THERMOSETTING AND THERMOPLSTIC POLYMERS

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POLYMERS

1. Fundamentals of Polymer Technology
2. Thermoplastic Polymers
3. Thermosetting Polymers
4. Guide to the Processing of Polymers

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

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
- Symbolized by TP

Thermosetting Polymers - Thermosets

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

Market Shares

- Thermoplastics are commercially the most important of the three types
  - About 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 molded into intricate part shapes, usually with no further processing
  - Very compatible with *net shape* processing
- On a volumetric basis, polymers:
  - Are cost competitive with metals
  - Generally require less energy to produce than metals
- Certain plastics are 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

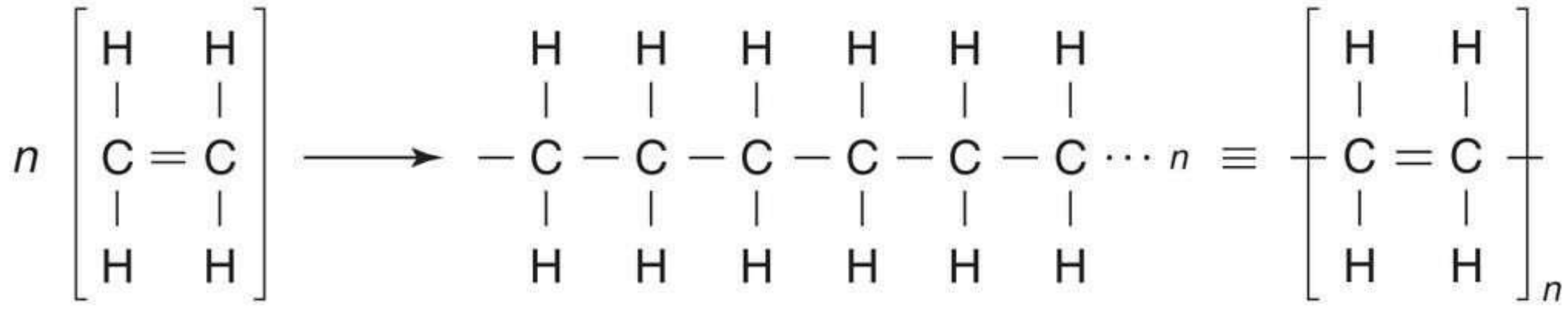
- Low strength relative to metals and ceramics
- Low modulus of elasticity (stiffness)
- Service temperatures are limited to only a few hundred degrees
- Viscoelastic properties, which can be a distinct limitation in load bearing applications
- Some polymers degrade when subjected to sunlight and other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

Polyethylene

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



(1) (2a) (2b)

Polymerization

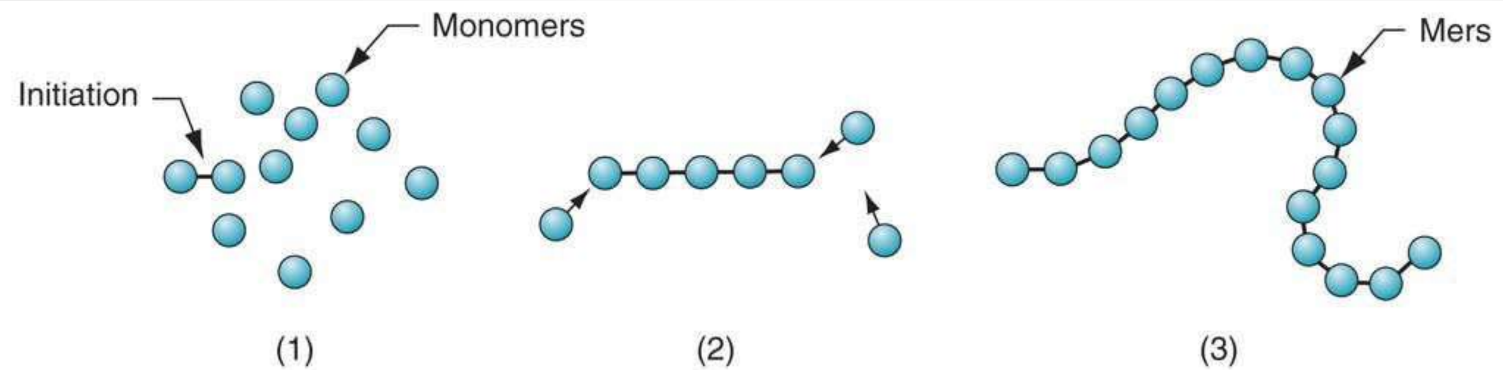
- As a chemical process, the synthesis of polymers can occur by either of two methods:
  1. Addition polymerization
  2. Step polymerization
- Production of a given polymer is generally associated with one method or the other

