# Polyethylene (PE)

It is simply consist of -CH<sub>2</sub> CH<sub>2</sub>- as repeating unit. The most common type of chain growth polymerization is free radical addition. PE is widly used in our society as a thin film for packaging or water bottles. There are two main types of PE, high density polyethylene (HDPE) and low density polyethylene (LDPE). HDPE is harder and stronger than LDPE, so it is used for gas tanks, heavy duty pipes, cabinets and so on. LDPE is much softer and usually transparent.

$$O \stackrel{\bullet}{-}O \stackrel{\bullet}{+} H - CH_3 \longrightarrow CH_3^* + HO - O \stackrel{\bullet}{-}CH_2^* \longrightarrow H_3C \longrightarrow CH_2^* \qquad Initiation reactions$$

$$CH_3^* + H_2C \longrightarrow CH_2 \longrightarrow H_3C \longrightarrow CH_2 \longrightarrow H_3C \longrightarrow CH_2^* \longrightarrow CH_2^*$$

LDPE was prepared in special reactors (autoclaves) at high pressure (1000-3000 atm) and  $80-300^{\circ}\text{C}$  by using peroxides as an initiator. At these conditions (6-8%) of the ethylene monomer (gas phase) converts to polyethylene. The unreacted is recycled again to the reactor.

HDPE was prepared by using Ziegler- Natta catalyst (coordination polymerization) at normal temperature of about 57-77°C in inactive organic solvent.

HDPE molecules are able to pack together closely, which leads to higher density, whereby their chains are almost linear and regular. LDPE molecules have side chains with different lengths because it was free radical polymerized.

It was found for each 50 carbon atoms in the main chin there are a side formed by chin transfer in the same molecule.



HDPE molecules able to arrange themselves in very close proximity

In contrast another types of PE according to their density can be found as:

### Very low density polyethylene (VLDPE):

has density range between (0.88-0.915~g/~ml.), while the density of LDPE is between (0.915-0.95g/ml). it has high amount of short chain branching made by copolymerization of ethylene with some olefins like 1-butene, 1-hexene and 1-octene.

#### **Linear low density polyethylene (LLPE)**

LLDPE can be produced with less than 300 psi and at about 100°C. It has a density from 0.915 to 0.925 g/mL. It is actually a copolymer of ethylene with about 8%–10% of an alpha-olefin such as 1-butene, 1-pentene, 1-hexene, or 1-octene. Through control of the nature and amount of alpha-olefin, we are able to produce materials with densities and properties between those of LDPE

and HDPE. LLDPE does not contain the long branches found in LDPE. Because of its toughness, transparency, and flexibility, it is used in film applications as packaging for cables, toys, pipes, and plastic streamers and containers.

### <u>Ultrahigh molecular weight polyethylene</u>

It is HDPE with chain of 100,000 ethylene units. This cause a physical cross- links between the long chain known as (( **inter- tangle**)) led to increase the mechanical properties and have high resistance to corrosion and radiation.

#### **Cross- liked polyethylene (PEX or XLPE):**

It is a medium to HDPE that contains cross-links to yield a thermoset material. The cross-linking causes a reduced flow and permeability and increase chemical resistance, so this material was used in some water pumping systems.

# Polypropylene

It is a type of the most produced polymers. It is quite similar to PE in the structure and in uses. It was used as plastics and fiber, it has high melt temperature, so it can be used in dishwasher-safe containers. The presence of CH<sub>3</sub> bonded to ethylene make the resulting free radical polymer as an a tactic polymer and random type of regularity as well as low molecular weight polymer because the CH<sub>3</sub> group can terminate the chain by chain transfer to it.

the most suitable polymerization method is by using coordination polymerization (Ziegler – Natta).

### Poly(vinyl chloride) PVC

The polymer is prepared by using free radical suspension polymerization (Batch techniques) at pressure of 9 atm. And temperature of 53°C. The gas vinyl chloride convert to liquid and continue the reaction until conversion of about 85%. The resulted polymer was isolated by using centrifuge and the unreacted monomer is recycled.

Using emulsion polymerization when the needed polymer is used in this phase.

The polymer PVC is stiff material, it can be formulated as a highly flexible material by adding material called plasticizers.

#### **Polystyrene**

It was known as Styrofoam which is the porous polystyrene.

Polystyrene was prepared by using bulk or suspension polymerization (free radical). It was a very brittle polymer, the development is by mixing the monomer with 5-10% butadiene rubber, then polymerized the styrene to get (**High impact polystyrene**).

The styrene can be copolymerized with other monomers to get new copolymer with new characteristics.

