Chapter 19

● Polymer Processing

• Processing – to describe the technology of converting raw polymer, or compounds containing raw polymer, to articles of a desired shape.

(a) Molding

i) injection molding
ii) reaction injection molding (RIM)
iii) reinforced RIM (RRIM)
iv) compression molding

(b) Extrusion

i) single -screw extrusion
ii) twin -screw extrusion
-blow extrusion

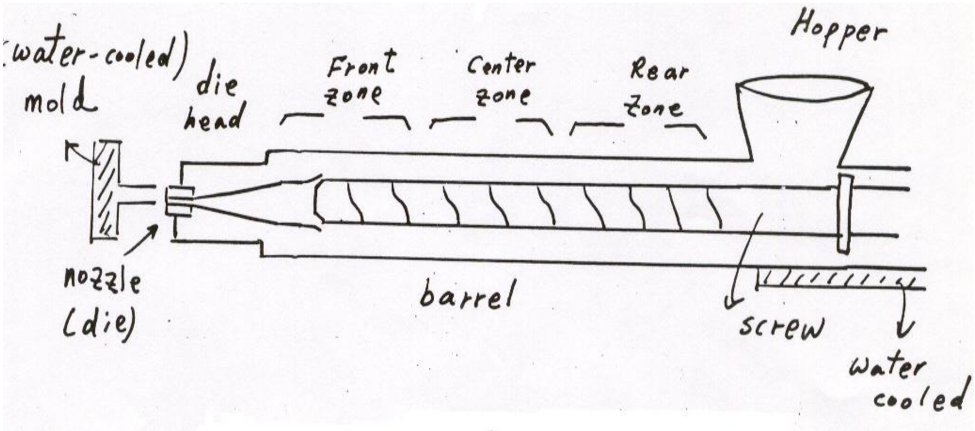
(c) blow molding

i) injection blow molding
ii) extrusion blow molding

(d) slush molding
(e) calendaring
(f) sheet forming
(g) stamping
(h) casting
(i) reinforced thermoset molding
(j) fiber spinning
(k) compounding

(a) molding

(i) injection molding



- 사용처 - TV cabinets, furniture, etc.
- Typical cycle time – (1/4~2min)
- used most of the thermoplastics
- for thermoset – polymer solidify through the curing(crosslinking) reaction.

The compound must be heated just enough in the barrel to achieve fluidity and injected into the mold before it begins to cure. Requires precise control of temp and cycle timing.

(ii) reaction injection molding (RIM) or liquid injection molding (LIM)

- a process developed recently to mold large polyurethane directly from the starting chemicals.

- the mixed stream begins to react as it flow into the mold, where the polymerization reaction is complete.

(ex) highly reactive polyol and isocyanate.

- initial mold temp = 150℃
- pressure to fill large molds = 100psi
- the streams are pumped through nozzles in a mixing head = 2500 psi