Addition Polymerization

- In this process, the double bonds between carbon atoms in the ethylene monomers are induced to open up so they can 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 to open the carbon double bond in some of the monomers

Addition Polymerization

- 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

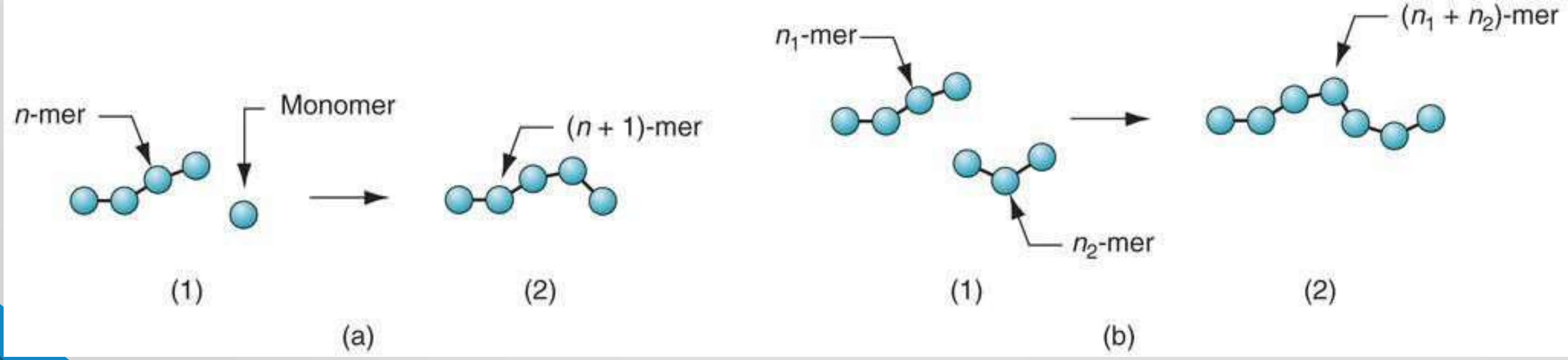


Step Polymerization

- 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 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

Step Polymerization

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



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 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 molecular weight must be interpreted as an average

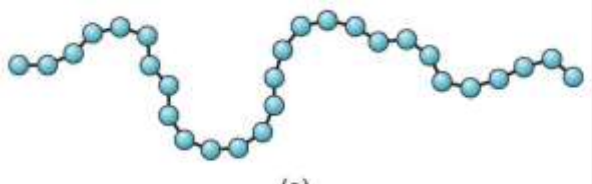
Typical Values of DP and MW

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

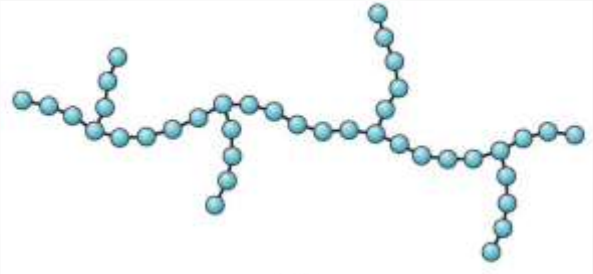
Polymer Molecular Structures

- 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, characteristic of elastomers
  - Tightly cross-linked, characteristic of thermosets

Polymer Molecular Structures


(a)

