23

PRINCIPLES OF POLYMER PROCESSING

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23.1 GENERAL

Most polymeric raw materials are available in the solid state as granules, flakes, or powders. Solid raw materials have to be transformed into a fluid or plastic state, which is accomplished by heating. Once in the plastic or fluid state, the material is shaped, after which the resulting shape is fixed by cooling (thermoplastics), or by a chemical reaction (thermosets). During processing, heat is supplied either from the outside, via electric heaters (extrusion or injection molding), infrared (IR) radiation (thermoforming), or direct flame (rotomolding), or generated by internal friction as the polymer mass is transported along the machine, first in the solid state and eventually in the highly viscous liquid state (extrusion or injection molding).

Two important polymer characteristics that affect processing are their low thermal conductivity, either in the solid or in the fluid state and their very high viscosity in the fluid state.

The low thermal conductivity makes heating and eventually cooling slow processes.

The high viscosity makes processing to require of powerful machines, capable of pumping a fluid (e.g., molten polyethylene at 180 °C) that is circa 1 million times more viscous than water; [$\eta_{(\text{water at } 20\,^{\circ}\text{C})}$ ~1 mPa s–vs–$\eta_{(\text{PE at } 180\,^{\circ}\text{C})}$ ~1 kPa s].

With respect to viscosity, it decreases with increasing temperature (Fig. 23.1). But in addition, considering that molten polymers are shear-thinning non-Newtonian fluids, their viscosity decreases with increasing shear rate, that is, increases the flow rate [1–3] (see Fig. 23.2).

Notwithstanding this fact, high pressures are required to transport the fluid mass through the transport channels or into the mold of a processing machine with an acceptable speed. Pressure levels of 50–150 MPa (500–1500 bars) are normal, so the machines have to be very robust.

The choice of the process depends, *inter alia*, on the requirements of the end product; with injection molding, narrower tolerances can be achieved than with thermoforming or rotomolding, for example. The nature of the polymer also plays a role; it depends, for instance, on the stability of the polymer at the high temperatures in a process. The length of the rubbery region on the temperature scale determines the ease of vacuum forming; too brittle a polymer is difficult to machine, for example.

A very important factor in the choice of a process is the *economy*. The manufacturing costs of the various processing techniques are very different and are strongly dependent on the number of articles to be made.

23.2 COMPOUNDING

Before the actual forming process, often the raw material has to be compounded, that is, blended with a number of other components.

To obtain a better dispersion, a blending process in the fluid state is necessary. To achieve this, various types of mixing devices are available, such as internal mixers and mixing extruders [4–8].

Internal mixers, such as the *Banbury* mixer (Fig. 23.3), and the laboratory *Brabender* or *Haake* mixers contain two connecting chambers, in which blades rotate in opposite directions with a narrow clearance to the walls, resulting

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Handbook of Polymer Synthesis, Characterization, and Processing, First Edition. Edited by Enrique Saldívar-Guerra and Eduardo Vivaldo-Lima.

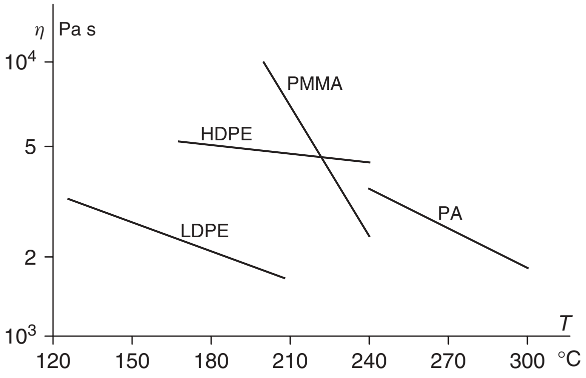

Figure 23.1 Melt viscosity as a function of temperature.

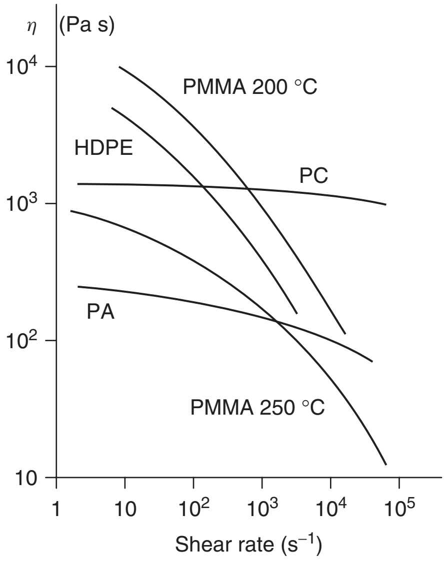

Figure 23.2 Melt viscosity as a function of shear rate.

in high shear rates. The chamber walls can be cooled or heated. After mixing, the material is removed from the chambers, milled into a sheet, and cut into ribbons or granulated for storage or further processing.

The other type of compounding device is the extruder. In addition to its use in fabrication, it is also used as a mixer. In essence, it is a screw pump in which the mass to be mixed is transported in a heated cylinder by a screw or, with twin-screw extruders, by two parallel screws. During this transport, melting and intensive mixing take place. At the end of the screw, the blend is forced through a die with a number of holes to produce spaghetti-like ribbons, which are then cooled down and cut into granules.

Most manufacturers of end products do not make the compounds by themselves but obtain them from the material supplier. In the bigger industries, compounding is sometimes carried out in-house, with the advantages of economy and of flexibility to tune their products to reach the best compromise of processability on the machines available and the desired properties of the end product.