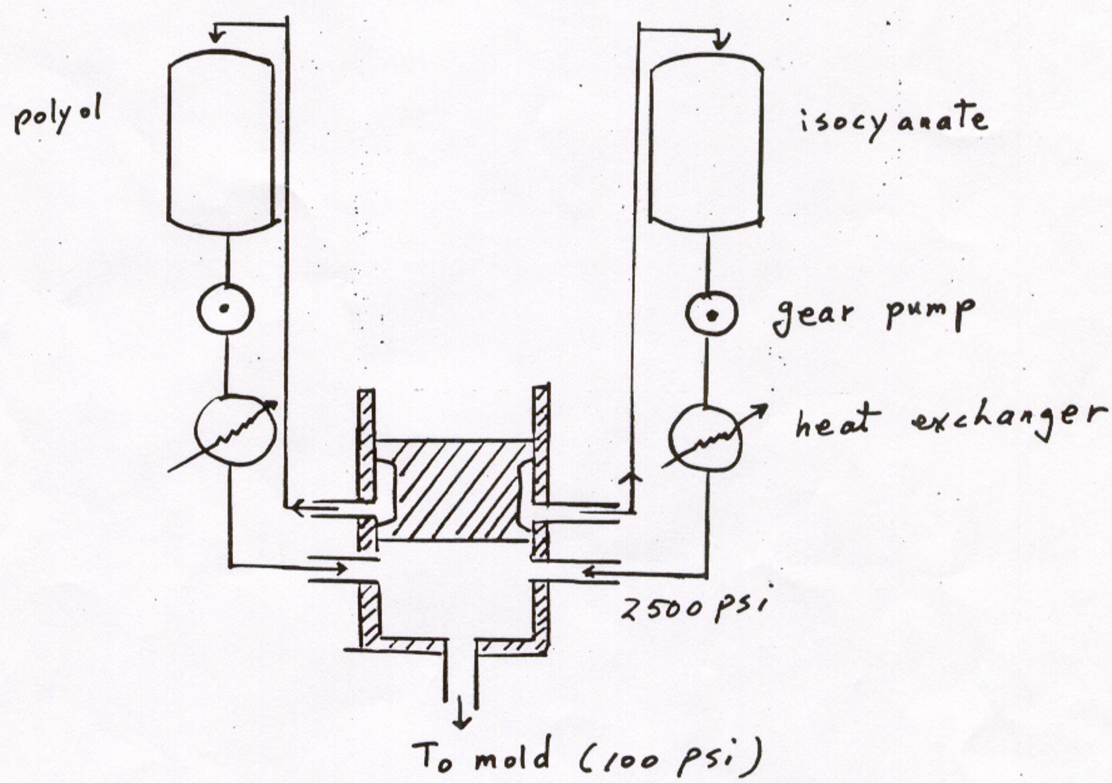


Fig. Reaction Injection Molding (RIM)

- the polyurethane may be formulated - flexible or rigid, solid or foamed
- 용도 : energy -absorbing front and rear panels for automobiles.
- cycle times – 2min, a mold -release agent needed.

(iii) Reinforced RIM

-reinforced materials , in which short reinforcing fiber are incorporated in one or both of the reactants.

(iv) compression molding

- this process is used for

1. thermosetting polymers
2. large thermoplastic pieces

3. ultra high molecular weight P.E
4. Teflon (Tetra fluoro ethylene)
5. Disc. Lenses – dimensional stability를 요구하는 경우.
6. filled resin –
   i) iron - filled phenolics
   ii) wood -flour filled urea -formaldehyde
   iii) α -cellulose filled melamine
   iv) unsaturated polyester

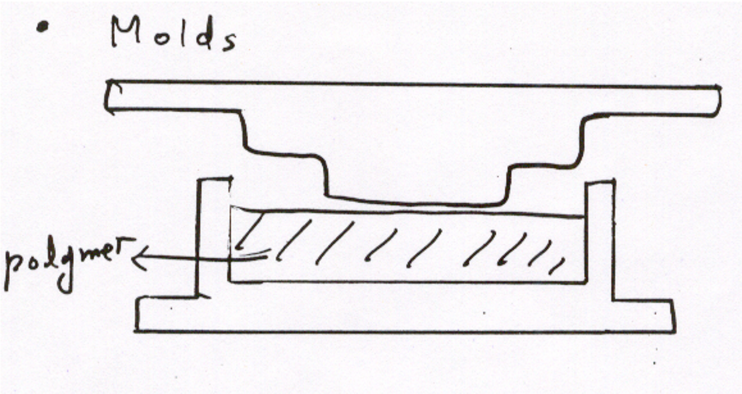
• advantages :

1. material flow is short
- residual stress 가 감소 : dimensional stability
2. simple mold – cheap
3. excessive shearing is avoided
- minimizing the mechanical property loss
- mold wear 가 적다.

• disadvantages :

1. shearing 이 작기 때문에 inhomogeneous하다.
2. curing 이 time dependent 하기 때문에 polymer 성형품의 thickness 가 크면 (>3/8 inch) uneven curing이 되기 쉽다.
3. preheating(mold) 때문에 long cycle time 이 필요 : need 1 min for 1/8 inch thickness.

