Lecture No. (1)

Introduction of Rubber Materials

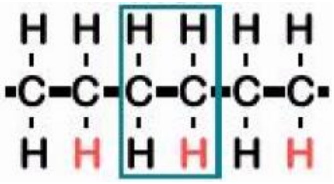
Polymer Structure

Polymers are found in nature as proteins, cellulose, silk or synthesized like polyethylene, polystyrene and nylon. Some natural polymers can also be produced synthetically such as natural rubber (poly isoprene).

Greek word Poly = many; Mer = unit ⇒ Polymer = many units. The term **polymer** denotes a molecule made up by the repetition of some simpler unit, called the **monomer**. For examples: ethylene ⇒ polyethylene**,** acrylic acid ⇒ poly (acrylic acid).

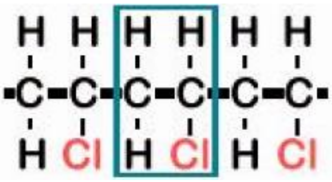
Many polymers structure usually basic makeup of only carbon and hydrogen (for example, polypropylene, polybutylene and polystyrene). Also, some polymers that, instead of having hydrogen atom, have other elements, which involved: oxygen, chlorine, fluorine, nitrogen, silicon, phosphorous, and sulfur are other elements that are found in the molecular makeup of polymers. Polyvinyl chloride (PVC) contains chlorine. Nylon contains nitrogen and oxygen. Teflon contains fluorine. Polyesters and polycarbonates contain oxygen. Vulcanized rubber contains sulfur. These are considered inorganic polymers, for examples:

monomer



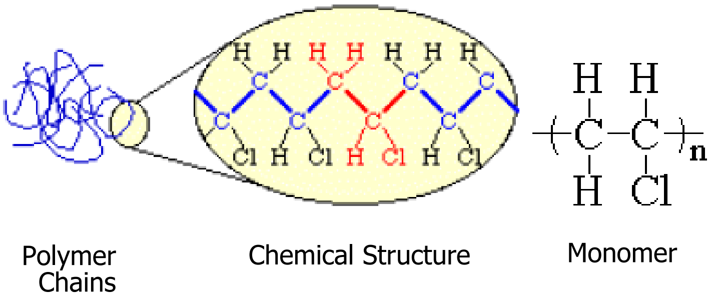
Polyethylene (PE)

monomer



Poly(vinyl chloride) (PVC)

The repeating structure results in large chainlike molecules, the number of repeating units or monomer per polymer chain called, **n**. **e.g.,** (PVC).



Advantages of Polymers (over metals or ceramics)

- Low density (specific gravity = 1.0 – 1.4) (7.85 for steel).
- Can be crystalline or semi-crystalline structure.
- Corrosion resistance.
- Easy to manufacture and make complex shapes at low temperature.
- Electrical and thermal insulation.
- Low cost.
- High toughness and ductility.
- Optics meaning can be transparent (preferred to glass because of light weight and toughness) such as aircraft windows are plastics.

Disadvantages of Polymers (relative to metals or ceramics)

- Low use temperature
- Low thermal and electrical conductivity.
- Low modulus of elasticity (low stiffness).
- Low tensile and compressive strengths (strength might be improved using composite structures).
- Fatigue sensitivity.
- Deformation is very sensitive to temperature.
- Creep at room temperatures.
- May swell with water.
- Toxicity, flammability.
- Solvent sensitivity (may be soluble or properties may change).
- U.V. light sensitivity (can break covalent bonds for some polymers).

Homopolymer

Homopolymers made up from only one type of monomer.

Copolymer

Copolymers made up of two or more types of chemically distinct monomers. It may be composed of two bi-functional units of two different monomers may be joined in a different fashion. Synthetic rubbers are often random copolymers, e.g., styrene butadiene rubber (SBR), which is used in automobile tires.

Alternating copolymer:

A copolymerization involving monomers A and B that results in -A-B-A-B-A-.

***Random copolymer**:*

A copolymerization where the sequence of A's and B's is random,
-A-A-B-A-B-B-A-B-A-B-B-B-A-.

Block copolymer:

Built from first one polymer, and then another, as in
-A-A-A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-B-.

***Graft copolymer**:*

Make up where a polymer of 'B' was grafted onto a polymer of 'A'.

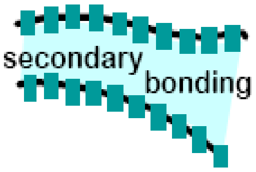
-A-A-A-A-A-A-A-A-A-A-
  |
  B
  |

Molecular Structure

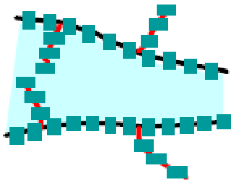
In each polymer the atoms are bound together by covalent bonds. However, the molecule chains, or segments of the same molecule, are attracted to each other by weak intermolecular forces, or termed secondary or Vander Waals forces.