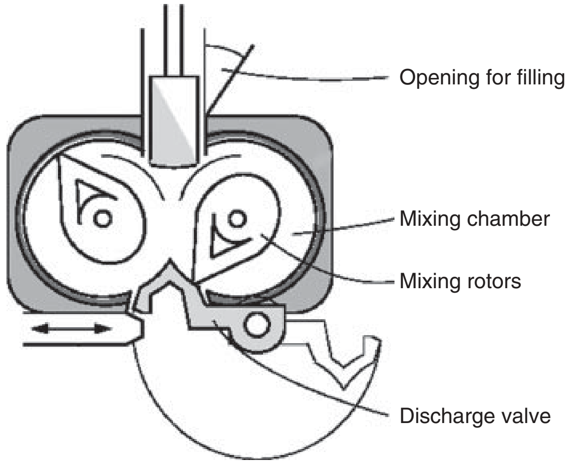

Figure 23.3 Simple sketch of a Banbury mixer.

23.3 EXTRUSION

The extruder is schematically represented in Figure 23.4. Its most essential part is the screw, which fits in a cylinder, provided with heating elements and cooling channels, so that a desired temperature profile can be established. At one end of the screw, there is the feed section for the raw material supply and, at the other end, the molten polymeric compound leaves the machine via the forming die [9–11].

In *extrusion*, the material is heated, molten, pressurized, and forced through a die, all along one and the same screw.

The controlling geometric parameters that characterize the extruder are the screw diameter D and the length to diameter ratio L/D. Extruders are categorized according to diameter, from which the output and the power demand for a given rotating speed of the screw are derived.

The diameters in use fall in the range of 2.5–30 cm, but most fall in the range of 5–15 cm. The ratio of the length to the diameter L/D is ~24, but has been moving to larger values (longer screws) of 36–42 in order to improve melt homogeneity.

The screw performs the following tasks:

- transport of raw material (granules, flakes, or powder);
- melting and thereby increasing the apparent density;
- mixing and homogenizing the polymer;
- pumping of the molten polymeric compound to the die and generating sufficient pressure to pass through the die.

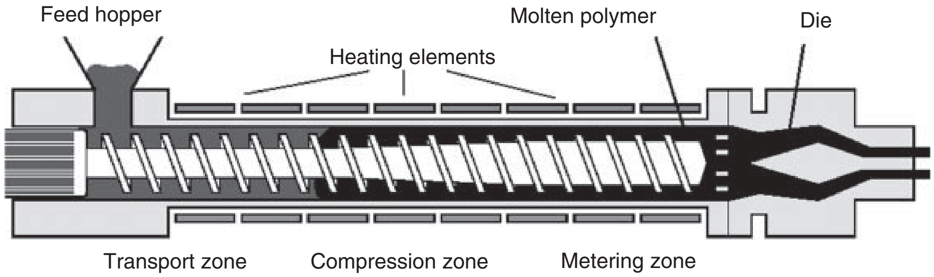

Figure 23.4 Simplified diagram of an extruder.

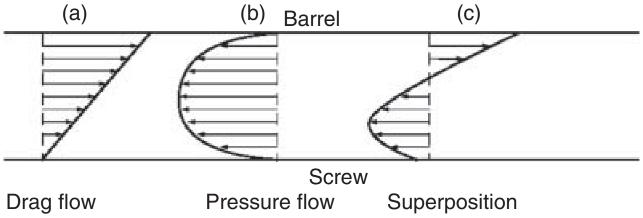

Figure 23.5 Velocity distribution in the screw channel of an extruder.

Each polymer has its own demands in relation to the granule size, *L/D* ratio, compression ratio,[1] melting behavior, risks of degradation, etc.

In the final part of the screw, where the fluid consists entirely of the molten polymer, the forward flow occurs as a result of the drag of a moving surface in contact with the molten polymer, and this can be visualized most easily by first imagining the screw at rest in a rotating cylinder and then unrolling the screw channel into a straight channel with a rectangular cross section. The cylinder wall then forms a lid on the channel, moving at a certain angle. Assuming the end of the channel is open, a velocity distribution along the direction of the channel would occur as depicted in Figure 23.5a. That is, $V = 0$ at the bottom of the channel, and $V = U$ (the component of the cylinder speed in the length direction).

But with a flow restriction at the end of the channel (the die), a backpressure P is built up. This will produce a backward flow along the last part of the screw channel as a result of the difference in pressure ΔP between the final part of the screw (high P) and the initial part of the screw (low P). This backward pressure flow would look as depicted in Figure 23.5b.

The combination of these two distributions is depicted in Figure 23.5c; a net flow results that governs the volumetric flow of the extruder. This flow Q can be estimated as follows: The drag flow to the right, Q_d, is proportional to the velocity V, that is, the rpm of the screw N, and is also dependent on the geometry of the screw channel, but not on the viscosity of the melt. So

$$Q_d = aN \tag{23.1}$$

The pressure flow in the opposite direction, Q_p, is proportional to the pressure P, inversely proportional to the viscosity η, and, again, dependent on the screw geometry. So

$$Q_p = b\Delta P/\eta \tag{23.2}$$

The net flow $Q = Q_d - Q_p$ is

$$Q = aN - b\,\Delta P/\eta \tag{23.3}$$

(which represents a straight line with a negative slope).

The flow through the die (after the tip of the screw) is solely dependent on the high pressure at the entrance of the die and the low pressure at the die exit (circa 1 bar).

The flow through the die would then be

$$Q_p = c\Delta P/\eta \tag{23.4}$$

(which represents a straight line with a positive slope and intersection at the origin).

A plot of the flow Q as a function of the pressure P is given in Figure 23.6. For a given screw geometry, the first equation, the screw characteristic, is given for two values of the rpm N, while the second equation, the die characteristic, is shown for two levels of the flow resistance in the die, $1/c$. Each combination gives rise to an intersection of the two lines, which is the working point of the extruder, from which the values of Q and P can be read.

In other words, the flow rate for a given screw/die combination is proportional to the rpm of the screw and independent of the pressure and viscosity. This treatment is valid only for a Newtonian fluid. In reality, polymers deviate from this simplified picture, though the general conclusions are not affected.