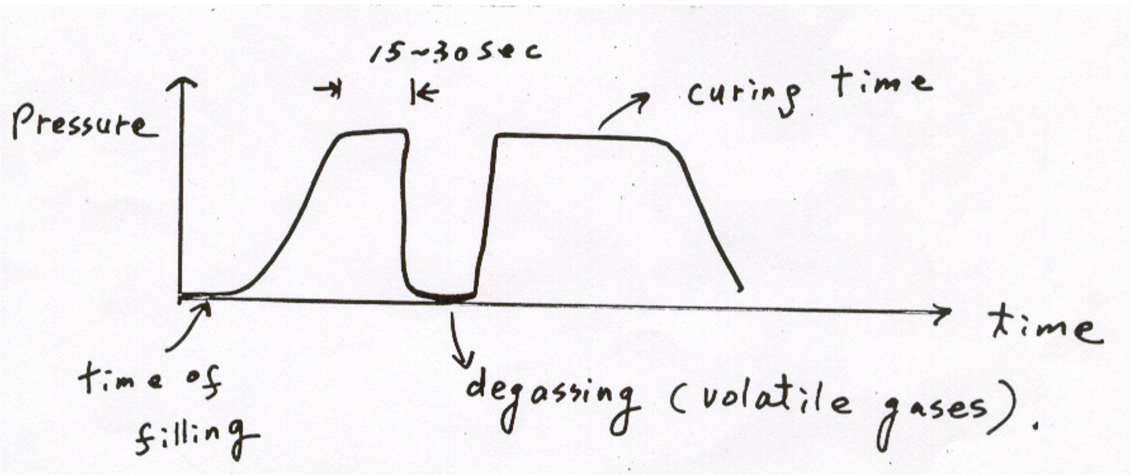
• Molds



-least expensive
-used for shallow part
-cure가 되면 부피가 감소(≅10%)

• Molding temp:

- urea -formaldehyde 140~150℃
- melamine -formaldehyde 140~165℃
- phenolic - formaldehyde 145~180℃



• curing time:

1. temperature, pressure,resin의 종류
2. thickness
3. preheating time 에 따라 달라진다.

보통30~60 sec/mm thickness

4. if curing time is insufficient :
   단단하지 못하고 mold에 붙는다.(adhere)흠이 생긴다.
5. if curing time is excessive color change(보통 검게 나타남)
   crazing brittleness.

- molding 가증한 점도: $5*10^8$ poise (phenolic, amino plaste)

이때의 압력은 20~40 Mpa – additive에 따라 pressure도 달라짐.

- flate part 를 만드는 pressure : 2000~4000 psi

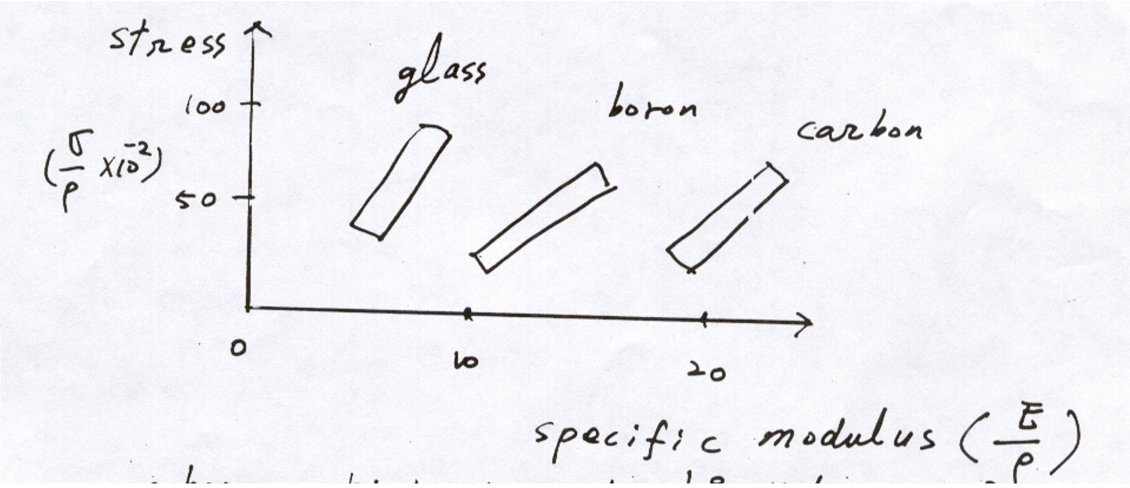
(ex) dish in 10 inch diameter :

