SME 2713
Processing of Polymers - 1

Outline

1. **Introduction**
    - What is polymers
    - Polymerization
    - Structures of polymers
2. **Polymer classifications**
    - Thermoplastic vs thermoset
    - Amorphous vs crystalline
    - Addition vs condensation
    - Commodity, engineering, high performance
3. **Properties of polymers**
4. **Processing methods for polymers**
5. **Types of polymers**
6. **General requirements for plastic products**

1. INTRODUCTION

Plastic refer to a family of synthetic materials made up of repetition of high weight molecules in a form of flexible chain.

These materials are soft and moldable during manufacture and can be formed in various shapes and sizes, such as sheets, films, fibers, filaments, adhesives, molding pellets and powder

1. INTRODUCTION

What is a "Polymer"

The word Polymer comes from the Greek "poly" meaning many, and "meros", parts or units. A polymer is an organic substance made up of many repeating units or building blocks of molecules called ***mers.*** You combine many monomers (one unit), i.e bonding atoms via covalent bonds, to create a polymer.

$$\sum_{1}^{n} n\ (mer) = polymer$$

Polymer is often used as a synonym for "plastic“. All plastics are polymers, but not all polymers are plastics. **Plastic actually refers to the way a material melts and flows.**

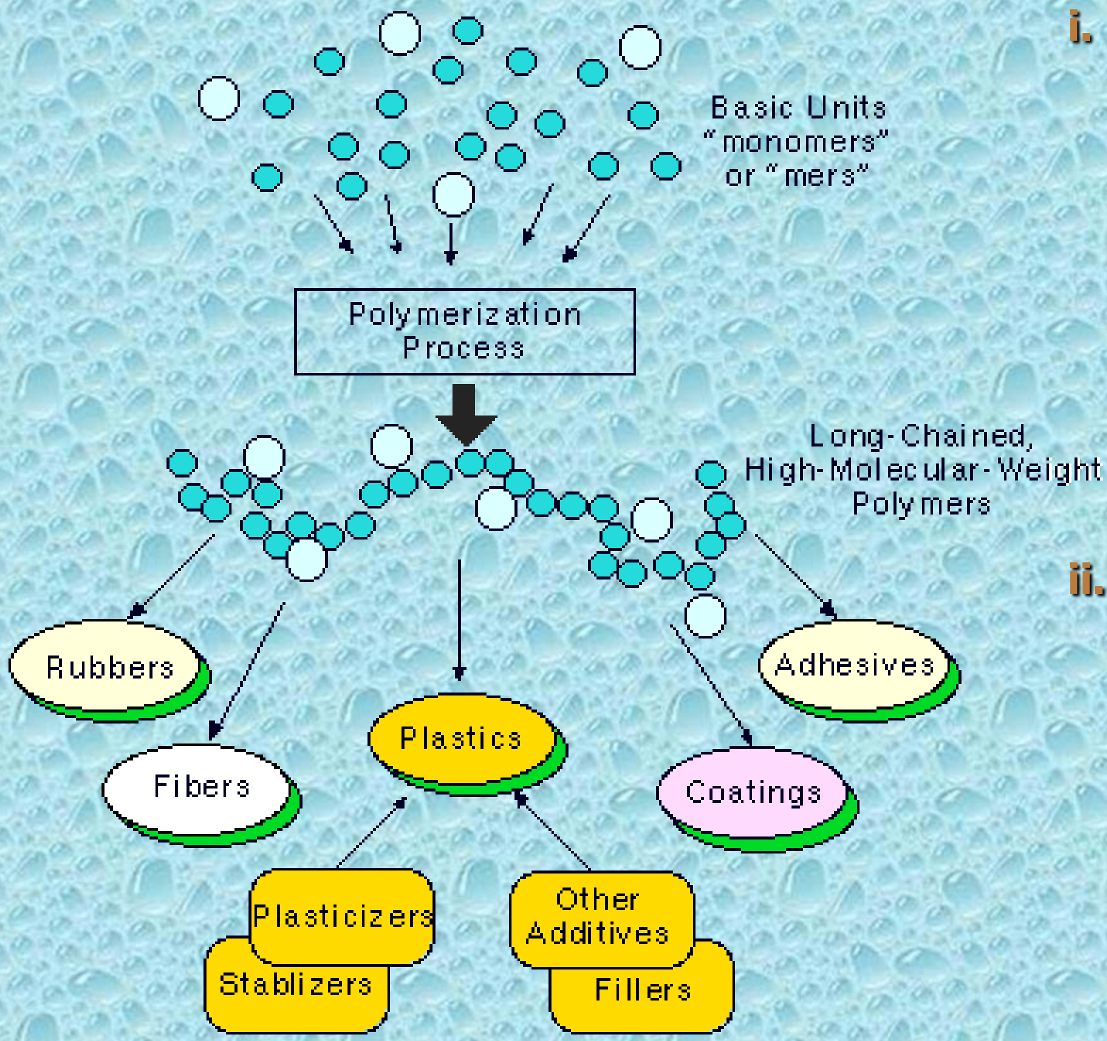
When in form ready for further working, they are called *resins*.

1. INTRODUCTION

Commercial polymers are formed through chemical reactions in large vessels under ***heat and pressure***. Other ingredients are added to control how the polymer is formed and to produce the proper molecular length and desired properties. This chemical process is called "polymerization".

Frequently, polymers, resins, plastics are used interchangeably.

Polymerization Reactions



i. **Chain polymerization**, also called ***addition*** polymerization, with the aid of **initiators**, to form Paraffin or Benzene.

ii. **Step reaction**, also called *condensation*, dissimilar monomers joined into short groups that gradually grow with by-product released.