Besides the single-screw extruder (SSE), there is the twin-screw extruder (TSE), that is, two parallel screws rotating within the same cylindrical housing [8].

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[1] Compression ratio = H/h, where H is the channel depth in the first, *deepest*, part of the screw and h is the channel depth in the last, *shallowest*, part of the screw.

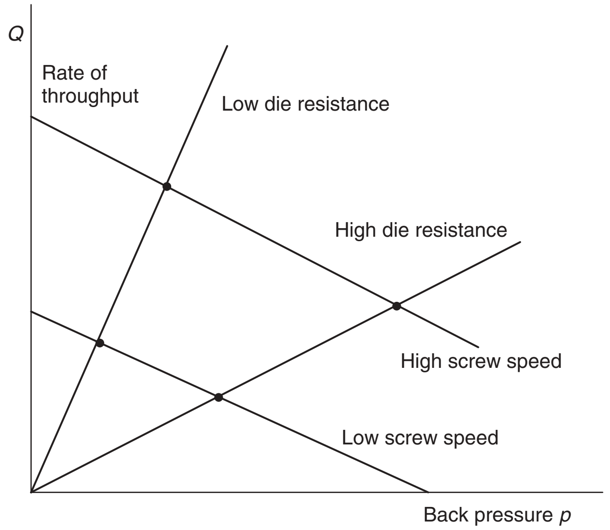


Figure 23.6 Variation of throughput versus backpressure at different rpms and die resistance.

TSE can either be **corotating**, that is, both screws rotating in the same direction, or **counter-rotating**, that is, each rotating in opposite directions.

In addition, TSE can either be **intermeshing** (Fig. 23.7), when the interaxis (I) is less than the sum of the radii of the two screws, that is, when the flights of one screw penetrate into the channel of the other screw and vice versa; or **nonintermeshing**, when the interaxis is equal to the sum of the radii of the two screws, that is, when the tip of the flights of one screw just touches the tip of the flights of the other screw.

In this respect, a high level of intermeshing will produce the maximum positive pumping action but minimum mixing and homogenizing. On the contrary, a low level of intermeshing will produce a diminished pumping action but a much better mixing and homogenization.

The mixing and homogenizing capacity of TSE is much greater than that of a SSE. They are preferred in the compounding industry.

The range of products that can be made by extrusion is very large: rods, pipes, hoses, sheets, films, profiles, filaments and fibers, wire coatings, etc.

Filaments and rods can be formed quite easily by using a die with a circular orifice.

Pipes and hoses require an annular orifice. After leaving the die, while still hot and malleable, the pipe/hose is fed into a calibrator (which is a cylinder with an inner diameter identical to the required pipe/hose outside diameter) in which, either by internal pressure or by vacuum suction, the pipe/hose is pressed against the highly polished inside surface of the calibrator.

Sheet extrusion requires a broad, slit die, in which an even distribution of the flowing polymer along its width and an equal flow resistance at each point has to be taken care of. Sheets are being extruded up to a width of 3–4 m and up to 3 cm thickness. If desired, sheets can be produced with a wave shape by passing the still-malleable extrudate between two profiled rolls.

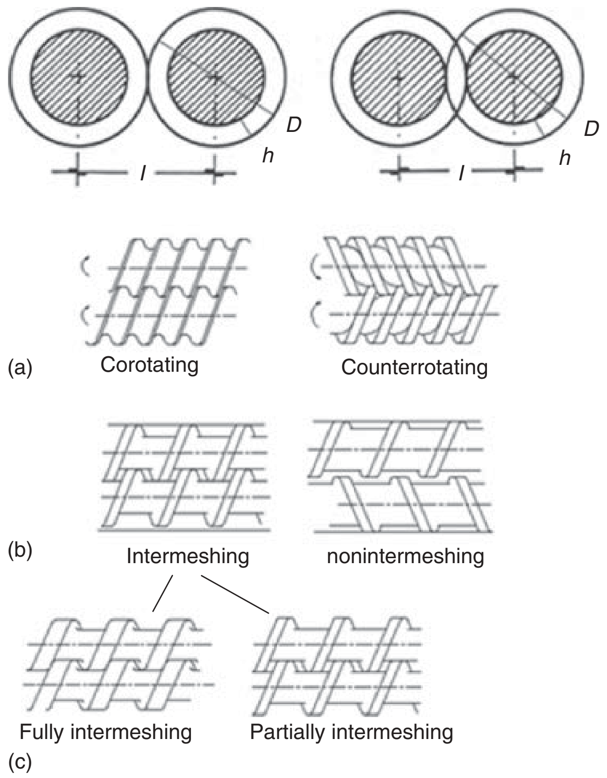


Figure 23.7 Simplified diagrams of twin-screw extruder configurations. I = interaxis = separation (distance) between the screw axes; D = screw diameters; h = screw channel depth.

Film extrusion can be done in a similar way, with a narrower die gap. After extrusion, sheets and films are cooled in a water bath or on polished cooling rolls.

Another application of extrusion is the coating of metal wires or profiles with a plastic layer. This is done on a large scale in the manufacture of electric wires and cables. For this purpose, a cross-head die is needed (Fig. 23.8). The same principle is used for plastic profiles containing a metal core.

An alternative way of producing a film is by the *blown film* process. An annular die is used from which the material emerges as a thin-walled tube, which is immediately blown up by internal pressure to a much larger diameter (Fig. 23.9).

The tubular film thus formed is laid flat and reeled, and can, by cutting and welding, easily be formed into plastic bags.