$$\frac{2500\,psi \times 5^2 (3.14) in^2}{2000 lb / ton} \cong 100 ton$$

- press :
  a) mechanical press
  b) hydrolic press (100 ton 이상인 용량에 사용)

- press 선정요건 :
  a) height between two plates
  b) effective surface
  c) working pressure(50~1000 ton)
  d) cost

- Fiber for reinforcement:
  - glass, carbon -fiber, boron



• boron : high temp 에 사용 (ϕ =100μm)

● The material to be molded with additives.
- additive 가 없으면 brittle, low impact
• filler –
1) wood flour (≅ ϕ =100μm)
2) cotton fabrics : impact resist 증가
3) silica,$CaCO_3$
4) glass, carbon fiber,boron

● Fiber reinforced plastics (FRP)
- adhesion between fiber and resin 이 중요
most inorganics have hydrophilic surfaces, while the polymers are hydrophobic : coupling agents are intended to help overcome these difficulties (Silanes) – vinyl triethoxysilane ($H_2C{=}CH{-}Si(OC_2H_5)_3$)

Step 1. Hydrolysis :

$H_2C{=}CH{-}Si(OC_2H_5)_3 + 3H_2O \longrightarrow H_2C{=}CH{-}Si(OH)_3 + 3C_2H_5OH$

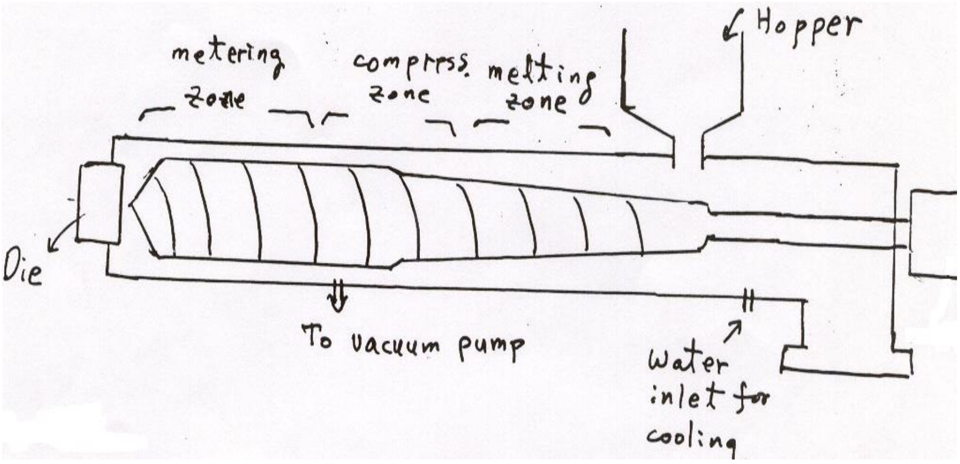
Step 2 Reaction with substrate :

$H_2C{=}CH{-}Si(OH)_3 + HO{-}▌ \longrightarrow H_2C{=}CH{-}Si(OH)_2O{-}▌ + H_2O$
(filler)

● Extrusion :

- thermoplastic items with a uniform cross-sectional area are formed by extrusion.

Products : pipe , hose and tubing, gaskets, wire and cable insulation, and sheeting, also for fiber.



←motor

Barrel

• melting zone : to convey the solid pellets forward from the hopper and convert them into molten polymer.

• compression zone : to compact and mix the molten polymer to provide a more or less homogeneous melt.