Linear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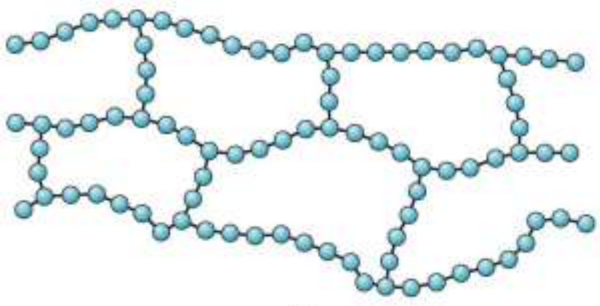
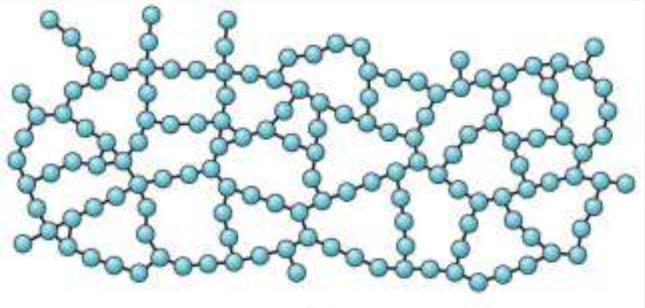
Branched


(c)

Loosely cross-linked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Tightly cross-linked

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

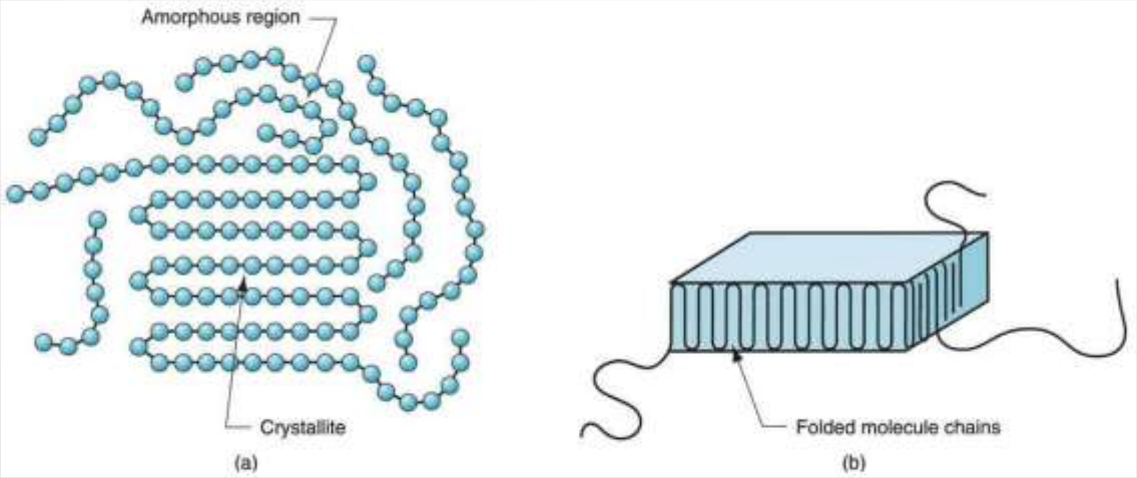
- Thermosets possess a high degree of cross-linking; elastomers possess a low degree of cross-linking
- Thermosets are hard and brittle, while elastomers are elastic and resilient
- Cross-linking causes the polymer to become chemically set
  - The reaction cannot be reversed
  - The polymer structure 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%

Crystalline Polymer Structure

- 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 & High Density Polyethylene

Polyethylene type	Low density	High density
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