Coextrusion is a process variant in which two or more extruders feed a single die. A laminar flow of two or more

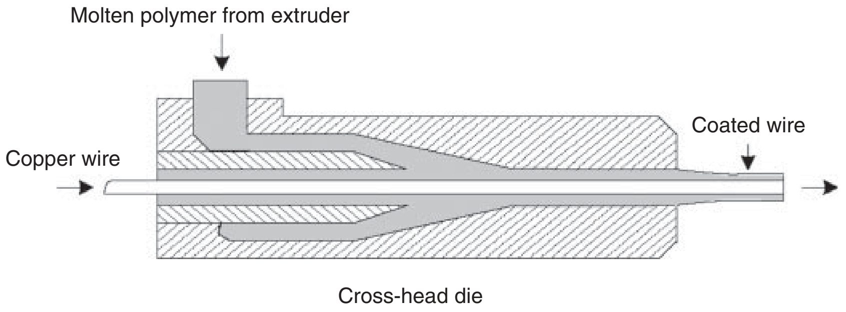


Figure 23.8 Wire coating.

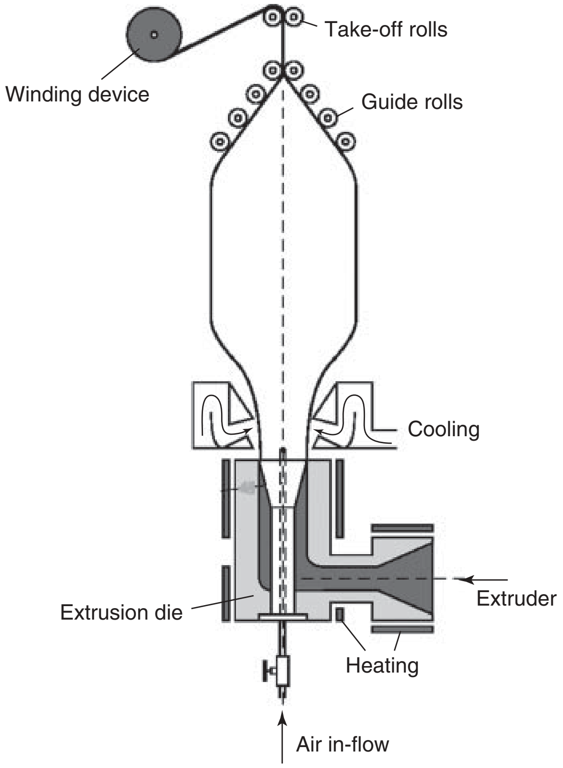


Figure 23.9 Film blowing.

adjacent polymer currents flow through the die to produce a multilayer film or laminate, for example, or a multilayer rod or pipe. Multilayer products can be composed of different polymers. For each polymer, a separate extruder is used.

A laminated film can be made by coextrusion, for example, in which one of the layers provides the strength, another acts as a gas barrier, and yet other layers promote adhesion, etc.

23.4 BOTTLE BLOWING

Blowing of *hollow articles* such as bottles and containers can be carried out online with the extrusion process. A thermoplastic tube emerging from the extruder die is, while still malleable, blown up against the inside of a mold comprising two halves, the walls of which are cooled [12, 13]. The neck of the bottle is calibrated with the aid of a mandrel and the bottom is sealed by the mold parts. The principle is indicated in Figure 23.10. Since the cooling time largely governs the cycle time, a series of moving molds are used. When the bottle has cooled down sufficiently, the mold is opened and moved back to the extruder to be filled again.

The blowing process, though simple, has a few disadvantages: the wall thickness is uneven and the weld at the bottom is deformed. These drawbacks are partly taken care of by a variant of the process, that is, the injection-molding blowing process. Here, a preform is made by injection molding, comparable to the extruded portion, but now more adjusted to the ultimate shape of the bottle. This preform is transported to a second part of the mold, in which it is blown up under pressure.

When using poly (ethyleneterephthalate) PET, the preform is injection molded and rapidly cooled in the mold so that it remains amorphous (PET crystallizes very slowly). By heating it above its T_g (65 °C), it passes into the rubbery state and can then be blown up and, simultaneously, longitudinally stretched. The biaxial orientation thus obtained accelerates the crystallization and, at the same time, results in a very fine crystalline texture so that a thin-walled, strong, transparent, and heat-resistant bottle is obtained.

23.5 INJECTION MOLDING

Injection molding is the most used technique for manufacturing end products directly from a thermoplastic raw material. In this process, articles are formed by injecting the molten polymer into a mold. This method is also used on rubbers and thermosets, though in these cases the mold is heated rather than cooled in order to promote the vulcanization or curing reaction [14–16].

Here, the material is heated by heat transfer from the cylinder wall as well as by internal friction. The material

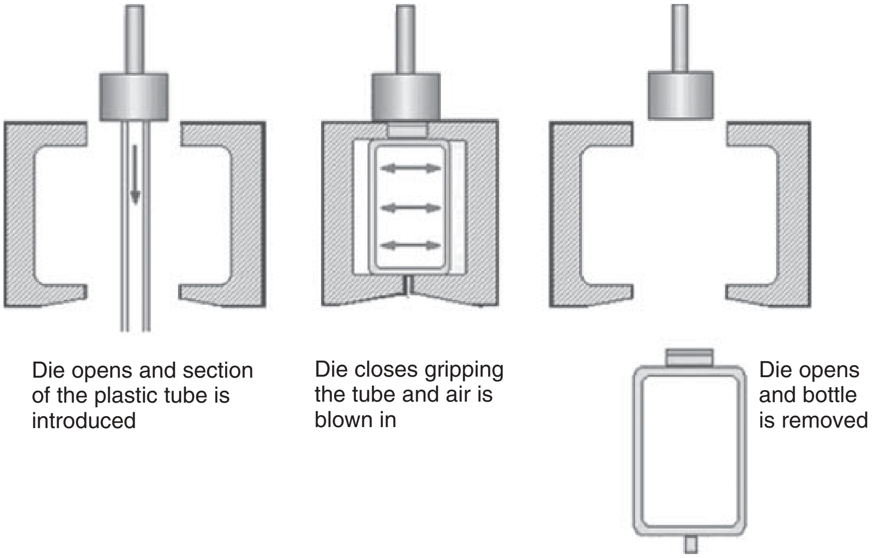


Figure 23.10 Bottle blowing.