• metering zone : to provide melt to the die.

- Die swell or extrudate swell : recovering stored elastic energy.
- Melt fracture : roughness or irregular, severely distored extrudate. When extrusion rate is increased.

• To decrease melt fracture – by increasing die length, smoothly tapering the entrance to the decreasing die temperature.

•Extruder screw diameter – 1 inch to 1 foot

•Extruder의 length to diameter ratio (L/D) – 20/1 to 36/1

- Counter rotating twin-screw extruders – capable of generating the high pressure
- Corotating twin-screw extruders – for excellent mixing and a narrow residence time distribution used extensively in polymer compounding (mixing) operations.

- Blow Extrusion :

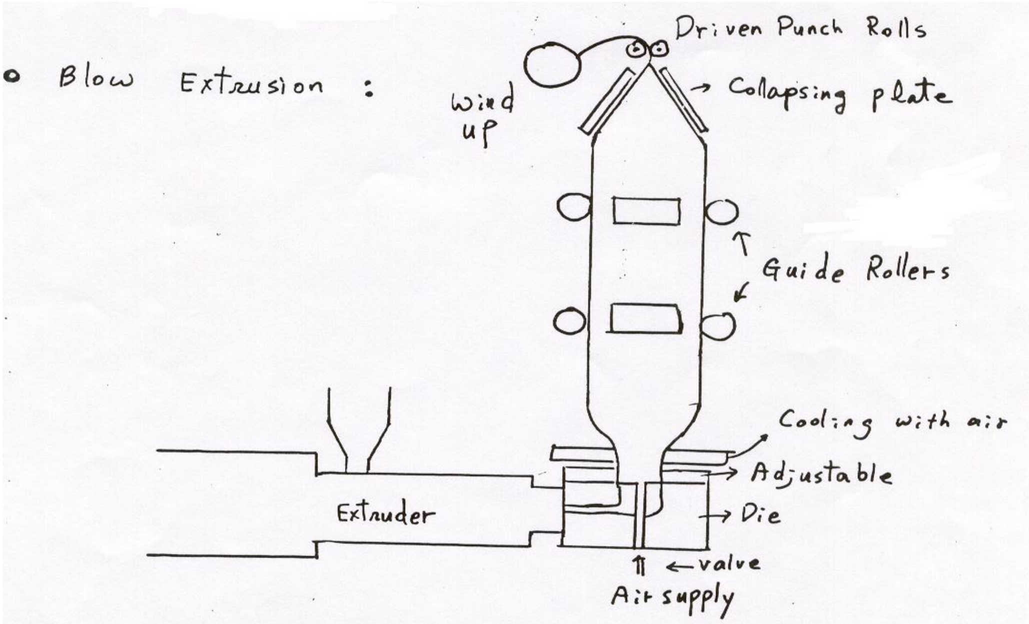


Fig. Blow Extrusion Film Line
(Modern Plastics Encyclopedia, McGraw-Hill)

- Blow Extrusion – most packing film is produced. A thin walled hollow cylinder is extruded vertically upward. Air is introduced to the interior of the cylinder, expanding it to a tube of film (0.01 inch thickness)

(ex) PE film

(EX) For LLDPE (Linear Low Density Polyethylene) at 410 ℉, 4.5 inch extruder feeds on 8 inch tubular film die to make 5 mil film (0.05mm) Head pressure is ≅ 5000 psi, this corresponds to $\dot{\gamma} \cong 670\ s^{-1}$.

Apparent shear rate $\longrightarrow$ $\dot{\gamma} = \frac{4Q}{\pi R^3}$

Where Q IS VOLUMETRIC FLOW RATE (cm^3/sec)

- LLDPE :

- (ethylene +high olefins) copolymerization.
- High pressure free radical process
- Cost down

(Advantages)

lower costs, good strength can be drawn to thin gauges.

(Disadvantages)

high melt viscosity (need high power) raising the melt temperature.

(용도) shopping bags, garbage bags.

