

Handbook of Thermoplastic Elastomers

Second Edition

**Edited by
Jiri George Drobny**



HANDBOOK OF THERMOPLASTIC ELASTOMERS



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Jiri George Drobny



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4 Processing Methods Applicable to Thermoplastic Elastomers

4.1 Introduction

Polymeric materials come in a variety of forms. They may be solids of different hardness, liquids, in solutions, or dispersed in water as latex or a suspension. Some are converted into finished products as received, i.e., without modifications; others are modified, dissolved, blended, or mixed to produce desired processing and performance characteristics. Thermoplastics are generally processed by methods shaping them in the molten state to desired shapes and sizes. Such methods are often referred to as *melt-processing methods*. Most thermoplastics are not subjected to cross-linking, which means that they can be remelted and shaped again. Thus, production scrap or used parts can be utilized again, at least as a partial replacement of virgin materials.

Thermoplastic elastomers (TPEs) are materials that can be generally processed by melt processing methods used for plastics. The following sections will describe in some detail processing methods used for the fabrication of products from thermoplastic materials. Because of the large number of types of thermoplastic elastomers, these processing methods may be applicable only to some of them. On the other hand, there are some techniques suitable specifically for TPEs. Specific processing methods and conditions used for individual TPEs and other relevant details are included in chapters discussing respective materials.

4.1.1 Properties Influencing Processing

4.1.1.1 Flow Properties

Thermoplastic elastomers, as any other thermoplastic materials, are formed into articles almost exclusively by melt processes that rely on the flow of the melted material at elevated temperatures. Injection molding, blow molding, extrusion, and rotational

molding/lining are all examples of melt processing. The most widely used melt processing methods, their advantages and disadvantages are listed in [Table 4.1](#). An understanding of melt flow is essential for success with these processes. The study of the flow of materials including that of polymers is known as *rheology*.

The rheology of a thermoplastics melt is complex, being very dependent on temperature and shear rate. This means that the melt viscosity—the characteristic that makes flow easy or difficult—can vary widely in the melt condition. The two key points about the flow of thermoplastics are that the behavior is non-Newtonian and that viscosities are very high. These characteristics are dictated by the long polymer chain molecular structure of the materials. One practical consequence is that considerable force is required to make a plastics melt flow into a mold or through a die. This explains why plastics processing machinery and molds must be very robust and are costly. Flow behavior pertaining to mixing is discussed in [Section 4.2.1.2](#).

To understand and control melt processes, it is necessary to define the way in which melt viscosity changes with temperature and shear rate. The *shear rate* is a measure of how fast the melt passes through a channel or orifice. A simple fluid such as water has a constant viscosity value regardless of shear rate. This is known as *Newtonian behavior*, in which the fluid can be described fully by a single constant—the viscosity. By contrast, the viscosity of a melt of a plastic at a constant temperature changes markedly as the shear rate changes. This is *non-Newtonian behavior*. There is no single viscosity value. The viscosity value for such a melt must always be related to the shear rate at which it was determined, and strictly it should always be referred to as the *apparent viscosity*, although this qualification is usually assumed rather than explicitly stated. An important consequence follows: For a viscosity to be truly useful in determining how a process will turn out, it

Table 4.1 Comparison of Molding Techniques and Extrusion for Thermoplastic Polymers

Process technique	Advantages	Disadvantages
Injection molding	The most precise control of shape and dimensions, highly automatic process, fast cycle times; the widest choice of materials.	High capital cost; is only good for large numbers of parts; large mold pressures (typically 140 MPa, or 20,305 psi).
Compression molding	Lower mold pressures (typically 7 MPa, or 1015 psi); does minimum damage to reinforcing fibers (in composites); large parts are possible.	Requires more labor; longer cycle than injection molding; less shape flexibility than injection molding; each charge is loaded by hand.
Transfer molding	Good for encapsulating metal parts and electronic circuits.	Some scrap with every part and each charge is loaded by hand.
Blow molding	Can make hollow parts (such as bottles); stretching action improves mechanical properties; fast cycle; requires low labor.	No direct control over wall thickness; cannot mold small details with high precision; requires polymer with high melt strength.
Rotational molding and rotolining	Labware that is shatterproof and will not contaminate samples; small to very large vessels; valve lining, bellows, items with complex geometry, containers.	A slow process, requires labor and involves numerous moving parts; a great deal of cleaning and surface conditioning is necessary.
Extrusion	Used for films, sheets, wraps, or long continuous parts (i.e., pipes, wire, and cable insulation).	Must be cooled below its glass transition temperature to maintain stability.