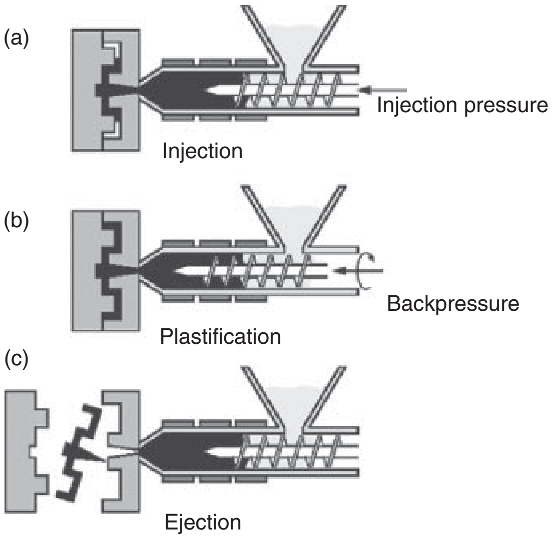


Figure 23.11 Reciprocating-screw injection-molding machine.

is transported and homogenized by an extrusion screw and, after reaching the screw tip, is injected into the mold at a very high pressure (sometimes up to 1500 bar) by the same screw, which now acts as a plunger (Fig. 23.11a). After the mold is filled, the transport channel is closed; the screw continues rotating, but now it transports the molten material to the front side while itself moving backwards (Fig. 23.11b). This takes place while the polymer in the mold cools down sufficiently to be demolded (Fig. 23.11c). In the mold, the product cools down under pressure. After complete solidification, the mold is opened and the product is ejected from it (Fig. 23.11c). The high injection pressure would push away the backside of the mold if this is not be pressed against the front side by a closing force, which has to be very high, for instance, for small machines 10–50 tons (100–500 kN) and for very big machines up to 10,000 tons (100,000 kN).

The *mold* is a very complicated tool. It comprises two halves: a fixed half attached to the stationary platen and a moving half attached to the moving platen. With complicated shapes, or with long flow paths, injection has to take place at several points. For the transport of the melt to these injection points, channels are present that are mostly heated ("hot runners") in order to prevent cooling of the melt before it enters the cavity. The mold cavity is surrounded by thick metal walls through which cooling channels run (with rubbers and thermosets, these channels are used for heating). The mold contains an ejection mechanism to remove the molding after opening.

The melt should be present at the appropriate temperature and pressure at each injection point to enable the desired flow pattern in the cavity. Unwanted phenomena such as poor welding lines, frozen-in orientations, or cooling stresses should be avoided.

The mold is kept closed during injection by a heavy hydraulically controlled closing mechanism. The magnitude of the required forces can be estimated as follows: With an injection pressure of, for example, 1000 bars, the pressure in the mold may, on average, amount to one-third of this value, say 300 bars. When the projected area of the mold is 500 cm^2, the maximum closing force is 1500 kN (150 tons). The size of an injection-molding machine is often characterized by its closing force; for smaller machines, this amounts, for example, to 200 kN, and for bigger ones 3000 kN and even up to 100,000 kN.

23.5.1 Limitations

A first requirement for a good injection-molding process is, of course, that the mold be completely filled. The pressure at which the molten polymer is injected should be sufficient not only to transport the melt through the injection channels at the desired speed but also to continue this transport within the mold through narrow channels with cooled walls. During this transport, the melt is cooled, so that the viscosity increases. Eventually, it solidifies, starting from the walls. If solidification has proceeded through the whole cross section of the channel, then further flow is impossible and incomplete molding results. The dimensions of the end product are limited by this phenomenon; the flow path, that is, the ratio of the maximum distance over which the melt is able to flow and the thickness of the channel, has an upper value. A practical rule of thumb is that, for well-flowing materials this ratio should not exceed about 300. When the length to diameter ratio of the object to be formed is higher, or when the polymer flows less well, then the solution could be to increase the number of injection points.

When the injection pressure is too high to be withstood by the closing mechanism of the mold, the mold halves will be pushed apart, allowing a small quantity of the melt to escape, which results in a very thin extension of the product ("*flash*"). At higher temperatures, that is, with lower viscosities, flash occurs at lower injection pressures as a result of better pressure transfer.

23.5.2 Defects

Shrinkage during solidification always tends to reduce the dimensions to values lower than those of the mold. The magnitude of this shrinkage is shown in Figure 23.12. It appears that for amorphous polymers a reduction in volume of circa 10% occurs when the polymer is cooled from the processing temperature to the ambient; for crystalline polymers, this reduction may amount to 20–25% (Fig. 23.12).

However, cooling and solidification take place under pressure; that is, the melt is compressed and, as a consequence, has undergone a decrease in volume because of its compressibility (Fig. 23.13). This compressibility facilitates the forced introduction of an additional small amount of polymer which will be able to compensate part of the normal shrinkage that occurs as a result of cooling and solidification and, in such a case, because of crystallization.

Figure 23.14 presents the relation between the volume and temperature at several pressure levels, showing the competition between compressibility and shrinkage for amorphous and semicrystalline polymers. These figures are valid for a certain rate of cooling. The effect of cooling rate and pressure are of importance. Higher pressures increase the glass transition temperature (T_g) as well as the crystallization temperature (T_c).