-extruder 의 온도 : LLDPE(230℃)
LDPE(200℃)

- Conventional LDPE :

-provide strong stable melts but are generally limited in their abilities to yield thin gauge films.

- LLDPE + LDPE Blends :

- used to produce more stale films in tubular film extrusions.
- Film producers are forced with choices between a wide range of PE and their blends, as well as a variety of suggested modifications to the film extrusion process.

- Blow Molding : or extrusion blow molding.

- a hollow cylindrical tube or parison is extruded, the parison is then clamped between halves of a water -cooled mold.
  (ex) plastic bottles (coca -cola etc.)
- compressed air expands the parison against the inner mold surfaces, and when the part has cooled sufficiently, the mold opens, the part is ejected, and the mold is returned to grab another parison.

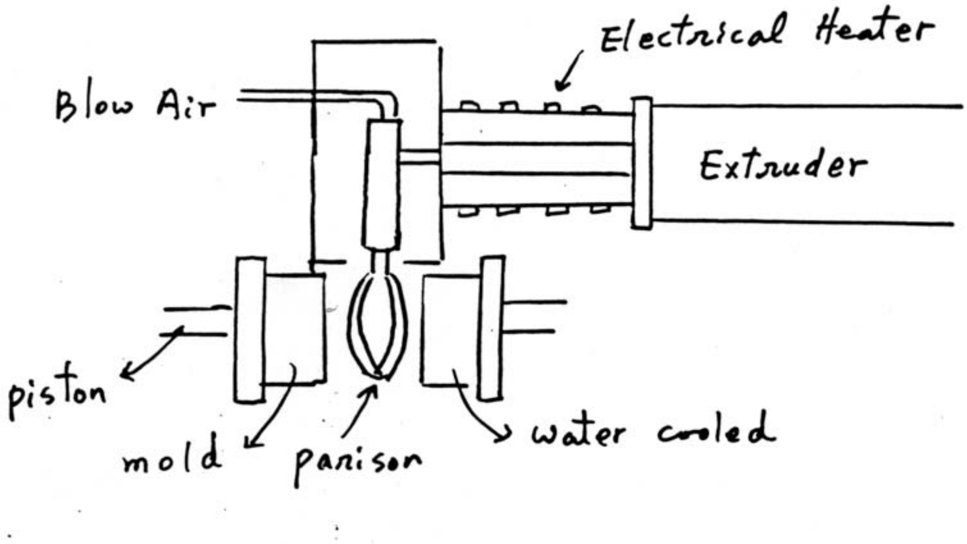


Fig. Extrusion Blow Molding.

(용도)bottle, big drums (55gals),vehicle part,
- offer light weight and great design flexibility

• Injection blow molding

- the parison is formed by injection molding, with the end closed and the threads molded on.

1st step : parisons (or preform) are injection molded and allowed to cool to room temp.

2nd step : reheated in a radiant -heat oven. Arod rapidly stretches the parison, orientating the polymer molecules in the axial direction.

3rd step : tangential orientation by blowing process. The resulting

biaxial orientation improves the toughness, creep resistance,clarity, and barrier property (resistance to permeation)
(ex) poly(ethylene terephthalate)(PET), soda -pop bottles.

• Rotational molding :

- used mainly of powdered plastics, polyethylene and nylons.
- A charge of powder is introduced to a heated mold, which is then rotated about two mutually perpendicular axes. This distributes the powder over the inner mold surfaces, where it fuses.

    1) rotational molding – requires of low molecular weight resin, because a low viscosity is needed to permit fusion of the powder.
    2) Blow molding – requires very high molecular weight linear polyethylene, to prevent excessive parison sag.

• Calendering :

polymer sheet (greater than 0.01 inch thickness) may be produced either by extrusion through thin film dies or by calendering.

- a calendaring consists of series of rotating heated rolls,between which the polymer compound (e.g. plasticized PVC) is squeezed into sheet form.
- Roll의 크기 (up to 3ft in diameter, 8ft in length)
- 용량(production) : up to 100yards/min.
  (e.g.) 장판, shower curtains. etc