1. INTRODUCTION

There are two main types of polymerization:

Addition polymerization is the straightforward addition of monomers of the same kind

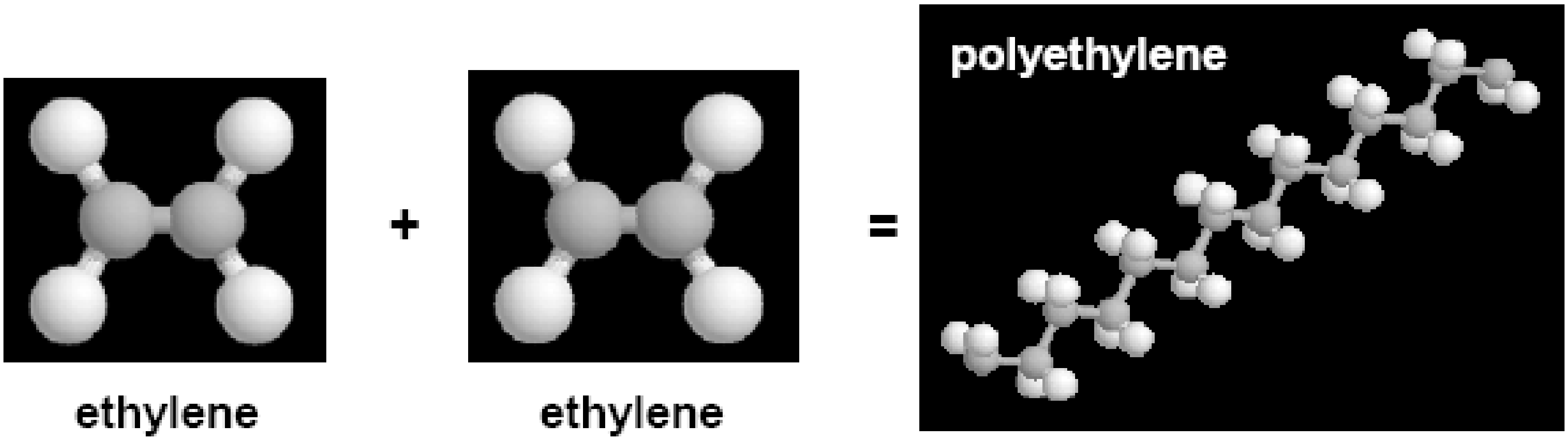
Homogeneous type A+A … → A-A-A-A- …

or of different kinds

Copolymer type A+B+A+B … → A-B-A-B- …

1. INTRODUCTION

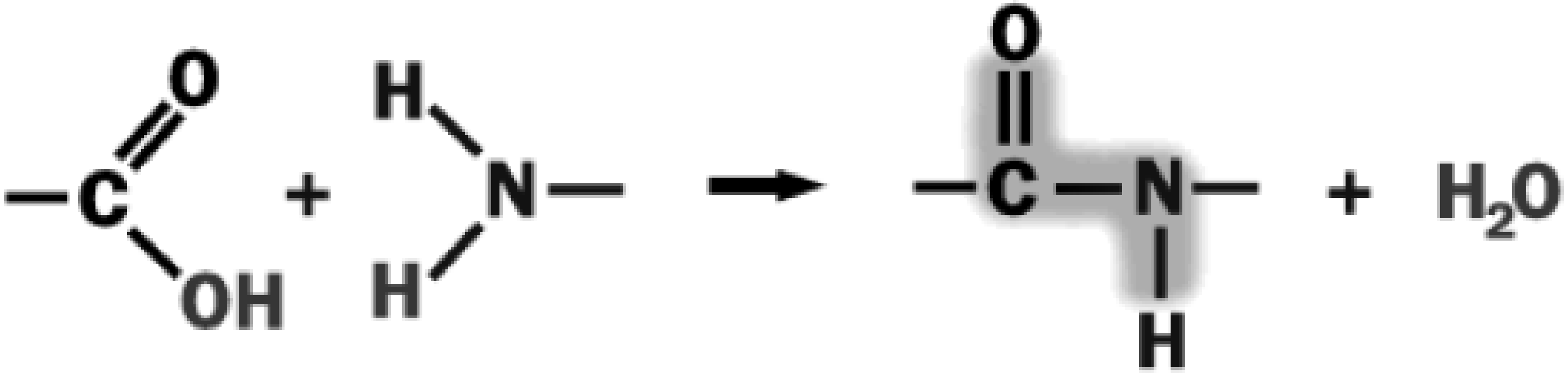
Polyethylene is an example of homogeneous addition polymerization.



1. INTRODUCTION

Condensation polymerization involves a polymerization reaction between two monomers with the expulsion of a simple by-product, such as water, hydrogen chloride, etc …

$$A+B \rightarrow AB + \text{simple by-product}$$



An example of a condensation reaction between two amino acids leaving water as a by-product

1. INTRODUCTION

- Polymers are an important class of materials
- They possess a very wide range of mechanical, physical, chemical and optical properties
- Compared with metals, polymers are generally characterized by **lower**;
  - Density, strength, elastic modulus, and thermal and electrical conductivity
  - And a higher coefficient of thermal expansion