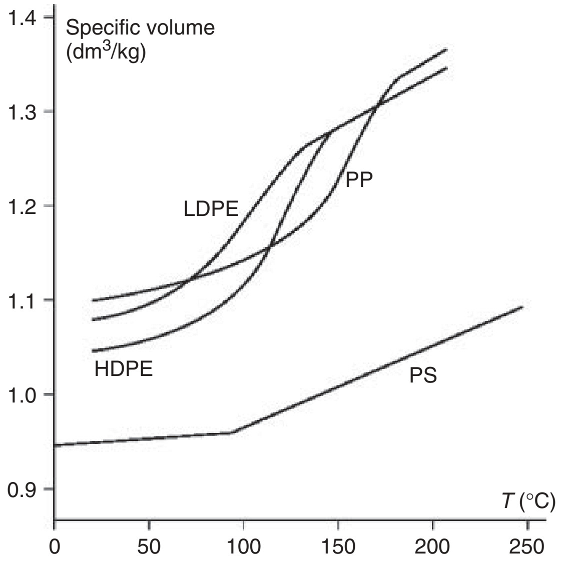


Figure 23.12 Relation between specific volume and temperature (no pressure applied).

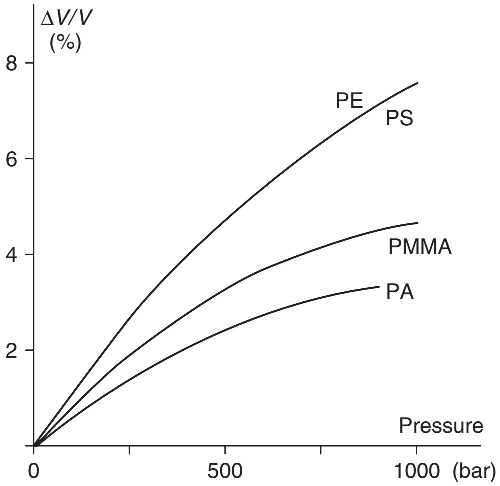


Figure 23.13 Compressibility of molten polymers.

Further reduction of shrinkage in injection molding is reached by maintaining the injection pressure for some time on the mold cavity, the so-called afterpressure. While the outer layers solidify and shrink, an extra amount of melt is pressed into the cavity, which further reduces the final overall shrinkage (Fig. 23.15). A rapid decrease in pressure down to zero (i) indicates a considerable final shrinkage when the end-pressure is high, and (ii) the afterpressure has been too high or applied for too long; the shrinkage is negative and the molding will be tightly clamped in the mold. The ultimate shrinkage is, for amorphous polymers,

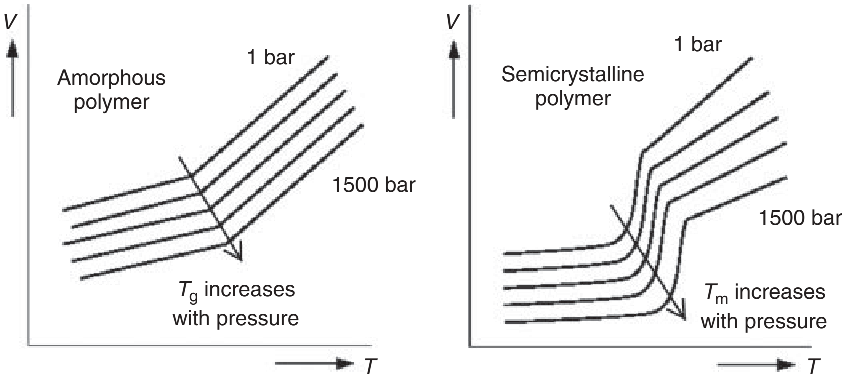


Figure 23.14 p,V,T diagrams for an amorphous and a semicrystalline polymer.

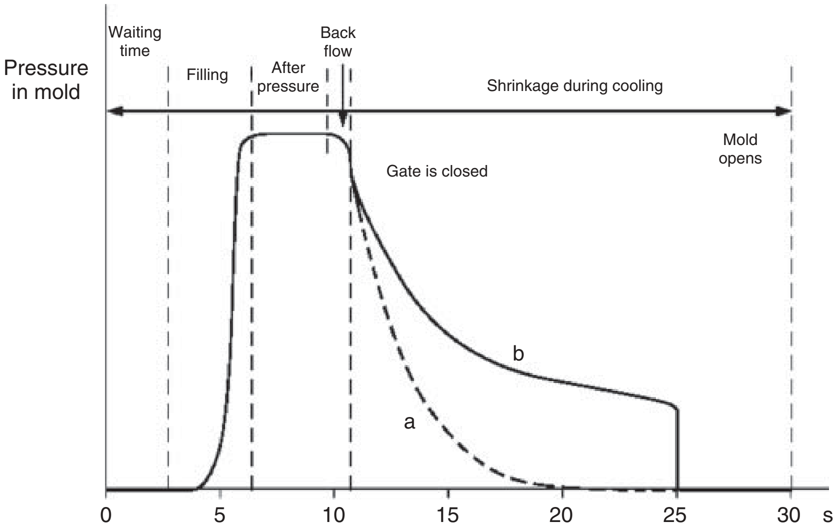


Figure 23.15 Variation of pressure within the mold during the molding cycle.

mostly between 0.3% and 0.7% and for semicrystalline polymers between 1% and 3%.

The shrinkage may vary from place to place depending on the rate of solidification. The simplest example is a solid block that solidifies rapidly on the outside; the hard skin formed this way prevents further shrinkage of the inner part. This results in internal stresses which may lead to tearing and void formation.

Another source of uneven shrinkage is a thickness difference in the molding. A thicker part cools more slowly and attains a higher density than a thin part. These shrinkage differences may give rise to warping of the molding. Also, at the opposite sides of a thicker part, sink marks may occur as a result of a higher local shrinkage.

