

1 Polymer Processing

1.1 Introduction

Polymeric materials – often called *plastics* in popular usage – are ubiquitous in modern life. Applications range from film to textile fibers to complex electronic interconnects to structural units in automobiles and airplanes to orthopedic implants. Polymers are giant molecules, consisting of hundreds or thousands of connected *monomers*, or basic chemical units; a polyethylene molecule, for example, is simply a chain of covalently bonded carbon atoms, each carbon containing two hydrogen atoms to complete the four valence sites. The polyethylene used to manufacture plastic film typically has an average molecular weight (called the *number-average molecular weight*, denoted M_n) of about 29,000, or about 2,000 $\text{—CH}_2\text{—}$ units, each with a molecular weight of 14. The symbol “ — ” on each side of the CH_2 denotes a single covalent bond with the adjacent carbon atom. (The monomer is actually ethylene, $\text{CH}_2=\text{CH}_2$, where “ $=$ ” denotes a double bond between the carbons that opens during the polymerization process, and a single “mer” is $\text{—CH}_2\text{—CH}_2\text{—}$; hence, the molecular weight of the monomer is 28 and the degree of polymerization is about 1,000.) The *ultra-high molecular weight* polyethylene used in artificial hips and other prosthetic devices has about 36,000 $\text{—CH}_2\text{—}$ units. Polystyrene is also a chain of covalently bonded carbon atoms, but one hydrogen on every second carbon is replaced with a phenyl (benzene) ring. Two or more monomers might be polymerized together to form a *copolymer*, appearing on the chain in either a regular or random sequence. The monomers for some common engineering plastics are shown in Table 1.1.

The polymers used in commercial applications are solids at their use temperatures. The solid phase might be brittle or ductile, depending on the chemical composition and, to some extent, on the way in which the polymer has been processed. The chemical composition of the backbone of some polymers, such as polyethylene, is such that crystallization can occur; other polymers, such as polystyrene, cannot form crystalline structures and solidify only as amorphous solids, or *glasses*. The *glass transition* occurs when the temperature is sufficiently low to prevent large-scale chain motion. Crystallization and glass transition temperatures are shown for

Table 1.1. Repeat units and transition temperatures of some common polymers

Polymer	Monomer	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$
Linear polyethylene (HDPE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ (-\text{C}-\text{C}-) \\ \quad \\ \text{H} \quad \text{H} \end{array}$	~ 110	134
Branched polyethylene (LDPE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ (-\text{C}-\text{C}-) \\ \quad \\ \text{H} \quad \text{H} \end{array}$	~ 110	115
Polystyrene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ (-\text{C}-\text{C}-) \\ \quad \\ \text{H} \quad \phi \end{array}$	90–100	none
Poly(ethylene terephthalate)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \quad \text{O} \\ \quad \quad \quad \\ (-\text{O}-\text{C}-\text{C}-\text{O}-\text{C}-\phi-\text{C}-) \\ \quad \\ \text{H} \quad \text{H} \end{array}$	70	260
Poly(methylmethacrylate)	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ (-\text{C}-\text{C}-) \\ \quad \\ \text{H} \quad \text{C}-\text{O}-\text{CH}_3 \\ \\ \text{O} \end{array}$	90–100	none

Note: ϕ denotes a phenyl group (a benzene ring); the substitution is in the para position in poly(ethylene terephthalate).

the polymers in Table 1.1. Polymers are very viscous in the liquid state, and molecular diffusion is slow; hence, the molecular reorganization necessary to permit crystallization can sometimes be so slow that a crystallizable polymer will reach the glass transition temperature and solidify as a glass before crystallization can occur. Indeed, there are always amorphous regions in any crystalline polymer.