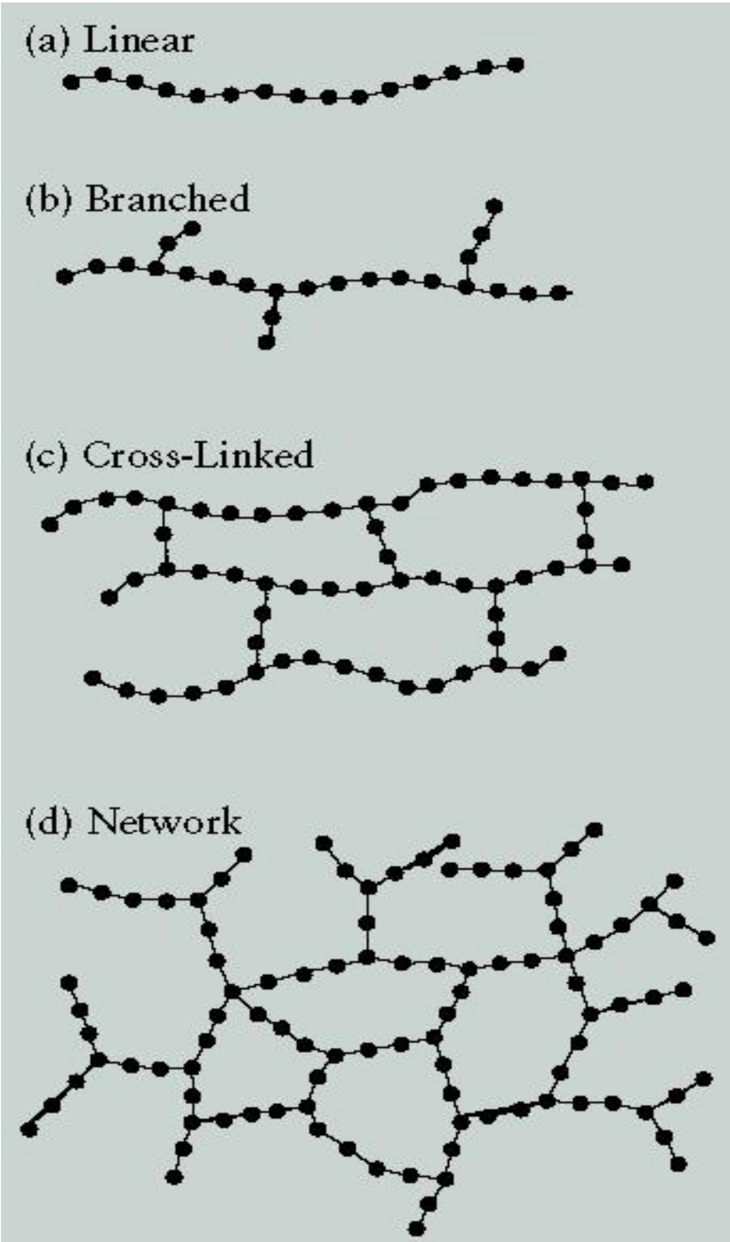
1. INTRODUCTION

- **General properties of polymers:**
  - **Lightweight**
  - **Corrosion resistant**
  - **Low in strength**
  - **Not suitable for high temperature (toxic fumes)**
  - **Relatively inexpensive**
  - **Readily formed into a variety of shapes**
  - **Some are transparent (replacement of glass)**
  - **Electrical insulators**
  - **Low coefficient of friction**

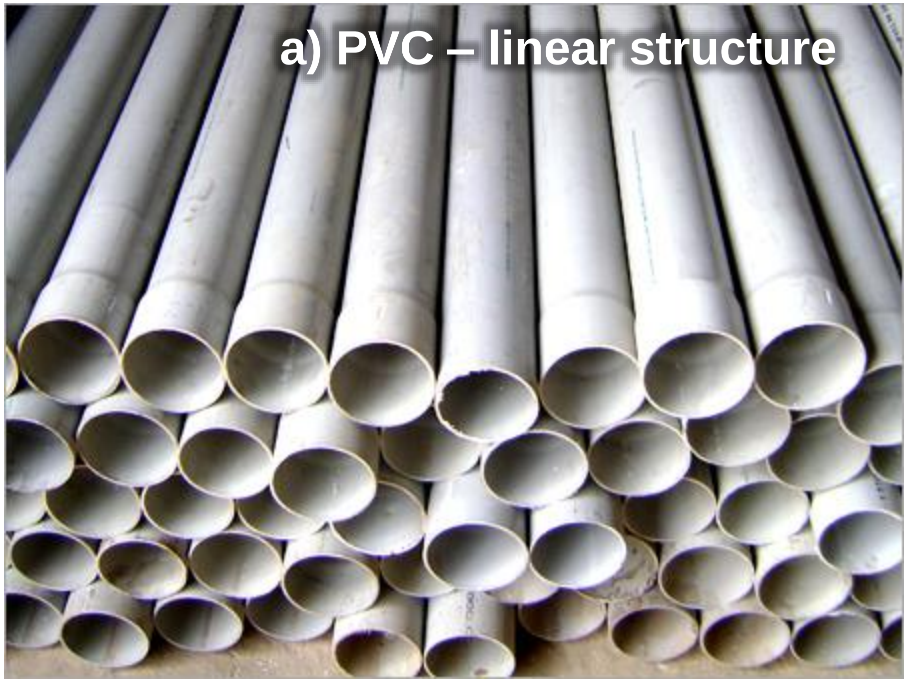
1. INTRODUCTION

- The properties of the polymer depend on the molecular structure (linear, branched, cross-linked, or network), the degree of crystalinity, and additives (which perform various functions, such as *improving strength, flame retardation, and lubrication*, as well as imparting flexibility, colour, and stability against ultraviolet radiation and oxygen).
- The **glass-transition** temperature separates the brittle and ductile (hard and soft) regions of polymers.

Illustration of Polymer Chains



Schematic illustration of polymer chains. (a) Linear structure. Thermoplastics such as acrylics, nylons, polyethylene, and polyvinyl chloride have linear structures. (b) Branched structure, such as in polyethylene. (c) Cross linked structure. Many rubbers and elastomers have this structure. Vulcanization of rubber produces this structure. (d) Network structure, which is basically highly cross-linked. Examples include thermosetting plastics, such as epoxies and phenolics.