Ebnesajjad S. *Fluoroplastics, volume 2, Melt processible fluoropolymers: the definitive user's guide and databook*. Norwich (NY): *Plastics Design Library*; 2003.

should be measured at about the same shear rate experienced in the process (see [Table 4.2](#)). Unfortunately, this is not true of the most popular and widely available measure of melt viscosity, the melt flow rate (MFR) or melt flow index (MFI).

The melt flow rate test is performed at a low shear rate, so MFR figures will be at their least inaccurate for medium to low shear rate processes like blow molding and thermoforming, and will be most inaccurate for injection molding. The quoted MFR value is the weight of polymer melt flowing through an

orifice in specified conditions, so the higher the MFR value, the lower the melt viscosity and the easier the material will flow. Even though MFR values are measured at an unrealistically low shear rate, it might seem that the test would accurately rank different materials for comparative ease of flow. Unfortunately, not even this can be guaranteed because of the varying degree of shear dependency shown by different materials and grades. The MFR test owes its continued survival mostly to tradition and the fact that it is cheap and easy to perform [1].

Table 4.2 Process Shear Rate Ranges

Process	Typical Process Shear Rate, s^{-1}
Injection molding (Section 4.4)	1000–10,000
Extrusion (Section 4.3)	100–1000
Transfer molding (Section 4.6)	1–100
Rotational molding/lining (Section 4.8)	<100
Compression molding (Section 4.5)	<1
Blow molding (Section 4.7)	—

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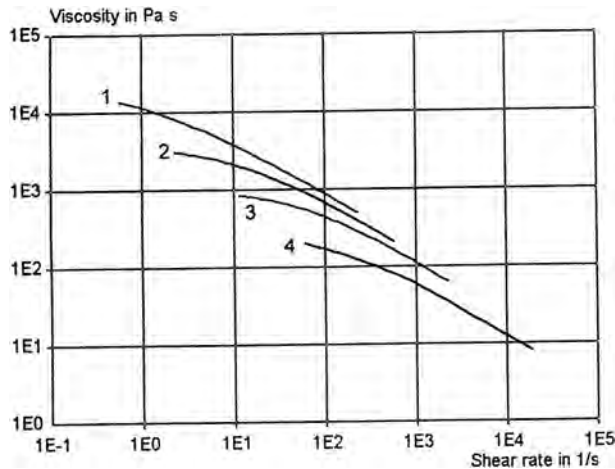


Figure 4.1 Example of viscosity curves at 260 °C for polypropylene. 1-Blow molding grade (MFR = 0.4); 2-Calenderfilm grade (MFR = 1.1); 3-Block copolymer molding grade (MFR = 5.0); 4-Thin wall molding grade (MFR = 19.0).

More reliable viscosity measurements can be made with high shear *rheometers*. Material testing is performed at shear rates similar to those experienced during extrusion or injection molding, so the resulting values have a direct bearing on process considerations (Fig. 4.1). Even then, it is not a simple matter to depict flow behavior. A number of viscosity models have been developed to describe this behavior, and while a detailed discussion is beyond the scope of this work, it is as well to be aware of some of these models because they are used in process simulation computer programs. These programs predict the effect of product and control parameters on the end product. The simplest version is known as the *Power Law Model*. More elaborate and accurate models are based on higher order versions of the power law, or on the *Carreau*, *Cross*, or *Ellis* models. Flow data corresponding to these models are still not widely published but can usually be obtained on request from materials suppliers. Developers of flow simulation software maintain extensive databases of plastics flow data, but these are not freely accessible [1]. The situation has improved with the development of *Campus*, the free industry-standard materials database that includes rheological data (www.campusplastics.com).

