross-links their molecules and permanently sets these polymers

Mechanical Properties of Thermoplastics

- Low modulus of elasticity (stiffness)
 - E is two or three orders of magnitude lower than metals and ceramics
- Low tensile strength
 - TS is about 10% of the metal
- Much lower hardness than metals or ceramics
- Greater ductility on average
 - Tremendous range of values, from 1% elongation for polystyrene to 500% or more for polypropylene

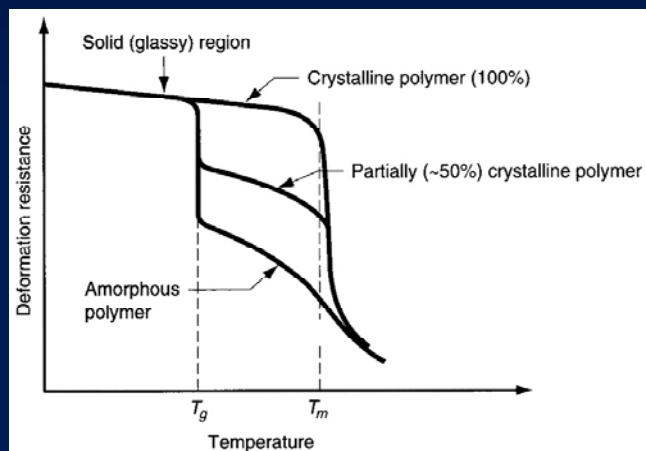


Figure 8.11 - Relationship of mechanical properties, portrayed as deformation resistance, as a function of temperature for an amorphous thermoplastic, a 100% crystalline (theoretical) thermoplastic, and a partially crystallized thermoplastic

Physical Properties of Thermoplastics

- Lower densities than metals or ceramics
 - Typical specific gravity for polymers are ~ 1.2
 - Ceramics specific gravity = ~ 2.5
 - Metals specific gravity = ~ 7.0
- Much higher coefficient of thermal expansion
 - Roughly five times the value for metals and 10 times the value for ceramics
- Much lower melting temperatures

More Physical Properties of Thermoplastics

- Specific heats two to four times those of metals and ceramics
- Thermal conductivities about three orders of magnitude lower than those of metals
- Insulating electrical properties

Commercial Thermoplastic Products and Raw Materials

- Thermoplastic products include molded and extruded items, fibers, films and sheets, packaging materials, and paints and varnishes
- The starting plastic materials are normally supplied to the fabricator in the form of powders or pellets in bags, drums, or larger loads by truck or rail car

Thermosetting Polymers (TS)

- TS polymers are distinguished by their highly cross-linked three-dimensional, covalently-bonded structure within the molecule
- Chemical reactions associated with cross-linking are called *curing* or *setting*
- In effect, the formed part (e.g., pot handle, electrical switch cover, etc.) becomes one large macromolecule
- Always amorphous and exhibits no glass transition temperature

General Properties and Characteristics of Thermosets

- Rigid - modulus of elasticity is two to three times greater than TP
- Brittle, virtually no ductility
- Less soluble than TP in common solvents
- Capable of higher service temperatures than TP
- Cannot be remelted - instead they degrade or burn

How Cross-Linking is Done in TS Polymers

- Three categories:
 1. Temperature-activated systems
 2. Catalyst-activated systems
 3. Mixing-activated systems
- Curing is accomplished at the fabrication plants that make the parts rather than the chemical plants that supply the starting materials to the fabricator

Temperature-Activated Systems

Curing is caused by heat supplied during part shaping operation (e.g., molding)

- Starting material is a linear polymer in granular form supplied by the chemical plant
 - As heat is added, the material softens for molding, but continued heating results in cross-linking
- Most common TS systems
- The term “thermoset” applies best to these polymers

Catalyst-Activated Systems

- Cross-linking in these systems occurs when small amounts of a catalyst are added to the polymer which is in liquid form
- Without the catalyst, the polymer remains stable
- Once combined with the catalyst it changes into solid form

Mixing-Activated Systems

- The mixing of two chemicals results in a reaction that forms a cross-linked solid polymer
- Elevated temperatures are sometimes used to accelerate the reactions
- Most epoxies are examples of these systems

Thermosetting vs. Thermoplastic Polymers

- TS plastics are not as widely used as the TP
 - One reason is the added processing costs and complications involved in curing
- Largest market share TS = phenolic resins with ~ 6% of the total plastics market
 - Compare polyethylene with ~ 35% market share
- TS Products: countertops, plywood adhesives, paints, molded parts, printed circuit boards and other fiber reinforced plastics

Elastomers

Polymers capable of large elastic deformation when subjected to relatively low stresses

- Some can be extended 500% or more and still return to their original shape
- Two categories:
 1. *Natural rubber* - derived from biological plants
 2. *Synthetic polymers* - produced by polymerization processes similar to those used for thermoplastic and thermosetting polymers

Characteristics of Elastomers

- Elastomers consist of long-chain molecules that are cross-linked (like thermosetting polymers)
- They owe their impressive elastic properties to two features:
 1. Molecules are tightly kinked when unstretched
 2. Degree of cross-linking is substantially less than thermosets