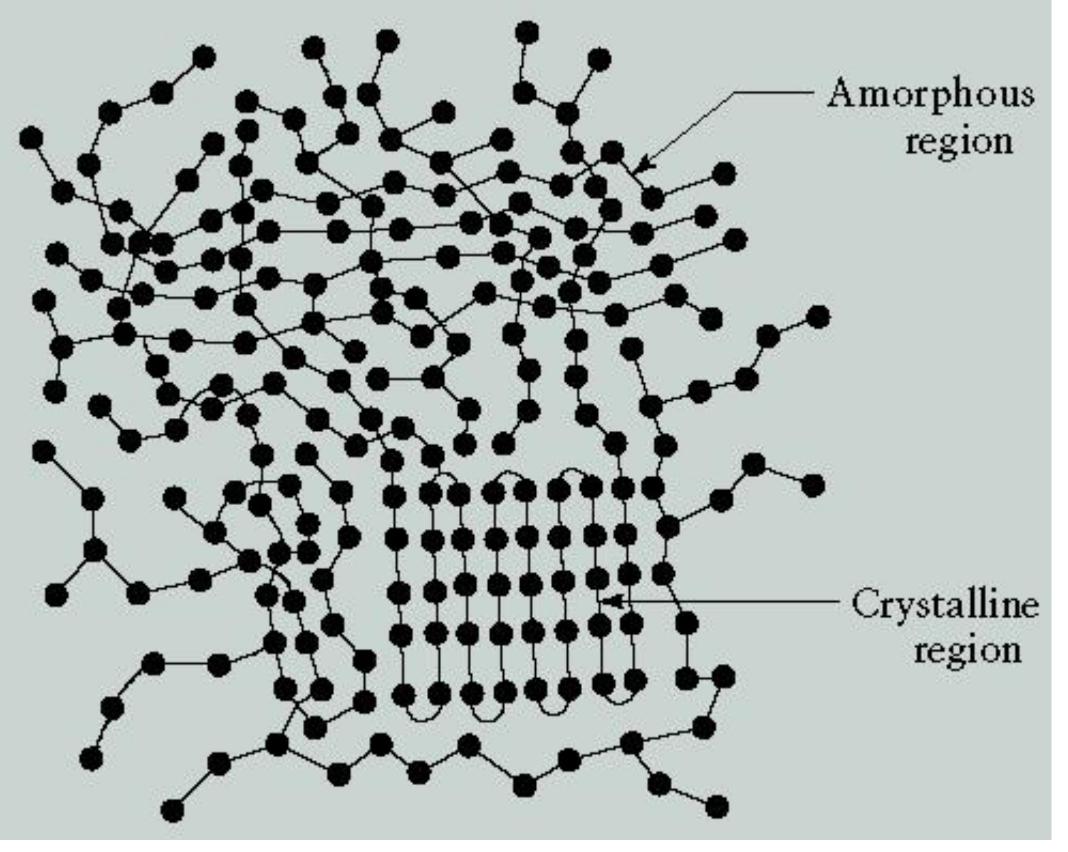

a) PVC – linear structure

b) PE – branched structure


c) Elastomer – cross linked structure

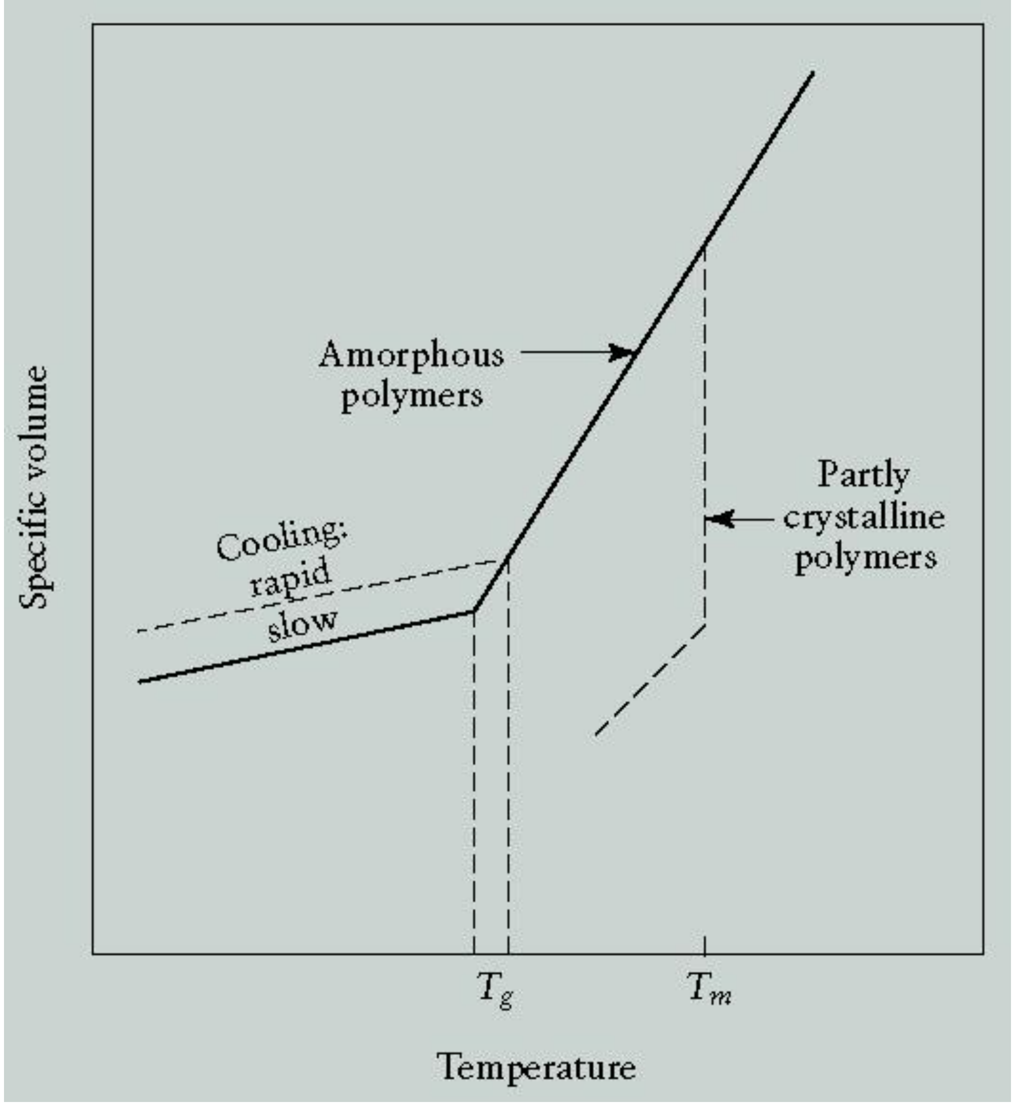
d) Thermosetting – Network Structure

Amorphous and Crystalline Regions in a Polymer



Amorphous and crystalline regions in a polymer. The crystalline region (crystallite) has an orderly arrangement of molecules. The *higher the crystallinity, the harder, stiffer, and less ductile is the polymer.*

Specific Volume of Polymers/Temperature



Specific volume of polymers as a function of temperature. Amorphous polymers, such as acrylic and polycarbonate, have a **glass-transition** temperature T_g, but do not have a specific melting point T_m. Partly crystalline polymers, such as polyethylene and nylons, contract sharply at their melting points during cooling.