A third type of flow measurement is sometimes available, although its popularity appears to be waning. *Spiral flow method* attempts to relate flow information directly to the injection molding process by using an industrial molding machine to run the

tests, in conjunction with a test mold in which a long flow channel is arranged in a spiral. The disadvantage is that reproducibility between different presses and molds is low. The spiral flow behavior of thermoplastic is characterized simply by the flow length observed under prescribed conditions of temperature, pressure, and flow rate. Flow length measurements are specific to test conditions and cannot be extrapolated to other circumstances. However, because the test is performed at typical process shear rates, it will reliably rank materials for ease of flow at the test conditions. Another drawback is that the test is rather unwieldy and time consuming.

4.1.1.2 Thermal Properties

The melt processing of thermoplastics involves first heating the material to a point at which it can be made to flow, and then cooling it again to a temperature at which the formed object is stable. This requirement constitutes a major energy demand in the forming process and is central to the efficiency and economy of the process. It is a common perception that thermoplastics are difficult to heat and even harder to cool, and that this is particularly true of thermoplastic elastomers. The perception is a sound one, and a study of thermal characteristics shows why this is so.

The heat energy or heat content of a system is a function of the mass of a material, its specific heat, and the temperature change. The quantity is often referred to as *enthalpy*. The heat energy to melt a thermoplastic is therefore proportional to the difference between its melt temperature and room temperature. Theoretically, the heat energy to be removed in cooling, in the case of a molding, is the difference between the melt temperature and the mold temperature. In practice, the component can usually be ejected at a higher temperature, and only a region near the surface needs to be at this temperature, so the heat to be extracted is considerably less.

The heat energy involved in heating and cooling varies considerably from one polymer to another (Table 4.3). An additional consideration is the fundamental difference between *amorphous* and *semicrystalline* plastics. For semicrystalline materials, the heat requirement for melting includes additional quantity for melting the crystalline structure. This is known as *latent heat of fusion* of the crystalline structure. For example, polypropylene has

Table 4.3 Process Heat Requirements of Different Thermoplastics

Polymer	Melt Temperature, °C	Mold Temperature, °C	Heat Required to Melt, kJ/kg	Heat Removed on Cooling, kJ/kg
Polystyrene	200	20	310	310
ABS	240	60	451	369
PMMA	260	60	456	380
Polyamide 6	250	80	703	520
Polyamide 6/6	280	80	800	615
Polypropylene	260	20	670	670
HD polyethylene	260	20	810	810

Maier C, Calafut T. *Polypropylene: the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 1998.

the heat of fusion 670 J/g or 570 kJ/kg and it is more than double of that of polystyrene and considerably greater than the energy requirement for materials with much higher melt temperatures, such as polycarbonate, PPO and PES. The cooling requirement for PP and HDPE is even more demanding. These thermal characteristics have a direct bearing on processing. They mean, for example, that cooling for a polypropylene mold must be much more efficient than that for most other plastics. The need is often overlooked, and it is responsible for the commonly experienced difficulty of overheating cores and pins.

The specific heat and thermal conductivity of plastics vary greatly with temperature. So indeed does density. These variations are not brought out in data sheets that deal only with solid properties and are not widely appreciated by plastics processors. It is still difficult to obtain information about the thermal properties of plastics in the melt state, even though this is important for plastics process calculations. A plot of enthalpy against temperature shows the extent of the variation and also clearly differentiates between amorphous and semicrystalline materials [2]. The enthalpy curve for the semicrystalline polymers shows a distinct discontinuity or “knee”. The rapid increase in enthalpy at this point corresponds to the latent heat of crystalline fusion. The curve for an amorphous material shows no such discontinuity. The enthalpy curves give a direct readout of the approximate heat energy to be added or removed when heating or cooling a plastics material and deserve to be more widely distributed. Table 4.4 gives guideline spot values for the thermal properties of thermoplastics melts. In reality, the values for density, specific heat, and thermal conductivity are temperature-related variables. The

