Polymer Processing

![Graph showing the relationship between molecular weight and property](image)

- Commercial polymers
- Tensile and impact strength
- Viscosity

Molecular weight, degree of polymerization
Polymer Processing

Shaping Polymers
  Extrusion
  Molding
Fibers
Coatings
Manufacturing Processes

• Continuous products with uniform cross sections:
  – Extrusion: Pipes, wall-siding, door molding
  – Film blowing: Irrigation hose, grocery bags
  – Calendering (continuous rolling to achieve desired thickness): Shower curtain, table cloths

• Cavity filling:
  – Injection molding
  – Compression molding (thermosets): Utensil handles
  – Blow molding: bottles, containers

• Gradually deposited layers:
  – Dipping
  – Fluidized bed coating
Thermoplastics

Glassy or Semicrystalline Polymer → Heating → Melted or Softened Polymer

Solidification

Extrusion through dies: linear products
Molding: Complex shapes

Linear vinyl polymers, Nylons, polyesters, polyarylenes polyimides.
Thermosets

Liquid Monomer(s), Oligomeric Precursors, Thermoplastic with curable groups Elastomer  →  Chemical reaction  →  Glassy Thermoset or Vulcanized Elastomer

Molding: Complex shapes-vulcanizing elastomers
RIM: Mixing two monomers or precursors
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeating Unit</th>
<th>$T_s$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethylsiloxane</td>
<td>$-\text{OSi(CH}_3\text{)}_2-$</td>
<td>-127</td>
<td>-40</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>$-\text{CH}_2\text{CH}_2-$</td>
<td>-125</td>
<td>137</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
<td>$-\text{CH}_2\text{O}$</td>
<td>-82</td>
<td>181</td>
</tr>
<tr>
<td>Natural rubber</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(polyisoprene)</td>
<td>$-\text{CH}_2\text{C(CH}_3\text{)}=\text{CHCH}_2-$</td>
<td>-73</td>
<td>28</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>$-\text{CH}_2\text{C(CH}_3\text{)}_2-$</td>
<td>-73</td>
<td>44</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>$-\text{CH}_2\text{CH}_2\text{O}$</td>
<td>-41</td>
<td>66</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>$-\text{CH}_2\text{CF}_2-$</td>
<td>-40</td>
<td>185</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>$-\text{CH}_2\text{CH}(\text{CH}_3)-$</td>
<td>-8</td>
<td>176</td>
</tr>
<tr>
<td>Poly(vinyl fluoride)</td>
<td>$-\text{CH}_2\text{CHF}$</td>
<td>41</td>
<td>200</td>
</tr>
<tr>
<td>Poly(vinylidene chloride)</td>
<td>$-\text{CH}_2\text{CCl}_2-$</td>
<td>-18</td>
<td>200</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>$-\text{CH}_2\text{CH(OOCCH}_3\text{)}-$</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>Poly(chlorotrifluoroethylene)</td>
<td>$-\text{CF}_2\text{CFCl}$</td>
<td></td>
<td>220</td>
</tr>
<tr>
<td>Poly(ε-caprolactam)</td>
<td>$-(\text{CH}_3)_2\text{CONH}$</td>
<td>52</td>
<td>223</td>
</tr>
<tr>
<td>Poly(hexamethylene adipamide)</td>
<td>$-\text{NH(CH}_3\text{)}_6\text{NHCO(CH}_3\text{)}_4\text{CO}$</td>
<td>50</td>
<td>265</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>$-\text{OCH}_2\text{CH}_2\text{OCO}$</td>
<td>61</td>
<td>270</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>$-\text{CH}_2\text{CHCl}$</td>
<td>81</td>
<td>273</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>$-\text{CH}_2\text{CH}\varnothing$</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>$-\text{CH}_2\text{C(CH}_3\text{)}(\text{CO}_2\text{CH}_3)$</td>
<td>105</td>
<td>200</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td></td>
<td></td>
<td>306</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>$-\text{CF}_2\text{CF}_2-$</td>
<td>117</td>
<td>327</td>
</tr>
</tbody>
</table>
Fig. 10.15-2 Construction of ZSK 300 showing modular barrel and screws (courtesy of Werner and Pfleiderer).
open cross-sections (channels)  closed cross-sections (tubes, pipes)  pellets
Stages in Compression molding cycle

The various stages of the compression molding cycle time can be represented as a function of the force required to close the mold at a constant rate. In the “plastication” stage (t<t_c) the force increases rapidly as the polymer feed is compressed and heated. The second stage flow commences, once the yield stress of the elastomer is exceeded. t_c is the point at which the mold fills and compression of the melt occurs. Ideally, to aid mold filling the majority of chemical reaction should take place after t_c.
Product Shaping / Secondary Operations

EXTRUSION

Shaping through die

→ Final Product (pipe, profile)

Secondary operation
- Fiber spinning (fibers)
- Cast film (overhead transparencies)
- Blown film (grocery bags)