Styrene – butadiene rubber (SBR): resulted by copolymerization of styrene with butadiene. The SBR contain 25% styrene . the method of preparing is suspension method at  $50^{\circ}$ C by using potassium persulfate as an initiator , so the copolymer called (**Hot rubber**). In contrast by using redox initiators at low temperature was used to yield another type of SBR called (**cold rubber**).

Nitrile rubber is a copolymer of styrene with butadiene and acrylonitrile, it was called (Acrylonitrile butadiene styrene rubber ABS). this rubber can resist the petroleum products, so it was used in storage tank and pipes for gasoline.

Emulsion polymerization method was used in preparing ABS. when acrylonitrile have 18% ratio, the copolymer have moderate resistance to oil when the ratio reached 40% the copolymer have high resistance to oil.

#### Poly(methyl methacrylate)

Known as the organic glass or prespex, because their films are transparent and hard, it was replaced the glass in many uses (laboratories, vehicles,....) and also in adhesive and paint industries.

Bulk polymerization method was used in preparing a film like glass of this polymer in presence of free radical initiator.

#### Poly(tetrafluoro ethylene)

Known as Teflon, have high thermal and chemical resistance and high electrical insulator.

Tetrafluoro ethylene monomer was polymerized by bubbling in water contain soluble initiator like ammonium persulphate at 40-80<sup>o</sup>C and 3-30atm.

### **Polymer processing**

It is the process whereby the raw materials are converted into products of desired shape and properties, thermoplastics are supplied as billets, marbels, or chips of a varying sizes and may contain some desired additives. When heated above Tg they soften and flow under pressure as viscous liquid that can be shaped to desired product.

Thermosetting are normally supplied as meltable or flowable prepolymer, oligomer or non-crosslinked polymers.

Polymer processing operations can be divided into the following broad categories:

- spinning (generally for fiber) - calendaring - coating - molding

#### Spinning:

It was the fiber technology. the polymer must shaped as filament or yarn. The dimensions of the filament are expressed in terms of a unit called ((tex)), which is of the fineness or linear density.

1 tex= 1g/1000m or  $10^{-6}kg/m$ .

Or using another unit as ((denier))

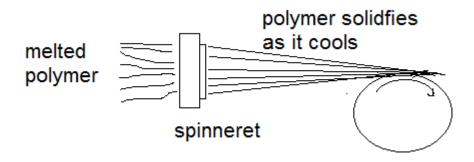
1 denier= 1g/9000m, 1denier= 0.1111 tex.

Three spinning processes are generally employed:

- melt spinning – dry spinning – wet spinning.

In melt spinning, the polymer is melted or extruded and pumped through a die having one or more holes. The die is called spinneret. The number and the shape of the holes are different. The number is from several to thousand holes. Shape of the holes is usually circular giving round fibers. The fiber stretching encourage the polymer chains to aline on a molecular level producing increased strength in the direction of the pull.

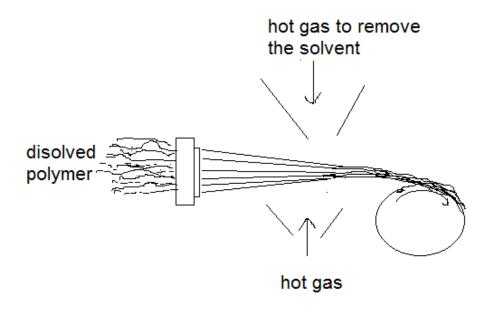
the polymers as chips or any shapes are heated forming melted polymer. In order to minimize the oxidation of this polymer, it was blanketed by inert gas.



#### **Dry spinning**

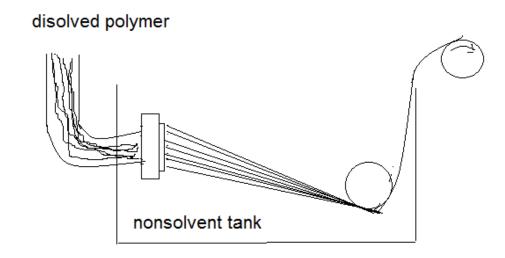
The used polymer is as a solution of 20 -40% concentration. The solution is filtered through a spinneret into a spinning cabinat through which

heated air is passed to dry the filament. For economical reasons, air is used as a hot gas and in sometimes nitrogen and superheated water are used.



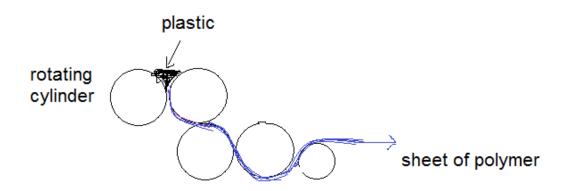
#### Wet spinning

It was the slowest spinning process. The used equipment in wet process is similar to that used in dry spinning but not necessary to heat the solution of the polymer to high temperature. The spinnerets are in tanks containing the non – solvent whereby the fiber are formed from the coagulation of the polymer solution by the active of the non- solvent. The holes in the spinneret are forced to be closer together allowing productivity to be increased.