latent heat of crystalline fusion is zero for amorphous polymers because the phenomenon is absent. *Freeze temperature* is the point at which the material becomes a solid. The *no-flow temperature* is not a fundamental property. Rather, it is a useful concept that has been introduced in flow calculations to compensate for shortcomings in viscosity models at low temperatures near to the solidification. Effectively, it is the temperature at which the viscosity of a not-quite-frozen polymer is held to be infinite. Reinforcements and fillers tend to reduce the specific heat and enthalpy of polypropylene, but the effect is not very great [2]. If figures are not available for reinforced grades, it would be reasonable to use data for base grades, which would then provide a small safety factor.

4.1.1.3 Shrinkage and Warping

Shrinkage and warping are complex consequences of melt processing. For semicrystalline plastics such as polypropylene, the situation is particularly complicated. Crystalline regions exhibit a greater shrinkage than the surrounding amorphous regions, so semicrystalline materials typically have a greater and more variable degree of shrinkage than amorphous materials.

Plastics melts are compressible, particularly at the high pressures used in injection molding and extrusion. The fundamental property is the relationship between pressure, volume, and temperature. Measurements describing this relationship for any material are known as PVT data and are usually shown graphically in the form of a PVT plot. The plot for polypropylene (Fig. 4.2) shows the now-familiar

Table 4.4 Approximate Thermal Melt Properties of Different Thermoplastics

Polymer	Melt Density, g/cm³	Specific Heat of Melt, kJ/kg-K	Thermal Conductivity of Melt, W/m-K	No-flow Temperature, °C	Freeze Temperature, °C	Latent Heat of Crystalline Fusion, kJ/kg
Polystyrene	0.88	1.8	0.13	130	95	0
ABS	0.89	2.1	0.15	140	105	0
PMMA	1.01	2.0	0.15	140	110	0
PA 6	0.95	2.7	0.12	220	215	200
PA 6/6	0.97	2.7	0.13	250	240	250
Polypropylene	0.85	2.7	0.19	140	120	235
LD polyethylene	0.79	3.2	0.28	110	98	180
HD polyethylene	0.81	3.3	0.29	120	100	190

Maier C, Calafut T. *Polypropylene: the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 1998.

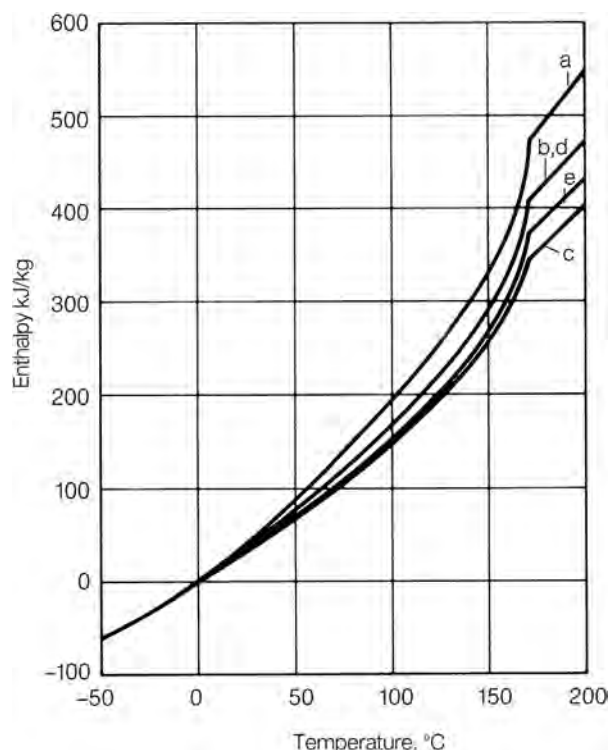


Figure 4.2 Example of a PVT plot for polypropylene homopolymers, measured during heating up.

discontinuity or “knee” in the curve that corresponds to the region of crystalline fusion. By contrast, PVT plots for amorphous materials reveal a simple change of slope at a point corresponding to the glass transition temperature.