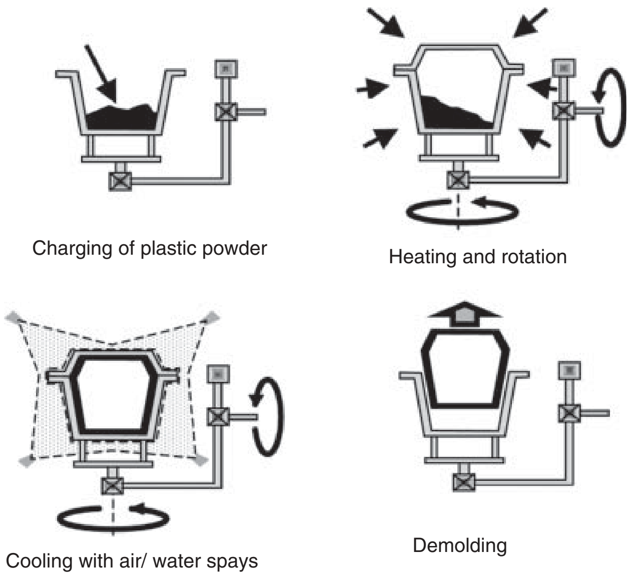
Shrinkage may also be anisotropic, for example, when chain orientation is present. This orientation is found in parts where the melt has been rapidly cooled under a high rate of strain. Shrinkage is higher in the orientation direction than across, so that, for instance, a flat disk injected from its center tends to deform into a saddle-like shape (warping).

The choice of the polymer plays a role, for instance, in the chain length and distribution, in orientations, and in the various process variables (injection pressure and temperature, afterpressure, mold temperature).

23.5.3 Rotational Molding

Molding of hollow articles is possible by rotation. Rotation about two perpendicular axes enables the formation of a hollow article (Fig. 23.16).

The starting material in these process is not necessarily in the liquid state; also polyvinyl chloride (PVC) pastes (plastisols) can be used, as well as even a well-flowing thermoplastic powder [17]. The particles will melt when in contact with the heated wall and will form a compact layer of material. The softened powder sticks to the wall, and other particles gradually complete the shaping process. Only the outer surface of an article made this way will be smooth, which is not objectionable for many applications.



Charging of plastic powder

Heating and rotation

Cooling with air/ water spays

Demolding

Figure 23.16 Rotational molding with two rotating axes.

This method is eminently suited for the manufacture of large objects such as containers and also nonclosed articles such as furniture, dashboard, etc. The material thickness in these articles varies between 1.5 and 15 mm, depending on the type of article.

Wall thickness fluctuations of up to 5% may occur as a result of the uneven temperature in the molten polymer during rotation. Also, because of rate of cooling which is not always reproducible, deviations in the dimensions of the finished product may amount to 5%. Requirements for this process are that the material can be molten completely, that the melt is of sufficiently low viscosity, and that the molten polymer does not degrade too rapidly. Besides plasticized PVC, high and low density polyethylene (HDPE and LDPE) are often used, as well as copolymers of PE such as EVA (ethylene-vinyl acetate). Cycle times vary between 3 and 40 min, depending on the wall thickness. Cycle time is predominantly controlled by the heating and cooling time.

A very promising development is the combination of the *in situ polymerization* mentioned earlier with the principle of rotational molding. This method is, in particular, used for the manufacture of large-sized polyamide-6 articles, starting with caprolactam. The big advantage compared with centrifugal casting is that one starts off with a low-viscous liquid and ends with a solid material. During the whole process, the temperature does not exceed the melting point of the polyamide (PA) formed. The article, therefore, does not need a cooling cycle before it can be taken out of the mold. An example is an oil tank of 1200 l with a wall thickness of around 4.5 mm, which requires 33 kg of caprolactam. The cycle time for heating, rotating, and simultaneous polymerization is around 13 min.

The molds are mostly made of steel or aluminum. Since the forces during rotational molding are relatively small, wall thicknesses of ~1.5 mm will be sufficient.

23.5.4 Compression Molding

Compression molding is the simplest technique to transform a raw polymeric material from the solid state into an end product. The material, as granules, flakes, or powder, is put between the two heated halves of the mold, which are then pressed together [18].

Thermoplastics, thermosets, and rubbers can be processed by compression molding. For thermoplastics, this technique is an exception.

Compression molding of thermoplastics is, in general, unattractive because the mold has to be heated (so the polymeric material melts and takes the mold form) and cooled (so the polymer part solidifies and can be taken out of the mold).

With thermosets, compression molding is commonly applied. The starting material is a molding powder comprising the resin, curing agent, and filler.

The powder is heated in the mold; it becomes a fluid and fills the mold completely, after which the curing reaction takes place.

In this case, if T is low (the curing reaction rate will be low), then η will be high and the material will require a high pressure to fill the mold or will probably not flow to fill the mold. On the contrary, if T is high (the curing reaction rate will be high), then η will be low but curing will probably start before the material fills the mold completely. When these effects coincide, the process fails. If the reaction time is longer than the time needed for flow, then a perfect molding is obtained, but the cycle time may be too long. Therefore, care must be taken in preparing an adequate formulation.

Molding powders cure, in general, at temperatures between 140 and 180 °C, under pressures between 200 and 600 bars. A substantial part of the temperature increase comes from the reaction heat, which may raise the temperature to above the temperature of the wall. This effect will be stronger with thicker articles.

A simple compression molding device is sketched in Figure 23.17.

In the case of thermosets, numerous articles are made by compression molding, such as bulb fittings, switches, wall plugs, crockery, and many other technical and household articles. The process is very economical because no expensive machines and molds are required and the cycle times are short (the finished article can be taken out of the mold without cooling down).