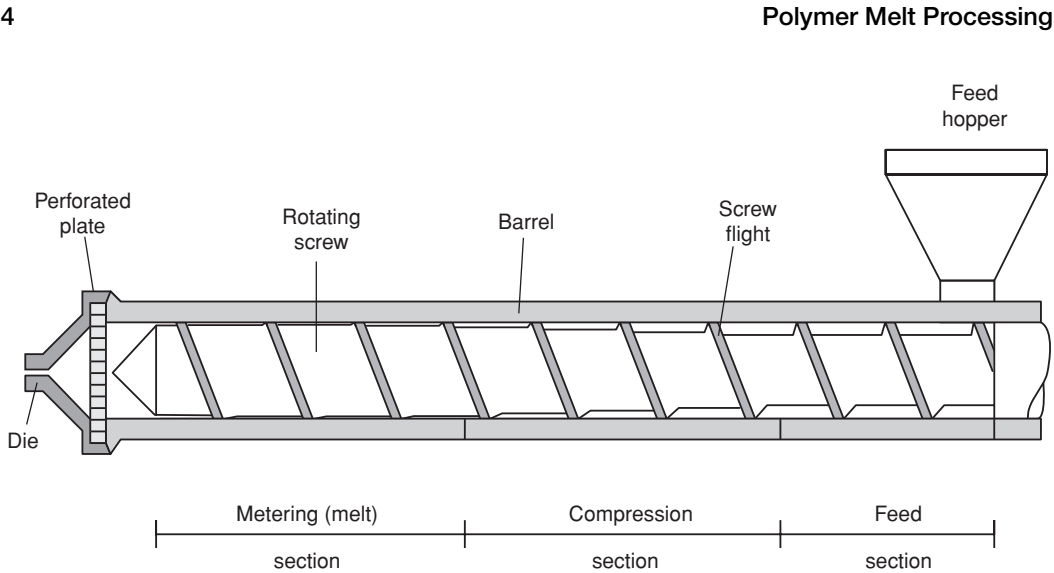
Polymers are often blended or contain additives to affect the properties of the solid phase; high-impact polystyrene, for example, is a blend in which particles of a rubbery polymer, typically polybutadiene or a styrene-butadiene copolymer, are dispersed in polystyrene. Many polymer composites used in molding applications contain solid fillers, such as calcium carbonate particles, glass fibers, or even nanoscale fillers like exfoliated clays or carbon nanotubes.

The polymer manufacturer, starting from raw materials like natural gas and other low molecular weight chemicals, produces the polymer – say, polyethylene – as a powder or in the form of chips or flakes, which are often converted (densified) into pellets by extrusion. This *resin* must be processed to produce the desired product – a molded part, for example. Most processing takes place in the liquid state. The resin must first be melted (we will use the term *melt* to denote the change from any form of solid to a liquid state, although technically only a crystal has a true melting

transition), then conveyed through one or more steps to form an object of the desired shape, and finally solidified again. A polymer pipe, for example, is produced by continuously extruding the molten polymer through an annular die and then cooling it quickly to retain the shape. An injection-molded part is produced by forcing the molten polymer into a mold of the desired shape, where the polymer cools until it has solidified, after which the mold is opened, the part removed, and the process repeated.

We typically draw the backbone carbons in a polymer chain in a straight line, but in fact sequential covalent bonds between carbon atoms form an angle of 109.5° , not 180° . Rotation about the bonds between adjacent carbon atoms permits substantial lateral motion of the chain, and any directional correlation of the backbone usually vanishes over lengths of five or ten monomer units; this distance is known as a *Kuhn length*. A single polymer molecule therefore has the appearance of a very long, flexible string of beads, or even simply a very long flexible rope, and the dynamics of isolated polymer molecules in dilute solutions are very well described by a statistical mechanics treatment of a string of beads undergoing random motion in the presence of Brownian forces. If these molecules are now packed together in a melt or a concentrated solution, it is clear that the motion of one string of beads is highly constrained by all the other strings in its neighborhood. The best visual picture is a bowl of spaghetti; if we put a fork into the bowl and attempt to move one strand, we impose a motion on all the other strands with which that strand is in contact, and we cause a macroscopic motion that tends to align the *entangled* strands. In a similar manner, the deformation we impose on a polymer melt during processing can induce orientation in the chains at a molecular level, and this orientation in turn manifests itself in the distribution of stresses, the ability of the melt to crystallize during cooling, and the mechanical and optical properties of the bulk material. The properties of the final shaped object thus depend in part on the chemical nature of the particular polymer and in part on the details of the mechanical process and the stress and thermal fields to which the melt has been subjected.