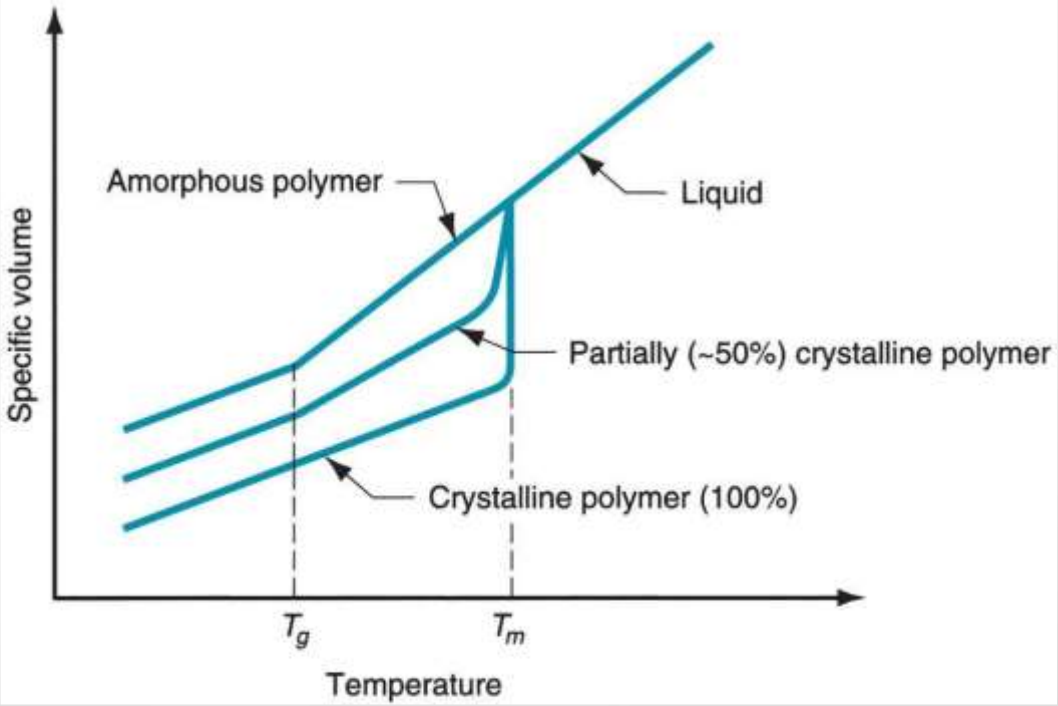
- Linear polymers consist of long molecules with thousands of repeated mers
  - Crystallization involves folding back and forth of the long chains upon themselves
- The crystallized regions are called *crystallites*
- Crystallites take the form of lamellae randomly mixed in with amorphous material
 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

Thermal Behavior of Polymers

- Specific volume (density)$^{-1}$ as a function of temperature



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

Thermoplastic Polymers (TP)

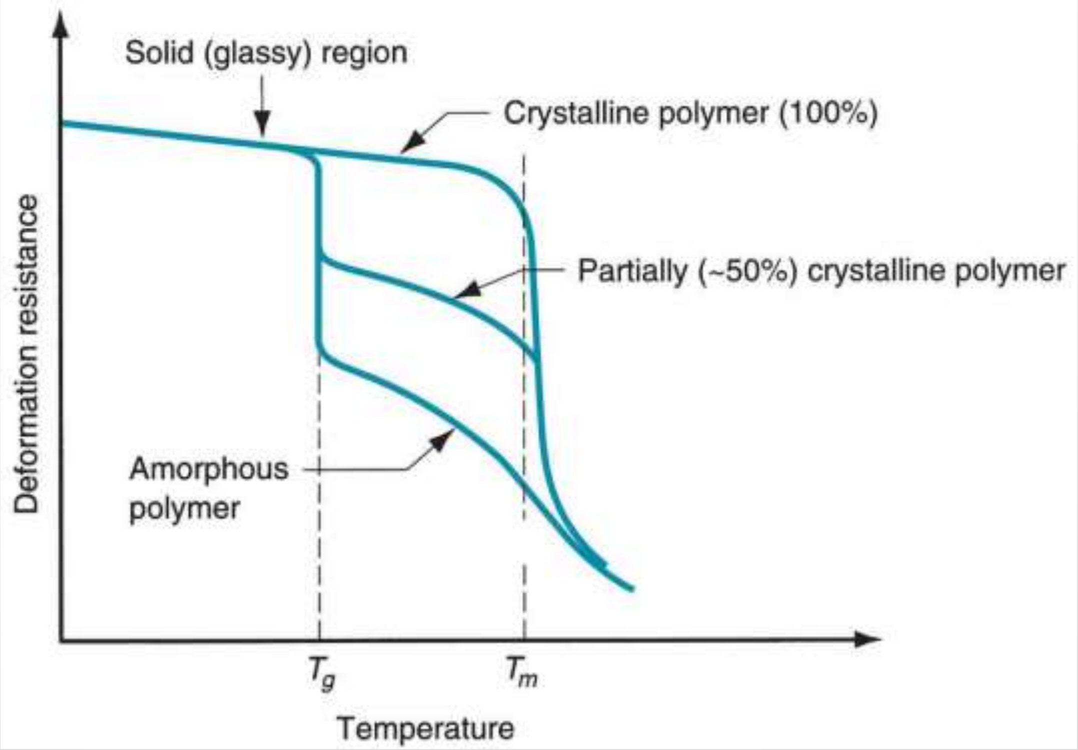
- Thermoplastic polymers can be heated from solid state to viscous liquid and then cooled back down to solid
  - Heating and cooling can be repeated many times without degrading the polymer
    - Reason: TP polymers consist of linear and/or branched macromolecules that do not cross-link upon heating
- 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 much lower than metals and ceramics
- Low tensile strength
  - *TS* is about 10% of metal
- Much lower hardness than metals or ceramics
- Greater ductility on average