Preform for other molding processes
- Blow molding (bottles)
- Thermoforming (appliance liners)
- Compression molding (seals)
Extrusion Blow molding

In extrusion blow molding, a **parison** (or tubular profile) is extruded and inflated into a cavity with a specified geometry. The blown article is held inside the cavity until it is sufficiently cool.
Blow Molding, Bottles

- Hollow plastic parts with relatively thin walls.
- Typical parts: Bottles, Bumpers, Bags, Ducting.
Injection Blow Molding

Injection blow molding begins by injection molding the parison onto a core and into a mold with finished bottle threads. The formed parison has a thickness distribution that leads to reduced thickness variations throughout the container. Before blowing the parison into the cavity, it can be mechanically stretched to orient molecules axially (Stretch blow molding). The subsequent blowing operation introduces tangential orientation. A container with biaxial orientation exhibits higher optical clarity, better mechanical properties and lower permeability.
Making Polymer Films

Solvent Free Process (Free standing films)
- Cast Extrusion
- Blow Film Extrusion

Solvent (Coating) Processes (later)
- Spincoating
- Dipcoating
- Liquid spray
- Thermal Spray
- Electrocoating
Cast Film Extrusion

• In a cast film extrusion process, a thin film is extruded through a slit onto a chilled, highly polished turning roll, where it is quenched from one side. The speed of the roller controls the draw ratio and final film thickness. The film is then sent to a second roller for cooling on the other side. Finally it passes through a system of rollers and is wound onto a roll.

• Thicker polymer sheets can be manufactured similarly. A sheet is distinguished from a film by its thickness; by definition a sheet has a thickness exceeding 250 µm. Otherwise, it is called a film.
3 layer cast film line

1) Extruder
2) Forming section
3) Casting section
4) Winder

One side is normally microscopically smooth, while the other side contains microscopic asperities which promote adhesion of coatings and printing media.
Polyester films:

Mylar = PETE Film

\[ \text{Teonex} = \text{PEN Film} \]

\[ \text{Mylar} = \text{PETE Film} \]

\[ T_g = 80 \, ^\circ\text{C} \quad T_m = 260 \, ^\circ\text{C} \]

\[ \text{Teonex} = \text{PEN Film} \]

\[ T_g = 120 \, ^\circ\text{C} \quad T_m = 262 \, ^\circ\text{C} \]
Polyester films:

Mylar® polyester films have a unique combination of physical, chemical, thermal, and optical properties:

• Strong, tough, brilliant, and clear.
• Ease of converting: laminating, extrusion coating, embossing, metallizing, printing, punching, corrugation, dyeing, stamping or forming.
• Ease of handling on high-speed equipment.
• Retain mechanical properties: stiffness, strength, toughness, dimensional stability, and optical clarity, over an exceedingly wide range of temperatures.
• Excellent temperature resistance.
• Readily combined with other materials.
• Strong tear-initiation and puncture resistance.
• Excellent oil, grease, or moisture barrier resistance.
• Excellent chemical resistance.
Coextrusion

- **Co-extrusion**
  - Two or more polymers extruded together through the same die
## Common Extrusions

<table>
<thead>
<tr>
<th>Multilayer Structure</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-side PVDC-coated Glassine/LDPE/Foil/LDPE</td>
<td>Nut, dehydrated soup mixes, dry chemicals, pharmaceutical powders</td>
</tr>
<tr>
<td>Paper/Foil</td>
<td>Tobacco</td>
</tr>
<tr>
<td>Paper/LDPE/Foil/LDPE</td>
<td>Wrappers for chewing gum, cigarettes, margarine/butter soap, carton overwrap, carton liner for sugar-coated cereal</td>
</tr>
<tr>
<td>LDPE/LDPE</td>
<td>Dry soup, drink mix</td>
</tr>
<tr>
<td>Nylon/PVDC/PE</td>
<td>Rice</td>
</tr>
<tr>
<td>Metallized Nylon/LDPE</td>
<td>Meat, cheese</td>
</tr>
<tr>
<td>PVDC-coated Nylon/Ionomer</td>
<td>Coffee</td>
</tr>
<tr>
<td>Polyester/PVDC/PE</td>
<td>Lunch meat and hot dogs</td>
</tr>
<tr>
<td>PVDC-coated PET/LDPE</td>
<td></td>
</tr>
<tr>
<td>PVDC/PVC</td>
<td></td>
</tr>
<tr>
<td>BOPP/LDPE</td>
<td></td>
</tr>
<tr>
<td>BOPP/PVDC-coated BOPP</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4.2. Common Multilayer Flexible Structures and Applications.**

*Handbook of Package Engineering-Hanlon, Kelsey & Forcino*
Blown Film Extrusion

- Film blowing is the most important method for producing Polyethylene films (about 90% of all PE film produced).
- In film blowing a tubular cross-section is extruded through an annular die (usually a spiral die) and is drawn and inflated until the frost line is reached. The extruded tubular profile passes through one or two air rings to cool the material.
- Most common materials: LDPE, HDPE, LLDPE