Our goal in this text is to use mathematical modeling to develop the basic principles necessary to understand polymer melt processing, to analyze and predict behavior, and ultimately to develop the tools needed to guide process operation and design. A mathematical model is an abstraction that captures the essential features of a physical process in a set of equations that can be manipulated, analytically or numerically, to explain and predict behavior. A good model is based on fundamental physical principles, with essential compromises between the detail required for fidelity to the underlying physical phenomena and the simplicity required for practical implementation. The level of the model is determined by the anticipated application. The academic tools we will employ in modeling polymer melt processes are fluid mechanics and heat transfer. The natural language of these subjects is multi-variable calculus, at a level commonly taught during the second year in U.S. science and engineering curricula; because we are interested in phenomena that vary spatially in more than one direction and may vary in time, the physical phenomena will be described by partial differential equations. The actual applications, however, in



contrast to the language itself and the formal structures of the models, require little or no experience in the solution of partial differential equations; indeed, simple quadratures of the type encountered in an introductory calculus course suffice for most situations that we will encounter.

1.2 Typical Processes

In the following sections we briefly describe some of the most important melt processes, and we will return to the modeling of these processes in subsequent chapters. We will be looking at generic features, and we will not focus on mechanical detail, which is of course very important in actual operation.

1.2.1 Extrusion

Extrusion is the most fundamental and most widely used unit operation in melt processing. An extruder is a device that pressurizes a melt in order to force it through a shaping die or some other unit. A ram extruder, for example, is simply a piston that forces a melt from a cylinder through a die. We are usually concerned with continuous extrusion over long periods of time, in which case a ram, which must operate in a semibatch mode (i.e., the cylinder must be refilled periodically), is not appropriate. The most common device for continuous extrusion is the single-screw extruder, shown schematically in Figure 1.1. The single-screw extruder is analogous to the meat grinder that was once a fixture in kitchens. In a meat grinder, chunks of meat are placed in a hopper and fall onto a rotating *Archimedes screw*. The meat is compressed and carried forward by the screw flights until it is forced through a perforated plate, producing the strands that make up “ground” meat. The counter-intuitive feature here, which we rarely think about in the context of a meat grinder, is that the meat enters at atmospheric pressure and is forced through the perforated

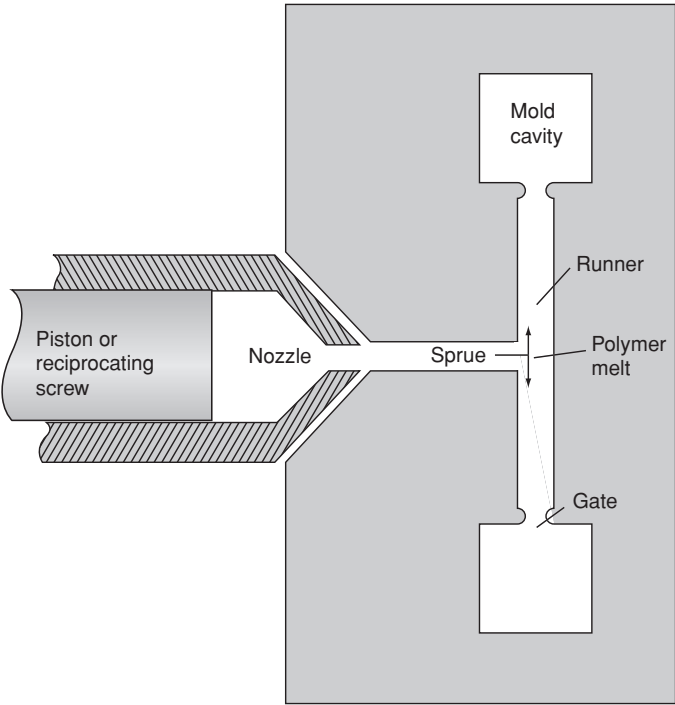


Figure 1.2. Schematic of injection molding.

plate to emerge at atmospheric pressure; hence, the pressure must *increase* from the hopper to the upstream side of the plate in order to provide the force necessary to push the meat through the plate. We are accustomed to thinking in terms of pressure *drop* in flow situations. Similarly, in a screw extruder the polymer, in the form of flakes, chips, or pellets, is fed through the hopper onto the screw, where melting takes place because of frictional and conductive heating and perhaps also deformation heating of the softening solid. The polymer is conveyed forward by the screw, becoming completely molten by the time it reaches the *metering section*. Pressure builds up in the flow direction until the end of the screw, where the polymer is forced through a shaping die. The pressure drop through the die must equal the pressure buildup along the screw.

Twin-screw extruders, in which the screws intermesh while conveying the polymer, are also in common use. Twin screws are very effective mixing devices, and they are commonly used for compounding blends and composites, as well as for reactive processes, in which a chemical reaction occurs in the extruder.