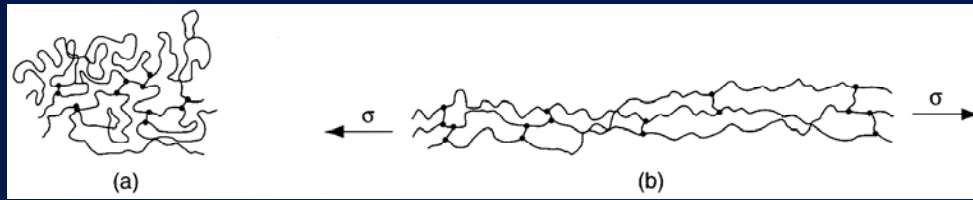


Figure 8.12 - Model of long elastomer molecules, with low degree of cross-linking: (a) unstretched, and (b) under tensile stress

Elastic Behavior of Elastomer Molecule

- When stretched, the molecules are forced to uncoil and straighten
- Natural resistance to uncoiling provides the initial elastic modulus of the aggregate material
- Under further strain, the covalent bonds of the cross-linked molecules begin to play an increasing role in the modulus, and stiffness increases
- With greater cross-linking, the elastomer becomes stiffer and its modulus of elasticity is more linear

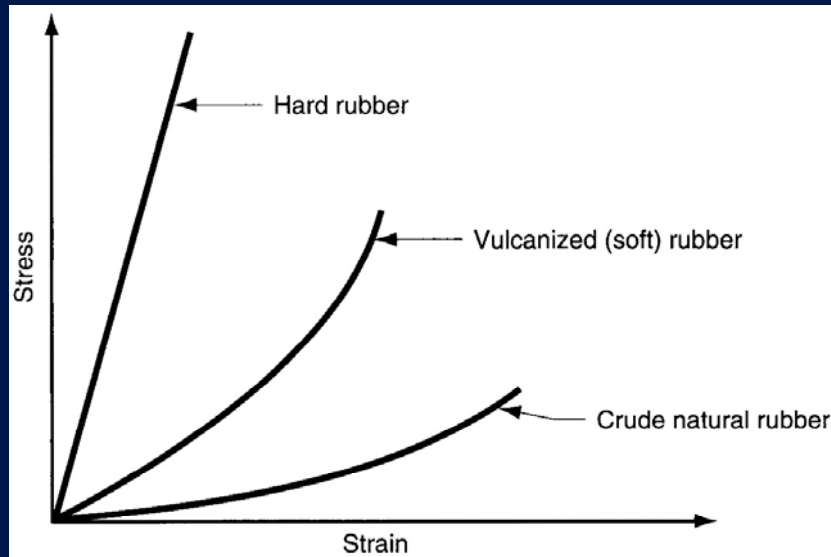


Figure 8.13 - Increase in stiffness as a function of strain for three grades of rubber: natural rubber, vulcanized rubber, and hard rubber

Vulcanization

Curing to cross-link most elastomers

- *Vulcanization* = the term for curing in the context of natural rubber (and certain synthetic rubbers)
- Typical cross-linking in rubber is one to ten links per hundred carbon atoms in the linear polymer chain, depending on degree of stiffness desired
 - Considerable less than cross-linking in thermosets

Natural Rubber (NR)

- NR consists primarily of polyisoprene, a high molecular-weight polymer of isoprene (C_5H_8)
- It is derived from *latex*, a milky substance produced by various plants, most important of which is the rubber tree that grows in tropical climates
- Latex is a water emulsion of polyisoprene (about 1/3 by weight), plus various other ingredients
- Rubber is extracted from latex by various methods that remove the water

Vulcanized Natural Rubber

- Properties: noted among elastomers for high tensile strength, tear strength, resilience (capacity to recover shape), and resistance to wear and fatigue
- Weaknesses: degrades when subjected to heat, sunlight, oxygen, ozone, and oil
 - Some of these limitations can be reduced through the use of additives
- Market share of NR ~ 22% of total annual rubber volume (natural plus synthetic)
 - Rubber volume ~ 15% of total polymer market

Natural Rubber Products

- Largest single market for NR is automotive tires
- Other products: shoe soles, bushings, seals, and shock absorbing components
- In tires, *carbon black* is an important additive; it reinforces the rubber, serving to increase tensile strength and resistance to tear and abrasion
- Other additives: clay, kaolin, silica, talc, and calcium carbonate, as well as chemicals that accelerate and promote vulcanization

Synthetic Rubbers

- Today, the tonnage of synthetic rubbers is more than three times that of NR
- Development of synthetic rubbers was motivated largely by world wars when NR was difficult to obtain
- The most important synthetic is styrene-butadiene rubber (SBR), a copolymer of butadiene (C_4H_6) and styrene (C_8H_8)
- As with most other polymers, the main raw material for synthetic rubbers is petroleum

Thermoplastic Elastomers (TPE)

A thermoplastic that behaves like an elastomer

- Elastomeric properties not from chemical cross-links, but from physical connections between soft and hard phases in material
- Cannot match conventional elastomers in elevated temperature strength and creep resistance
- Products: footwear; rubber bands; extruded tubing, wire coating; molded automotive parts, but no tires

Guide to the Processing of Polymers

- Polymers are nearly always shaped in a heated, highly plastic state
- Common operations are *extrusion* and *molding*
- Molding of thermosets is more complicated because of cross-linking
- Thermoplastics are easier to mold and a greater variety of molding operations are available
- Rubber processing has a longer history than plastics, and rubber industries are traditionally separated from plastics industry, even though processing is similar