Polyethylene

\[ T_g = -124 \, ^\circ \text{C} \quad T_m = 137 \, ^\circ \text{C} \]
Blown film process II

http://www.bpf.co.uk/bpfindustry/reifenhauser_gallery.cfm
Blown film process

http://www.bpf.co.uk/bpfindustry/process_plastics_blown_film.cfm
• **Sheet & film extrusions**
  • Cast vs. blown film

<table>
<thead>
<tr>
<th></th>
<th>Blown Film</th>
<th>Cast Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Required melt flow rate</td>
<td>lower</td>
<td>higher</td>
</tr>
<tr>
<td>Process temperature</td>
<td>lower</td>
<td>higher</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>more (slower cooling)</td>
<td>less (rapid cooling)</td>
</tr>
<tr>
<td>Optics</td>
<td>hazy, less gloss</td>
<td>better, glossy</td>
</tr>
<tr>
<td>Gauge variation</td>
<td>± 5 to 10%</td>
<td>± 2%</td>
</tr>
<tr>
<td>Output</td>
<td>lower</td>
<td>higher</td>
</tr>
<tr>
<td>Web control</td>
<td>size adjustable</td>
<td>neck-in, more rework</td>
</tr>
<tr>
<td>Flatness</td>
<td>less</td>
<td>better</td>
</tr>
</tbody>
</table>

Blown film is less expensive and more widely used
Blow Molding

Blow molding produces hollow articles that do not require a homogeneous thickness distribution. HDPE, LDPE, PE, PET and PVC are the most common materials used for blow molding. There are three important blow molding techniques:

- Extrusion blow molding
- Injection blow molding
- Stretch-blow processes

They involve the following stages:

- A tubular preform is produced via extrusion or injection molding
- The temperature controlled perform is transferred into a cooled split-mould
- The preform is sealed and inflated to take up the internal contours of the mould
- The molding is allowed to cool and solidify to shape, whilst still under internal pressure
- The pressure is vented, the mold opened and the molding ejected.
Lamination processes

Figure 14.10
A representative wet-bond laminator.

Figure 14.9
Extrusion laminating uses an extruded melt to bond two materials.

Fundamentals of Packaging Technology-Soroka
Natural Rubber

• Raw material extracted from trees
Natural Rubber

- Material is processed
Natural Rubber

• Latex is then dried, sorted and smoked
Natural Rubber

• The difficulties with natural rubber
  – Strength
  – Availability
  – Bacterial breakdown
  – Creep
  – Residual proteins = immune response
Styrene Butadiene Rubber (SBR)
Oil-Resistant Elastomers

• NBR—Nitrile Butadiene Rubber
  – Copolymerization of butadiene and acrylonitrile
  – More expensive than SBR or BR
• CR—Chloroprene rubber (neoprene)
  – Thermal stability
  – Non-flammable
Thermoplastic Elastomers (EPM and EPDM)

• Many of the properties of thermoset elastomers
  – Resiliency
  – Elasticity

• More easily processed
  – Injection molding, extrusion and other standard thermoplastic processes
  – Highly compatible with polyolefins
  – EPDM is crosslinked very lightly and may not be completely melted
Silicones
Elastomer Processing

- Compounding
  - Banbury mixer
Elastomer Processing

- Preforming
- Molding
- Dipping
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Properties at Break</th>
<th>Compressive Strength</th>
<th>Flexural Strength</th>
<th>Impact Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength (Mpa)</td>
<td>Modulus (Mpa)</td>
<td>Elongation (%)</td>
<td>Strength (Mpa)</td>
</tr>
<tr>
<td>Polyethylene, low density</td>
<td>8.3-31</td>
<td>172-283</td>
<td>100-650</td>
<td>-</td>
</tr>
<tr>
<td>Polyethylene, high density</td>
<td>22-31</td>
<td>1070-1090</td>
<td>10-1200</td>
<td>20-25</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>31-41</td>
<td>1170-1720</td>
<td>100-600</td>
<td>36-52</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>41-52</td>
<td>2410-4140</td>
<td>40-80</td>
<td>1170-1720</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>36-52</td>
<td>2280-3280</td>
<td>1.2-2.5</td>
<td>48-76</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>48-76</td>
<td>2240-3240</td>
<td>2-10</td>
<td>48-76</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>14-34</td>
<td>400-552</td>
<td>200-400</td>
<td>12</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>76-83</td>
<td>-</td>
<td>60-300</td>
<td>48-72</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>48-72</td>
<td>2760-4140</td>
<td>50-300</td>
<td>72-131</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>66</td>
<td>2380</td>
<td>110</td>
<td>93</td>
</tr>
</tbody>
</table>

\(^{a}\)Values taken from Aranoff,\(^{12a}\) converted to SI units, and rounded off.

\(^{b}\)To convert megapascals to pounds per square inch, multiply by 145.

\(^{c}\)Izod notched impact test (see Chap. 5). To convert newtons per centimeter to foot pounds per inch, multiply by 1.75.