1.2.2 Injection Molding

Injection molding is a semibatch operation shown schematically in Figure 1.2. The process is conceptually very straightforward: Molten polymer is forced into a closed mold from a ram extruder or a screw extruder with a reciprocating screw and allowed to solidify, after which the mold is opened, the part is removed, and the

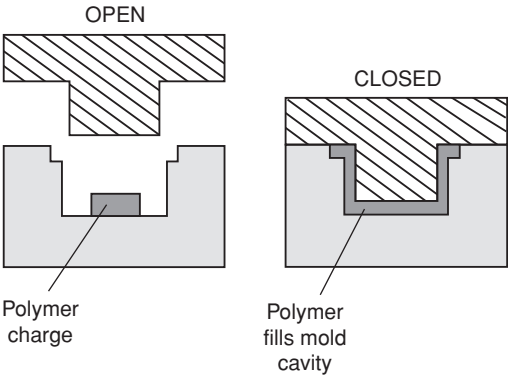


Figure 1.3. Schematic of compression molding.

process is repeated. There are a number of practical issues, however. The mold walls are typically cold, so the polymer is cooling during the filling cycle. If the mold is filled too slowly and too much solidification occurs, the mold cavity will be closed off before filling is complete. Indeed, incomplete filling can occur even without solidification because of a large melt viscosity increase from cooling during the filling process. Incomplete filling is a particular problem in the manufacture of complex molded parts, like those used for electronic interconnects. In addition, the flow inside the mold is very important. The flow plays a significant role in determining the morphology of the finished part, which in turn determines the physical properties. Many molds have inserts around which the polymer must flow, or multiple “gates” to facilitate filling, and the weld lines where the flow fronts meet can be mechanically weak points; hence, design to ensure optimal placement of the weld lines is an important consideration. Finally, it is common to fill more than one mold cavity from a single extruder, as indicated in the schematic. Flow balancing to ensure equal flow to all molds is therefore very important. Very high pressures can be reached in injection molding; polymer melts are usually considered to be incompressible, but this is one application where compressibility of the melt may be important because of the very high pressures. The high pressures also have implications regarding mechanical design; leakage around the mold face can be important because of inadequate pressure to keep the mold sealed, for example.

1.2.3 Compression Molding

Compression molding, shown schematically in Figure 1.3, is also conceptually simple. Polymer is placed between two mold faces and flows out to fill the cavity as the mold is closed. The charge for compression molding of large parts – an automotive hood, for example – often consists of stacked layers of *sheet molding compound*, which is a fiber-filled polymer sheet that can be handled at room temperature. The plies may be oriented in various directions to achieve desired fiber orientation in the final product, especially if the fibers are long (*continuous fibers*). When the fibers are short, the fiber orientation distribution is determined by the flow field during mold

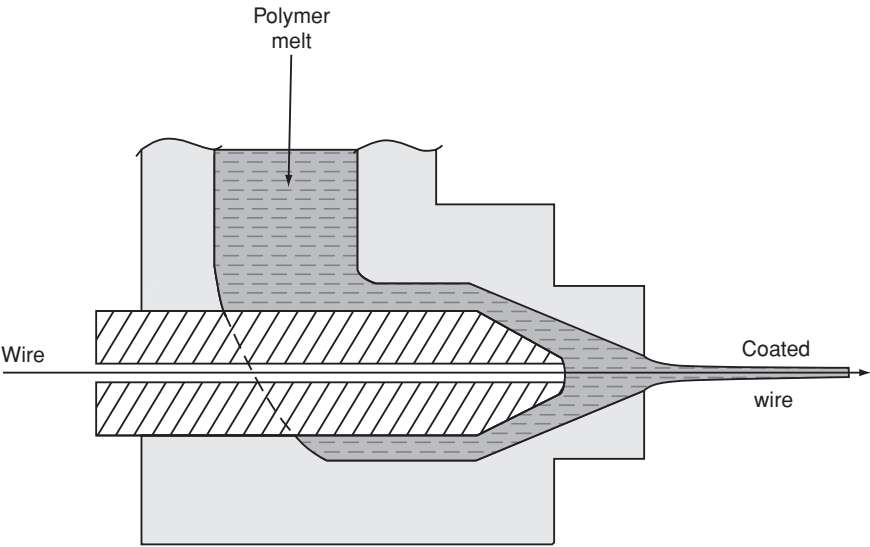


Figure 1.4. Schematic of a “cross-head” wire coating die.

closing. The programming of mold closing, especially in a large mold that might weigh several tons, is an interesting exercise; the feedback signal controlling the rate of closure can be position, force, or some combination of both. Compression molding is usually carried out with *thermosetting* polymers, which polymerize during the processing.