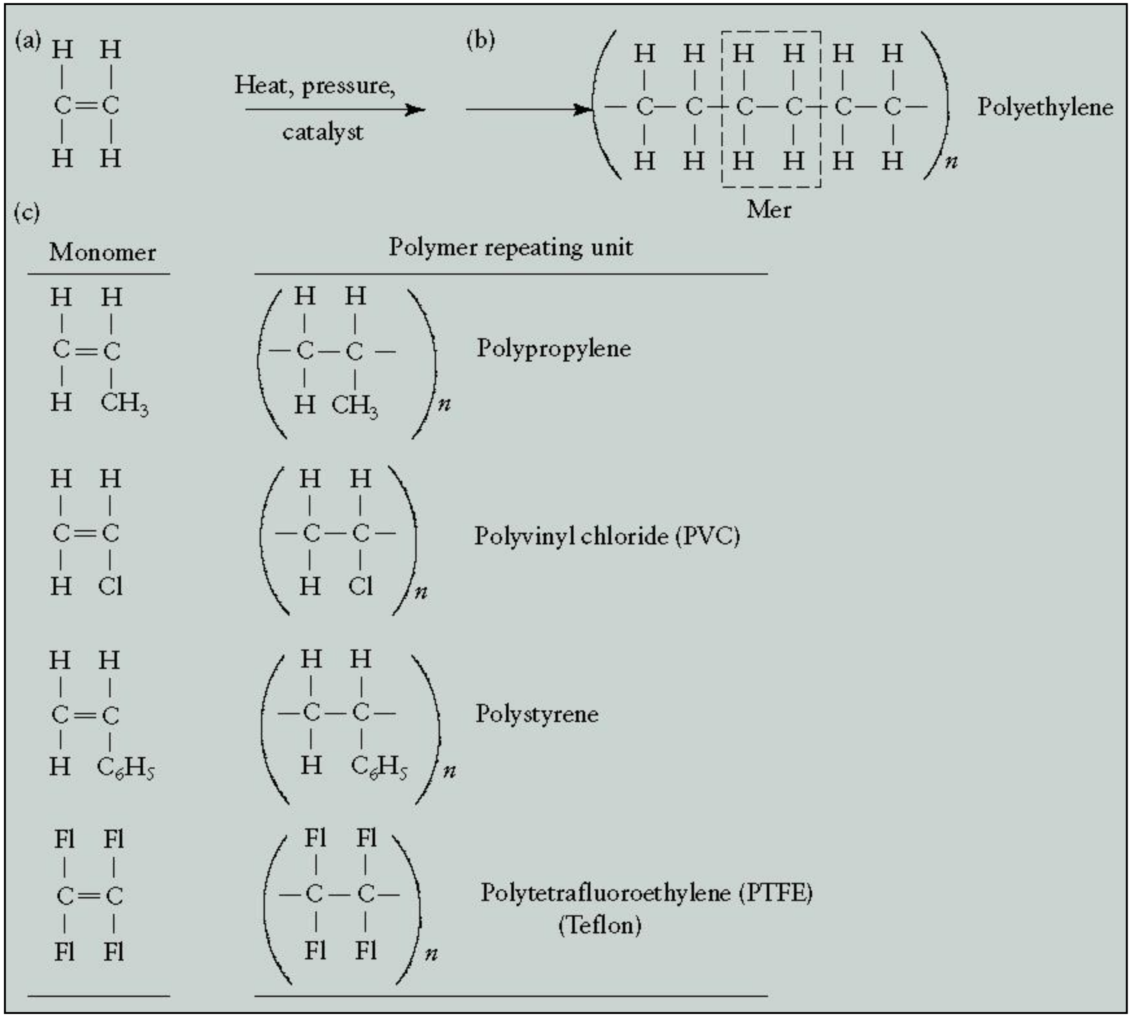
Glass Transition and Melting Temperatures

Glass-transition and melting temperatures of some polymers.

MATERIAL	T_g (°C)	T_m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene		
High density	-90	137
Low density	-110	115
Polymethylmethacrylate	105	-
Polypropylene	-14	176
Polystyrene	100	239
Polytetrafluoroethylene	-90	327
(Teflon)	87	212
Polyvinyl chloride	-73	-
Rubber		

1. INTRODUCTION

Polymer structures and molecules



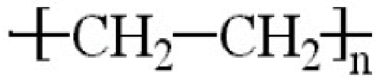
Basic structure of polymer molecules: (a) ethylene molecule; (b) polyethylene, a linear chain of many ethylene molecules; (c) molecular structure of various polymers. These molecules are examples of the basic building blocks for plastics.

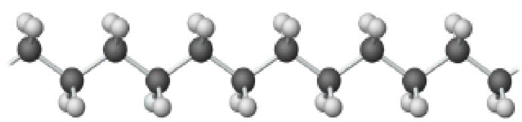
1. INTRODUCTION

Polymer Molecules

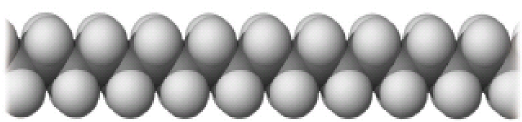
Polyethylene (PE)

- trash bags, electrical insulation
- thermoplastic





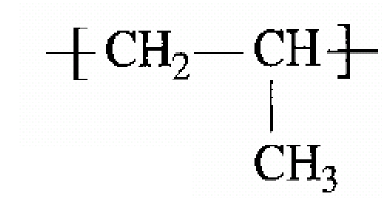
Ball-and-stick model

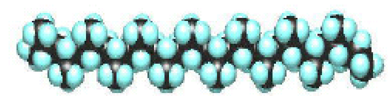


Space-filling model

Polypropylene (PP)

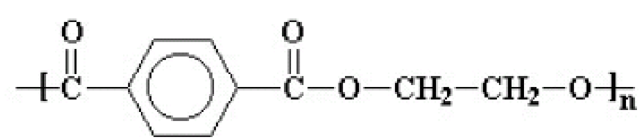
- margarine tubs, food containers
- thermoplastic





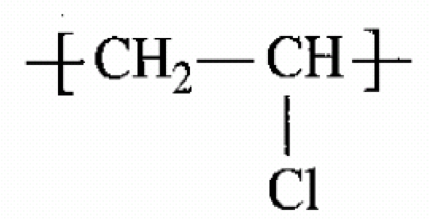
Polyester (PET)

- bottles
- carpets
- thermoplastic



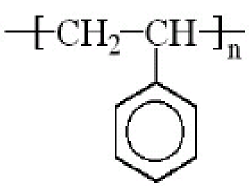
Polyvinylchloride (PVC)

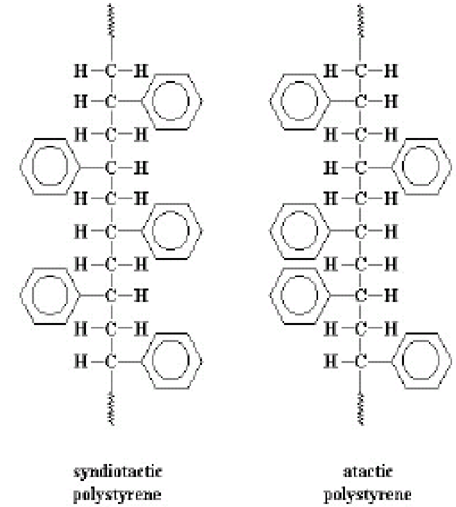
- credit cards
- pipes
- thermoplastic



Polystyrene (PS)

- coffee cups (styrofoam)
- clear plastic boxes
- thermoplastic

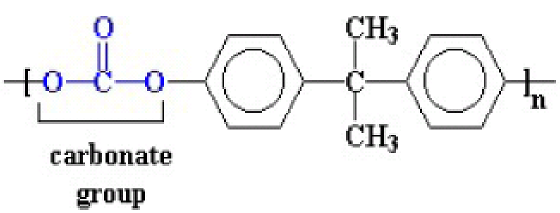




Syndiotactic polystyrene has a regular structure, so it can pack into crystal structures. The irregular atactic polystyrene can't.