#### **Calendaring**

This process is used to form films and sheets of thermoplastic polymers. The procedure include pressing the pellets or the thick plates of the polymer between a hot rotating cylinders. In order to get a thin films, many cylinders are used, also some pigments are used to color the sheets.



## **Coating**

This process was used to coat any surface body (metals, wood,......) with a thin layer of polymer to isolate it from the surrounding. The method include using solution of the polymer as a molten or solution or

suspended of the polymer. There are many methods can be used in coating as:

i- spray coating: spraying the dilute polymeric solution by using sprayer on the body many times until get the suitable layer of polymer after the solvent vaporized.

ii- dip coating: The body was dipped in the molten or emulsion polymer. The thickness of the layer can be increased by increasing the number of dipping.

iii- painting coating: by using brush. The used polymer solution must have high viscosity.

#### **Molding**

It is a general technique that can be used with plastics and thermosetting materials. There are many techniques methods of molding according to the wanted product and type of the polymer.

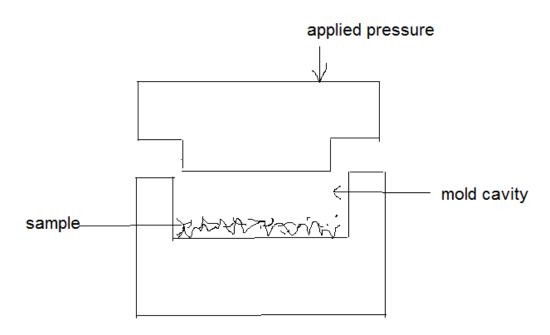
#### 1) Molding by casting:

it was in making special shapes of polymer, sheets, tubes and rods from thermoplastic and thermoset polymers. In this method, the polymer or the pre polymer is heated to fluid, poured into a mold, cured at a specific temperature and removed from the mold. Sheets and films can be done on a wheel or conveyor belt, whereby the polymer is spread to the desired thickness onto the conveyor belt as the temperature increased. The films is dried and then stripped off.

#### 2) compression molding:

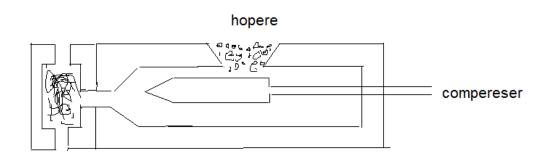
The thermoplastic or pre thermoset materials are heated sufficiently to soften and flow it to inter the mold cavity. The soften material is hold against the mold by pressure. The thermoset material is cooled below the

Tg to taking the shape, while the thermoset is held until the cross-linking occurs and locking in the shape.



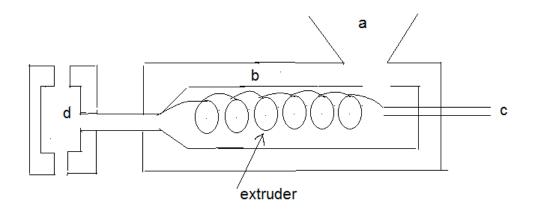
#### 3- injection molding:

A traditional injection apparatus consist of a hopper feed the molding powder to a heated cylinder. The molten material passes from a nozzle through a tapered sprue and a small gate into the cooled mold cavity. The polymer in the mold is easily broken off. A hydraulic press is used in the heated cylinder to push the polymer to the tapered.



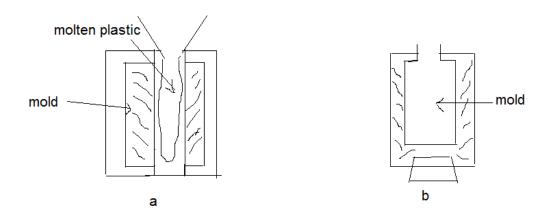
Now another technology is used (extruder). As in figure below, the hoper (a) feeds the molding powder to the heated cylinder (b) where the polymer is melted and forced by a reciprocating plunger(c) (or screw). The molten material moved toward the spreader into a cool, closed two —

piece mold (d). the cooled part is ejected when the mold opens and then the cycle is represent.



### 4-) Blow molding:

The molten polymeric material was extruded to a mold as a cylinder. The mold is blow with air to be cooled(a) and the material have the shape of the mold(b).



### 5- ) rotational molding:

'the mold (or cavity) is filled with a material, either a solid powder or a liquid. The mold is closed in a heated oven, and then rotate biaxially. The mold is then cooled, opened and the article recovered.

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