1.2.4 Coating

There are many types of coating operations. We will focus here on the coating of wire and film, shown schematically in Figure 1.4. A wire or film (the *substrate*) is passed through the die. The thickness of the coating for a given die geometry is determined by the substrate speed and the upstream pressure, since both parameters contribute to the polymer flow rate. Coating uniformity is an important consideration here, especially when the visual appearance of the coating is important; small variations in coating thickness in certain wavelength ranges can have a large impact on reflectivity, for example. The interior design of the die is important in order to prevent regions of melt recirculation, in which the organic polymer spends long times in the die at high temperature, since polymer degradation can occur and produce coating defects when the degraded polymer finally leaves the die. In some film extrusion coating processes, the polymer is extruded onto the moving substrate, rather than being contacted inside the die. This latter process, in which the extruded melt is stretched as it passes from the die to the sheet, is very similar to fiber spinning, which is described next. An instability known as *draw resonance*, in which the film thickness varies periodically, is a major concern in this process and one that we shall discuss subsequently.

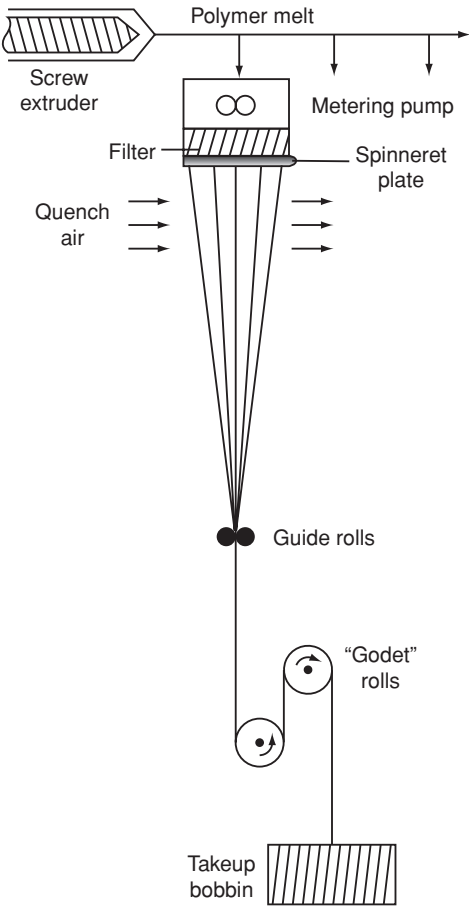


Figure 1.5. Schematic of fiber spinning.

1.2.5 Fiber Spinning

The melt spinning process for the manufacture of textile fibers is shown schematically in Figure 1.5. Let us first focus on a single filament. The polymer from the extruder, after passing through a filter to remove small gel particles, is forced through a small hole known as a *spinneret*, which is typically on the order of 200–400 μm in diameter. The jet, which might be at a temperature of 290 °C for poly(ethylene terephthalate), or PET, the polyester typically used in textile fibers, emerges into an ambient environment that is below the solidification temperature, which for poly(ethylene terephthalate) is about 80 °C. The filament is taken up on a roll moving at a much higher linear velocity than the extrusion velocity; the take-up speed is typically in excess of 3,000 m/min (50 m/s, or about 120 mph), while the average linear velocity through the spinneret is typically two orders of magnitude smaller. Mass conservation therefore requires that the filament at the point of takeup be drawn down in area by a factor roughly equal to the ratio of the takeup velocity to the extrusion velocity (“roughly” because the densities at the spinneret and takeup will be different because of the large temperature difference). The

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filament solidifies between the spinneret and the takeup, and the drawdown will occur mostly in the melt phase.

The mechanics of this process clearly depend on the interplay between the fluid mechanics causing melt stretching and the very high rate of air cooling; cooling affects the viscosity and hence the resistance of the fluid to stretching. The high speeds involved introduce aerodynamic considerations; air drag and filament inertia are important contributors to the filament mechanics, and the nature of the boundary layer in the air stream around the filament plays a significant role. In most cases the spinneret plate contains a large number of holes, and the individual filaments are taken up together as a *yarn*. The cooling air therefore contacts each filament in a different way, causing each filament to deform differently. Stretching flow is an efficient means of polymer chain orientation, which helps determine the final fiber morphology and properties; different stretching histories on different filaments will therefore cause some property variation within the yarn.