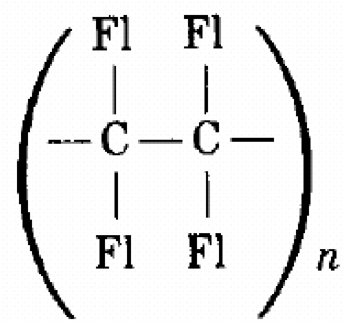
Polycarbonate (PC)

- Lexan
- thermoplastic



Polytetrafluroethylene (PTFE)

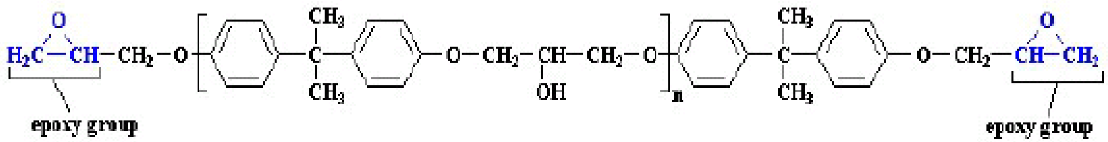
- Teflon
- bearings
- coatings
- thermoplastic



1. INTRODUCTION

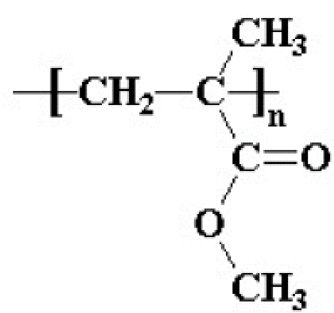
Epoxy

- adhesive
- composite matrix
- thermoset



Polymethylmethacrylate (PMMA)

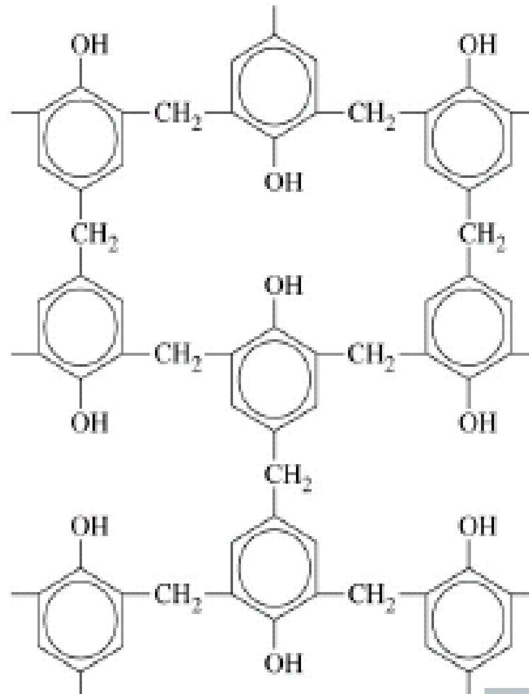
- Lucite, plexiglas
- thermoplastic



1. INTRODUCTION

Bakelite

- Leo Baekeland
  - 1863–1944
  - first synthetic polymer (1907)
  - made from phenol and formaldehyde

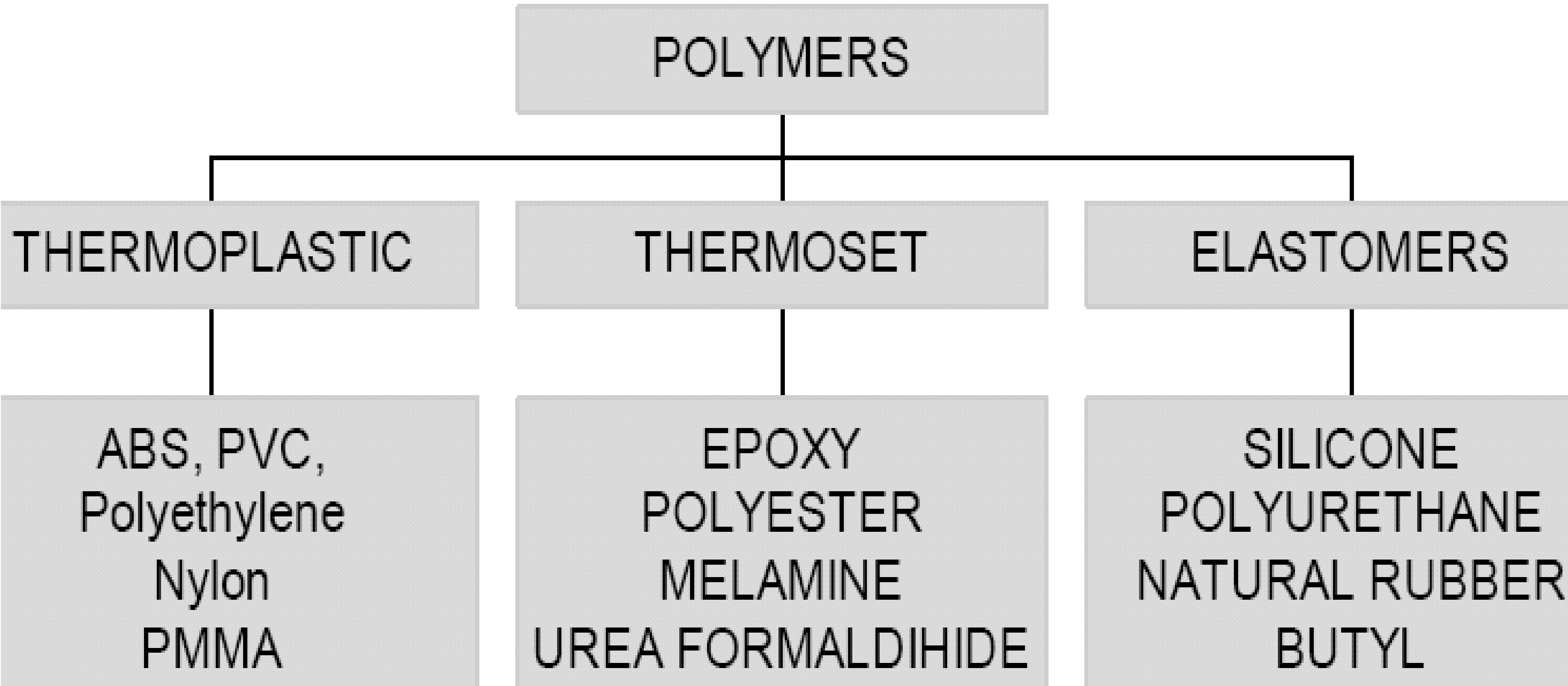


2. POLYMER CLASSIFICATION

There are many ways in which polymer properties or behavior are classified to make general descriptions and understanding easier. Some common classifications are:

- Thermoplastic vs thermoset
- Amorphous vs crystalline
- Addition vs condensation
- Commodity, engineering, high performance

2. POLYMER CLASSIFICATION



2. Classification of polymers

Thermoplastic vs. Thermoset:

Thermoplastics can be heated and formed, then re-heated and re-formed repeatedly. The shape of the polymer molecules is *generally linear*, or *slightly branched*, allowing them to flow under pressure when heated above the effective melting point.

Thermosets undergo a chemical as well as a phase change when they are heated. Their molecules form a *three- dimensional cross-linked network*. Once they are heated and formed they *can not be reprocessed* - the three- dimensional molecules can not be made to flow under pressure when heated.

Thermoplastics are branched chain polymers which are obtained by addition or condensation polymerization.

These polymers may be softened, hardened and resoftened by application of heat. This method of heating and cooling is used in the re-shaping of these polymers and makes them easily re-cyclable.

Some common thermoplastics are:

- polyethylene
- polypropylene
- polyvinyl chloride (PVC)
- polystyrene
- cellulose
- nylon

Characteristics of Thermoplastic Polymers

- Anisotropic
- Soften and melt upon heating
- Ductile
- High fracture energy
- More easily repaired than thermosets
- Good environmental resistance
- High melt viscosities
- No chemistry during fabrication
- Potential for recycling
- Indefinite shelf life

Thermosets belong to the three dimensional cross-linked or network polymers, making them stronger and harder than the linearly structured thermoplastics.

Thermosets are usually products of condensation polymerization and will undergo setting and hardening on heating and cooling.

However, unlike thermoplastics, once they have been set and hardened, they cannot be reproduced.

This is mostly due to the loss of part of the molecule (the by-product in the condensation reaction).

Common thermosetting materials include polyesters, epoxies, polyurethanes, phenol-formaldehyde, and melamine-formaldehyde.

Characteristics of Thermosetting Polymers

- Isotropic
- Do not melt upon heating
- Decreased stiffness at high temperatures
- Brittle (though yield in compression)
- Low fracture energy
- Sensitive to damage
- Environmentally stable
- Low viscosity before setting
- Limited shelf life

Amorphous vs Crystalline:

- Polymers with nearly linear structure, which have simple backbones, tend to be flexible and fold up to form very tightly packed and ordered areas called crystals.
- Crystalline polymers include: polyethylene, polypropylene, acetals, nylons, most thermoplastic polyesters, and in some cases polyvinyl chloride.
- Crystalline polymers have higher shrinkage, are generally opaque or translucent, good to excellent chemical resistance, low friction, good to excellent wear resistance.

Amorphous vs Crystalline:

- Polymers with bulkier molecular chains or large branches or functional groups tend to be stiffer and will not fold up tight enough to form crystals. These polymers are referred to as "amorphous" and include: polystyrene, polycarbonate, acrylic, ABS, and polysulfone.
- Amorphous polymers have low shrinkage, good transparency, gradual softening when heated (no melting point), average to poor chemical resistance, high friction, and average to low wear resistance.

Addition vs. Condensation:

Polymers such as nylons, acetals, and polyesters are made by condensation or step-reaction polymerization where small molecules (monomers) of two different chemicals combine to form chains of alternating chemical groups. The length of molecules is determined by the number of active chain ends available to react with more monomer or the active ends of other molecules.

Polymers such as polyethylene, polystyrene, acrylic, and polyvinyl chloride are made by addition or chain-reaction polymerization where only one monomer species is used. The reaction is begun by an initiator which activates monomer molecules by the breaking a double bond between atoms and creating two bonding sites. These sites quickly react with sites on two other monomer molecules and so on. This continues until the **initiator** is used up and the reaction stops. The length of molecules is determined by the number of monomer molecules which can attach to a chain before the initiator is consumed and all molecules with initated bonding sites have reacted.

Commodity, Engineering, High Performance:

- **Commodity polymers** have relatively *low physical properties*. They are used for consumer products which require low cost, disposability, packaging or container related, low stress and *low temperature resistance*, limited product life, and high volume production. (e.g. PE, PS, PP)

- **Engineering polymers** have properties towards the *high end* of the spectrum. ***Strength and thermal resistance are the most significant***. Their price may range from two to ten times as much as a commodity polymer.
- They are used in: housings, brackets, load bearing members, machine enclosures, and applications requiring wear resistance, long life expectancy, flame resistance, and the ability to endure cyclic stress loading. (e.g. PC, POM, PBT)

Polyoxymethylene POM

polybutylene terephthalate (pbt)

Polycarbonates (PC)

- The properties of **high performance polymers** are at the highest end of the spectrum, generally with very *high strength and thermal resistance*. They tend to be very expensive, priced above most engineering polymers.
- They are used in high temperature, high stress applications, in harsh environments, and low to medium volume production. (e.g. PEEK, PEI, LCP)


Polyether ether ketone (PEEK)


Liquid-crystal polymers (LCPs)

3. Properties of Polymers

- Polymers are characterized in many ways –
  - by chemical or physical structure,
  - by strength or thermal performance,
  - by optical or electrical properties,
  - etc.
- Most textbooks will give qualitative and some quantitative data on polymer properties.

- Properties can vary widely however, between manufacturers, for different performance grades, due to additives and reinforcements, or other reasons.
- For more precise data, contact a representative from a polymer producer, compounder, or distributor for a spec sheet on a particular material and grade.
- Often grades are offered to suit the needs of specific types of applications.