Compression molding of *rubbers* is not essentially different. The starting material is a blend of a rubber, vulcanization additives, and fillers. The compound is heated

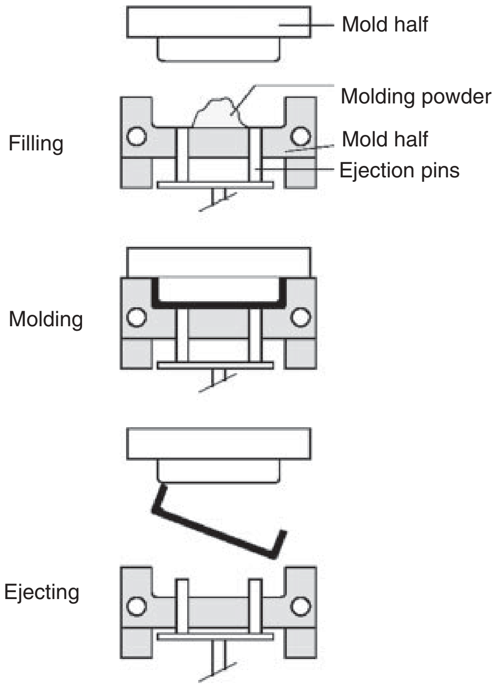


Figure 23.17 Simplified diagram of compression molding.

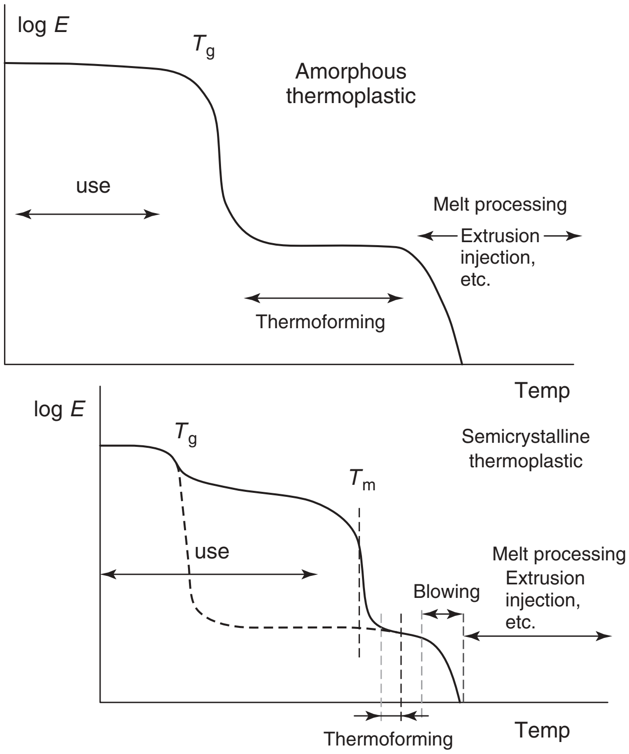


Figure 23.19 Temperature regions in which various processing techniques can be applied.

to become malleable, and is forced to flow into a mold, where it is kept at a high temperature until the vulcanization reaction is completed. Also here, there is a competition between flow and curing; premature vulcanization interferes with good processing. Tires are made this way.

23.6 THERMOFORMING

The starting material usually comes from extrusion, for instance as a laminate or a film.

When starting with a laminate, this is first heated to above its softening temperature, then formed, and finally cooled [19]. The technique most frequently applied for forming is vacuum forming; the force required for deformation is brought about by a vacuum below the heated laminate, which sucks the laminate onto the mold. This process is depicted in Figure 23.18. Heating is mostly achieved with infrared radiation and cooling is achieved with air or water sprays.

An important factor with thermoforming is that the polymer should show a pronounced *rubbery region* on the temperature scale. For this reason, amorphous polymers such as PVC, PS, poly(methyl methacrylate) (PMMA), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), etc. are well suited for thermo forming. With semicrystalline polymers, the rubbery region is largely masked by the crystallinity (Fig. 23.19). With PE and polypropylene (PP), thermoforming is, therefore, a critical operation, in which the processing conditions should be very carefully controlled.

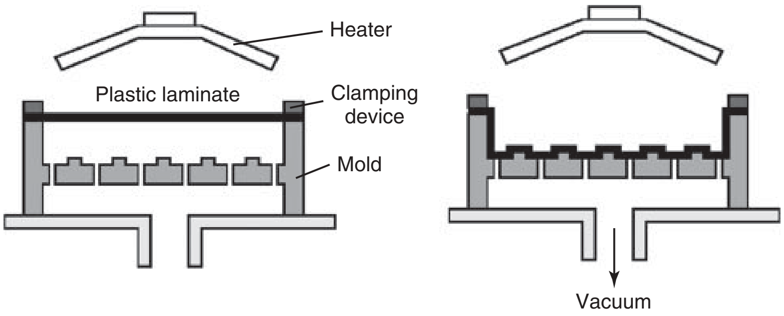


Figure 23.18 Simplified diagram of thermoforming.

Only high-molecular grades show sufficient rubbery behavior above their melting point to enable a thermoforming process. PA, PET, and poly(butylene terephthalate) (PBT), however, will be very difficult to shape using this technique.

With thicker articles or with complex shapes, vacuum does not always provide a sufficiently high force to produce the required deformation. Therefore, air pressure or plugs are sometimes applied, either simultaneously or consecutively. Typical areas of application are cups and trays for food packaging, articles with a larger area such as lighting ornaments, casings for appliances and machines, kitchen dressers, bath tubs, rowing boats, etc. The molds for thermoforming are simpler and cheaper than for injection molding. Cast aluminum is excellently suited for thermoforming molds; experimental molds can be made from timber or gypsum.

Thermoforming shows two important drawbacks. First, the pattern of deformation results in highly uneven wall thicknesses in the finished article. In a cup, for example, the lower brim may be half as thin as the middle or the upper rim. Second, the fact that deformation takes place in the rubbery condition. In this condition, straining is accompanied by chain orientation, which is frozen in upon rapid cooling. When the article is heated to above its T_g, it tends to recover its original shape and deforms, but at lower temperatures it shows a strong tendency to shrink.

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