The primary operating concern is filament uniformity and the avoidance of breaks. The melt zone below the spinneret but prior to solidification is short, typically on the order of one meter. The residence time in the melt zone is therefore on the order of fractions of a second. Feedback control of the average filament diameter on this time scale is not feasible. Furthermore, each extruder feeds many spinning stations, and a fiber plant will contain hundreds of stations. Thus, this process essentially operates in an “open loop” mode, with operator adjustments taking place over time scales that are very long relative to the time a fluid element spends on the line. Models are very helpful in defining process operating strategies, and major process improvements have been effected with the guidance of spinline models.

Polymer films are formed in a number of ways, but one common film process looks like a two-dimensional version of the spinning process, in which a molten sheet is extruded into air and stretched, after which the film is solidified and taken up on a cold roll. Film processes tend to operate at much lower speeds than fiber processes, but the basic mechanics are the same except near the edges of the film, where three-dimensional effects are important.

1.2.6 Film Blowing

The blown film process, shown schematically in Figure 1.6, is commonly used to manufacture biaxially oriented films and plastic bags. A thin cylindrical film is extruded through an annular die. The inside pressure is slightly above ambient, causing the film to expand (like a rubber balloon). The film is flattened at “hauloff” and taken up at a linear speed higher than the linear extrusion velocity, so stretching occurs both in the “machine direction” and in the transverse direction. Solidification occurs prior to hauloff. The flattened annular film is slit on the sides if film is the desired product or processed further to form periodic seals if bags are the product. The blown film process is very sensitive to operate, and the aerodynamics around the air ring seem to have a major effect on bubble stability.

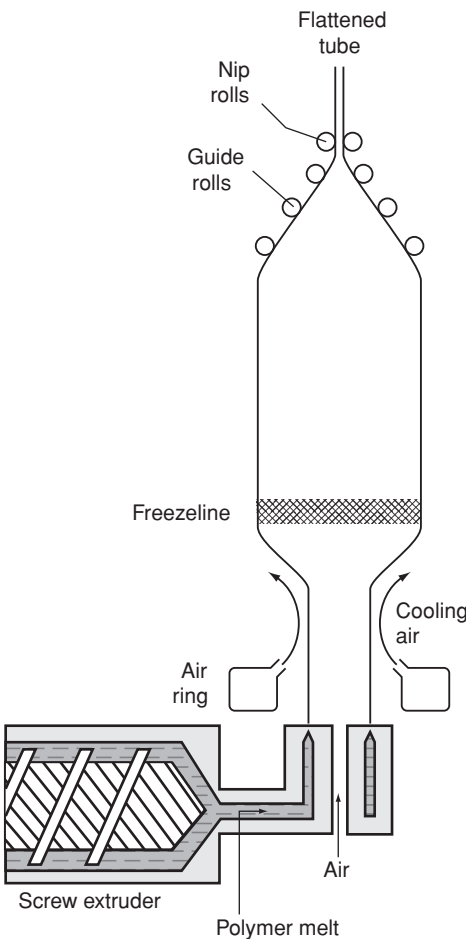


Figure 1.6. Schematic of the blown film process.

1.2.7 Blow Molding and Thermoforming

The blow molding process, which is used for the manufacture of bottles and industrial components such as automotive fuel tanks, combines elements of a number of the previous processes. A tube that is closed at one end, known as a *parison*, is first formed, either by injection molding or by extrusion. The heated parison is then pressurized and stretched to conform to the shape of the mold, where it solidifies. The blowing portion of the cycle is a biaxial stretch.

Classical thermoforming is a similar process in which a sheet is heated and deformed by vacuum from inside the mold or by pressurization from outside to stretch and conform to the shape of the mold. Some thermoforming processes utilize a mechanical device for part or all of the deformation of the sheet. Thermoforming is used to produce high-volume thin-walled products such as drinking cups and food packaging as well as large items like cargo bed liners for pickup trucks.

The modeling of the inflation and solidification portions of blow molding and thermoforming do not introduce major new concepts beyond those incorporated in