In general, covalent bonds give the thermal and chemical stability of polymers. On the other hand, secondary forces determine most of the physical properties we associate with specific compound. Melting, dissolving, vaporizing, adsorption, diffusion, deformation, and flow involve the making and breaking of intermolecular bonds so that molecules can move one another or away from each other.

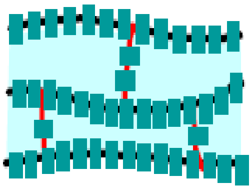
Individual chains of polymers can also be chemically linked by covalent bonds (crosslinked) during polymerization or by subsequent chemical or thermal treatment during fabrication. Once formed, these crosslinked networks resist heat softening, creep, and solvent attack, but cannot be thermally processed.



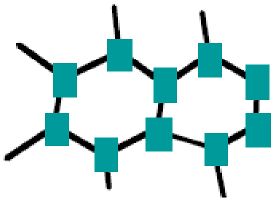
Linear



Branched



Cross-Linked



Network

Linear Polymers**:** For examples: polyethylene, poly (vinyl chloride) (PVC), polystyrene, polymethyl methacrylate, nylon, fluorocarbons (teflon).

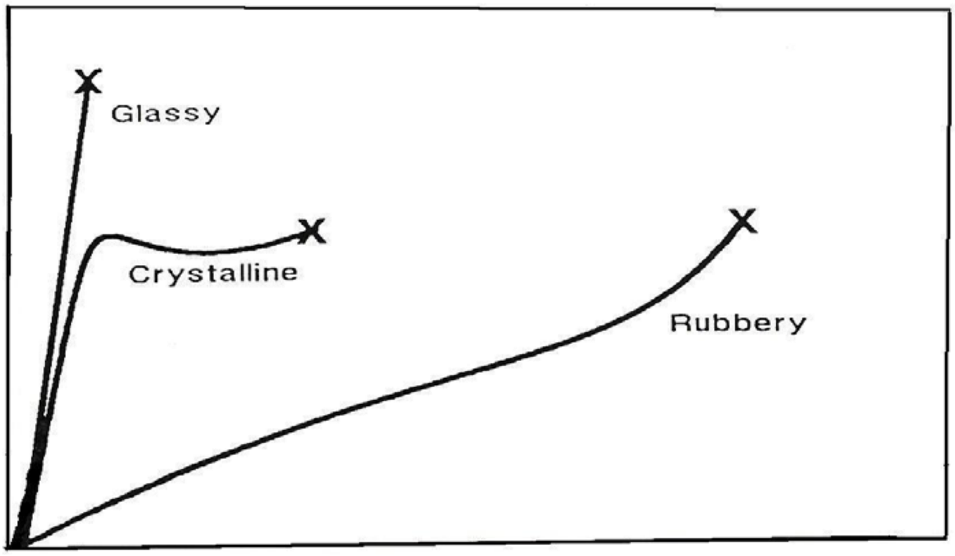
Branched Polymers**:** For examples: elastomers or rubbers.

Cross-linked Polymers**:** For examples: thermosetting polymers, many elastomers or rubbers are also cross-linked (vulcanized).

Network Polymers**:** For examples: epoxy, phenol-formaldehydes.

Classification of Polymers Depending on Thermal Behavior

Polymeric materials is composed of very large molecules can be classified according to behavior with rising temperature to (thermosets, thermoplastics and elastomers), the attention has been paid to elastomer (rubber) in this study. The tensile stress-strain diagrams for three types of polymer as shown in (Figure 1).

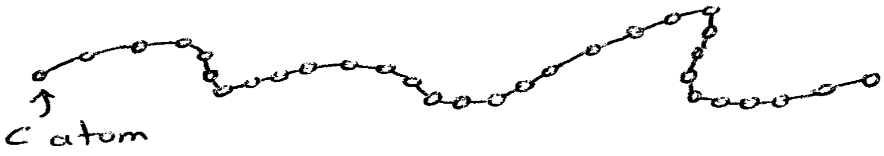


(Figure 1): Tensile Stress-Strain Diagram for three Types of Polymer: Glassy (Thermosets); Crystalline (Thermoplastics); and Rubbery.