Strength vs. Temperature

- Deformation resistance (strength) of polymers as a function of temperature



Physical Properties of Thermoplastics

- Lower densities than metals or ceramics
  - Typical specific gravity for polymers are ~1.2 (compared to ceramics (~ 2.5) and metals (~ 7)
- Much higher coefficient of thermal expansion
  - Roughly five times the value for metals and 10 times the value for ceramics
- Much lower melting temperatures
- Insulating electrical properties
- Higher specific heats than metals and ceramics

Commercial Thermoplastic Products and Raw Materials

- Thermoplastic products include
  - Molded and extruded items
  - Fibers and filaments
  - Films and sheets
  - Packaging materials
  - Paints and varnishes
- 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

Applications of Thermoplastic (TP)

- They are useful for a variety of applications, including consumer goods, machine parts and packaging and storage materials.
- Acrylic - It serves as a sturdy substitute for glass for such items as aquariums, motorcycle helmet visors, aircraft windows, viewing ports of submersibles, and lenses of exterior lights of automobiles
- Nylon - Nylon fibers are useful in making fabrics, rope, carpets and strings for musical instruments
- Polypropylene - Polypropylene (PP) is useful for such diverse products as reusable plastic containers, diapers, sanitary pads, ropes, carpets, plastic moldings, piping systems, car batteries.
- Teflon - Teflon is the brand name given by DuPont Corp. for a polymer called polytetrafluoroethylene (PTFE), which belongs to a class of thermoplastics known as fluoropolymers. It is famous as a coating for non-stick cookware.

Thermosetting Polymers (TS)

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

General Properties of Thermosets

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

Cross-Linking 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 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, material softens for molding, but continued heating causes cross-linking
- Most common TS systems
  - The term “thermoset" applies best to these polymers

Catalyst-Activated Systems

Cross-linking occurs when small amounts of a catalyst are added to the polymer, which is in liquid form

- Without the catalyst, the polymer remains stable and liquid
- Once combined with the catalyst it cures and changes into solid form

Mixing-Activated Systems

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

TS vs. TP 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 of 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

Applications of Thermosetting (TS)

- Epoxies :
- Characteristics: Excellent combination of mechanical properties and corrosion resistance; dimensionally stable; good adhesion; relatively inexpensive; good electrical properties.
- Application: Electrical moldings, sinks, adhesives, protective coatings, used with fiberglass laminates.
- Phenolics :
- Characteristics: Excellent thermal stability to over 1500 C; may be compounded with a large number of resins, fillers, etc.; inexpensive.
- Application: Motor housing, telephones, auto distributors, electrical fixtures

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

Reference

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THANK YOU.