Properties of Polymers

MATERIAL	UTS (MPa)	*E* (GPa)	ELONGATION IN 50 mm (%)	POISSON's RATIO (ν)
ABS	28-55	1.4-2.8	75-5	-
ABS (reinforced)	100	7.5	-	0.35
Acetals	55-70	1.4-3.5	75-25	-
Acetals (reinforced)	135	10	-	0.35-0.40
Acrylics	40-75	1.4-3.5	50-5	-
Cellulosics	10-48	0.4-1.4	100-5	-
Epoxies	35-140	3.5-17	10-1	-
Epoxies (reinforced)	70-1400	21-52	4-2	-
Fluorocarbons	7-48	0.7-2	300-100	0.46-0.48
Nylon	55-83	1.4-2.8	200-60	0.32-0.40
Nylon (reinforced)	70-210	2-10	10-1	-
Phenolics	28-70	2.8-21	2-0	-
Polycarbonates	55-70	2.5-3	125-10	0.38
Polycarbonates (reinforced)	110	6	6-4	-
Polyesters	55	2	300-5	0.38
Polyesters (reinforced)	110-160	8.3-12	3-1	-
Polyethylenes	7-40	0.1-0.14	1000-15	0.46
Polypropylenes	20-35	0.7-1.2	500-10	-
Polypropylenes (reinforced)	40-100	3.6-6	4-2	-
Polystyrenes	14-83	1.4-4	60-1	0.35
Polyvinyl chloride	7-55	0.014-4	450-40	-

Approximate range of mechanical properties for various engineering plastics at room temperature.

Processing Methods for Polymers

There are **many** processing methods for polymers. Commercial processing equipment can range from a few thousand dollars to many millions of dollars.

In addition to the equipment itself, tooling is generally required to make a particular shape.

Molding

- Compression Molding
- Transfer Molding
- Injection Molding
- Gas Assisted Injection Molding (GAIN)
- Reaction Injection Molding (RIM/SRIM)
- Injection/Compression Molding

- Blow Molding
- Extrusion Blow Molding
- Injection Blow Molding
- Injection Stretch Blow Molding
- Rotational Molding

Extrusion

- Rod, Pipe, Sheet, Profile Extrusion
- Coextrusion
- Extruded/Blown Film
- Extruded Foam
- Pultrusion

Casting

- Cast Film
- Cast Shape
- Vacuum Casting
- Lay-Up

Forming

- Vacuum forming
- Thermoforming
- Pressure Forming

Coating

- Powder Coating
- Dispersion Coating
- Extrusion Coating and Laminating
- Spray Coating
- Dip Coating

Calendaring

Types of polymers

Polymers are commonly refered to by both their names and abbreviations. Commercial polymers are also frequently refered to by the trade names of their manufacturer.

ABS - acrylonitrile-butadiene-styrene terpolymer
BMC - thermoset polyester bulk molding compound
EVA - ethylene-vinyl acetate copolymer
LCP - liquid crystal polymer
PA - polyamide, commonly called nylon
PAN - polyacrylonitrile
PAS - polyarylsulfone
PBD - polybutadine
PBT - polybuylene terephthalate

Types of polymers

PC - polycarbonate
PE - polyethylene see also:
HDPE - high density PE
LDPE - low density PE
LLDPE - linear low density PE
VLDPE - very low density PE
HMW-HDPE - high molecular weight HDPE
UHMWPE - ultrahigh-molecular-weight polyethylene
PEEK - polyetheretherketone
PEK - polyetherketone
PEI - polyetherimide
PES - polyethersulfone
PET - polyethylene terephthalate

Types of polymers

PET-G - glycol modified PET
PI - polyisoprene
PS-b-PI - polystyrene/polyisoprene block copolymer
PI - polyimide
PK - polyketone
PMMA - polymethyl methacrylate, commonly called acrylic
PMP - polymethylpentene
POM - polyoxymethylene, commonly called acetal
PP - polypropylene

PPA -	polyphthalamide
PPO/PPE -	polyphenylene oxide, polyphenylene ether
PPS -	polyphenylene sulfide
PS -	polystyrene
EPS -	expanded polystyrene
HIPS -	high impact polystyrene
PSO,PSU -	polysulfone
PTFE -	polytetrefluoroethylene
PU,PUR -	polyurethane
PVA -	polyvinyl alcohol
PVAc -	polyvinyl acetate
PVC -	polyvinylchloride, commonly refered to as vinyl

Why are polymers good?

- Light weight
- High corrosion resistance
- Strong. Emerging as structural polymers (T<150-250C).
- Electrical insulation
- Can be coloured
- Easily formed into complex, 3D shapes
- No further machining necessary
- Available in different opacity
- Good damping property
- Sales of plastics, on a volume basis, has grown more than double the steel production in the U.S.

General Requirements for Plastics Product

DESIGN REQUIREMENT	TYPICAL APPLICATIONS	PLASTICS
Mechanical strength	Gears, cams, rollers, valves, fan blades, impellers, pistons.	Acetals, nylon, phenolics, polycarbonates, polyesters, polypropylenes, epoxies, polyimides.
Wear resistance	Gears, wear strips and liners, bearings, bushings, roller-skate wheels.	Acetals, nylon, phenolics, polyimides, polyurethane, ultrahigh-molecular-weight polyethylene.
Frictional properties		
High	Tires, nonskid surfaces, footware, flooring	Elastomers, rubbers
Low	Sliding surfaces, artificial joints.	Fluorocarbons, polyesters, polyimides
Electrical resistance	All types of electrical components and equipment, appliances, electrical fixtures.	Polymethylmethacrylate, ABS, fluorocarbons, nylon, polycarbonate, polyester, polypropylenes, ureas, phenolics, silicones, rubbers.
Chemical resistance	Containers for chemicals, laboratory equipment, components for chemical industry, food and beverage containers.	Acetals, ABS, epoxies, polymethylmethacrylate, fluorocarbons, nylon, polycarbonate, polyester, polypropylene, ureas, silicones.

DESIGN REQUIREMENT	TYPICAL APPLICATIONS	PLASTICS
Heat resistance	Appliances, cookware electrical components	Fluorocarbons, polyimides, silicones, acetals, polysulfones, phenolics, epoxies.
Functional and decorative	Handles, knobs, camera and battery cases, trim moldings, pipe fittings.	ABS, acrylics, cellulosics, phenolics, polyethylenes, polpropylenes, polystyrenes, polyvinyl chloride.
Functional and transparent	Lenses, goggles, safety glazing, signs, food-processing equipment, laboratory hardware.	Acrylics, polycarbonates, polystyrenes, polysulfones.
Housings and hollow shapes	Power tools, housings, sport helmets, telephone cases.	ABS, cellulosics, phenolics, polycarbonates, polyethylenes, polypropylene, polystyrenes.