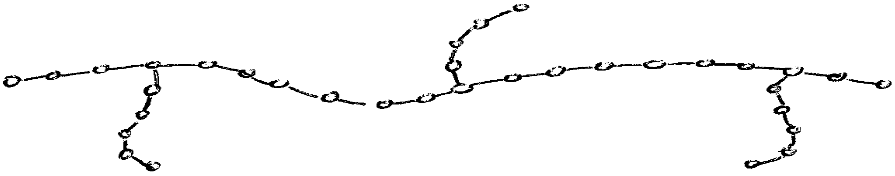
The polymer chains can be free to slide one another (thermoplastic) or they can be connected to each other with crosslinks (thermoset). Thermoplastics (including thermoplastic elastomers) can be reformed and recycled, while thermosets (including crosslinked elastomers) are not reworkable.

Thermoplastics

This polymers that soft and flow when heated; thus, easily reshaped and recycled. This property is due to presence of long chains with limited or no crosslinks. In a thermoplastic material the very long chains are held together by weak Vander Waals forces. When the material is heated the intermolecular forces are weakened so that it becomes soft and flexible, finally at high temperatures, it is a viscous melt (it flows). When the material is allowed to cool it solidifies again during the moulding process, usually under the application of pressure only. For examples: polyethylene (PE), polypropylene (PP), poly (vinyl chloride) (PVC), polystyrene (PS), poly (ethylene terephthalate) (PET), nylon (polyamide), unvulcanized natural rubber.



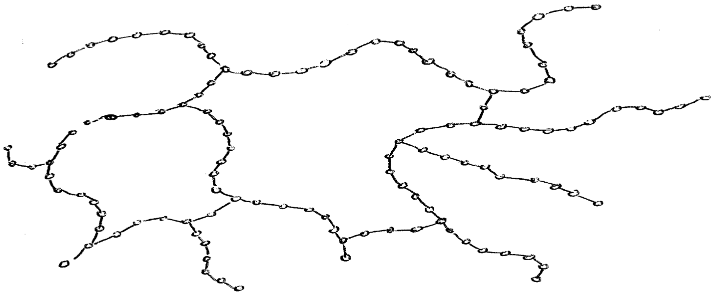
linear



branched

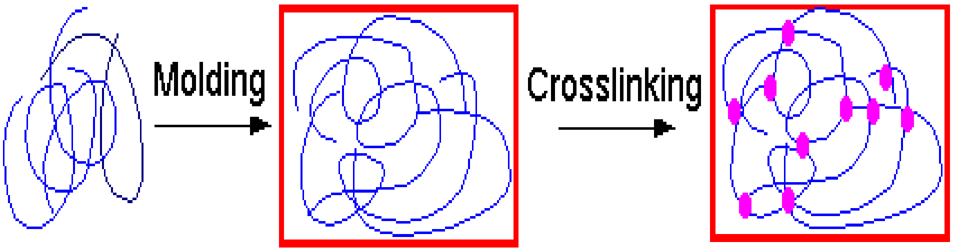
Thermosets

This polymer that decomposes when heated; thus, cannot be reformed or recycled. Presence of extensive crosslinks between long chains induces decomposition upon heating and became thermosetting polymers is brittle.



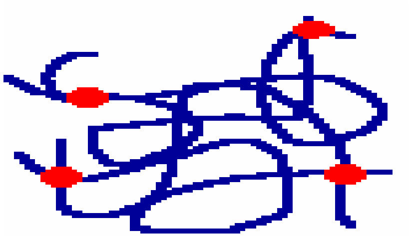
crosslinked

A thermosetting polymer is produced by a chemical reaction which has two stages. The first stage results in the formation of long molecule chains similar to those present in thermoplastics, but still capable of further reaction. The second stage of the reaction (crosslinking of chains) takes place during moulding, usually under the application of heat and pressure. During the second stage, the long molecular chains have been interlinked by strong covalent bonds so that the material cannot be softened again by the application of heat. If excess heat is applied to these materials they will char and degrade. For examples: epoxy, polyesters, phenol-formaldehyde resins, vulcanized rubber.



Elastomers

The polymer chains in elastomers are above their glass transition at room temperature, making them rubbery and undergo high flexible and elastic deformation.



Elastomeric polymer chains can be crosslinked, or connected by covalent bonds. The crosslinking in elastomers is called vulcanization, and is achieved by irreversible chemical reaction, usually requiring sulfur and high temperatures. Unvulcanized elastomers like natural rubber (polyisoprene) are a thermoplastic have poorly resistant to wear and in hot weather become soft and sticky, but in cold weather hard and brittle.

Sulfur compounds are added to form chains that bond adjacent polymer backbone chains and crosslinks them. The vulcanized rubber is a thermosetting polymer and makes elastomers reversibly stretchable for small deformations. When shorter stretched, the polymer chains become elongated and ordered along the deformation direction. The crosslinks guide the elastomer back to its original shape and the chains randomize again.