The PVT curves make it clear that shrinkage occurring as a result of melt processing is not just a function of thermal expansion and contraction but is also related to the compressibility of the melt. In practice, this relationship is made complex because process conditions will determine the extent to which the melt is compressed. Furthermore, process conditions are unlikely to be uniform throughout the part. For example, polypropylene shrinkage is related to the degree of crystallinity in the material and hence to the cooling rate. A greater degree of crystallinity leads to a higher rate of shrinkage and also to a greater differential between shrinkage in the flow direction and shrinkage measured transversely to flow. The differential effect is another consequence of the viscoelastic property of long-chain molecules. During flow, the molecules are aligned to a limited extent in the flow direction and are extended to a degree proportional to shear rate. On cooling, a partial recovery of this extension gives rise to

a higher shrinkage value. The effect is more pronounced in materials with a wide distribution of molecular weight. It is the differential shrinkage that is responsible for warping, the name given to the distortion of an apparently correctly formed part during and after cooling.

A further difficulty is that shrinkage takes place over a period of time. In the case of an injection molding, the greater part of total shrinkage is evident virtually immediately after ejection from the mold, but shrinkage will continue for more than 24 h. During this time, further crystallization and relaxation of internal stresses result in small dimensional changes. Thereafter, further changes take place very slowly, but the effect is dependent on temperature and will occur more rapidly if the part is exposed to elevated temperatures. The sum of all these considerations means that it is impossible to state a simple and precise design figure for the shrinkage. Shrinkage can be minimized by using high viscosity, controlled rheology, or nonnucleated grade types. Warpage can be limited by using materials with a narrow molecular weight distribution, particularly the controlled rheology types. Although it is a volumetric phenomenon, shrinkage is usually expressed as a linear quantity either as a percentage or as a linear ratio (mm per mm, for example) (Table 4.5).

The effect of fillers and reinforcements on shrinkage depends largely on the physical form of the additive. Particulate fillers such as talc or glass beads tend to counteract the effect of molecular orientation and so not only reduce shrinkage but also reduce shrinkage differentials and hence the tendency to warp [3].

Fibrous reinforcements also reduce shrinkage, but because during flow the fibers become partially oriented, the reduction is much greater in the flow direction than in the transverse direction [3]. This results in an increase in shrinkage differentials, although the increased tendency to warp is opposed to an extent by the greater stiffness of the reinforced material. In complex moldings, the varying flow patterns make it very difficult to anticipate shrinkage correctly by any means other than computer analysis. Even then, it is wise to design the product assembly to be tolerant of a degree of distortion and inaccuracy.

4.1.2 Preprocessing

Before any thermoplastic is processed into semi-finished or end products, and irrespective of the

Table 4.5 Approximate Shrinkage Range of Different Thermoplastics

Polymer	Shrinkage, %	Shrinkage, mm/mm	Range, %
SAN	0.4–0.6	0.004–0.006	0.2
ABS	0.4–0.7	0.004–0.007	0.3
Polystyrene	0.4–0.7	0.004–0.007	0.3
PVC-U	0.4–0.8	0.004–0.008	0.4
PET	1.6–2.0	0.016–0.020	0.4
PMMA	0.3–0.8	0.003–0.008	0.5
Polyamide 6	0.2–1.2	0.002–0.012	1.0
Polyamide 6/6	0.8–2.0	0.008–0.020	1.2
Polypropylene	1.2–2.5	0.012–0.025	1.3
HDPE	1.5–3.0	0.015–0.030	1.5
LDPE	1.0–3.0	0.010–0.030	2.0

Maier C, Calafut T. *Polypropylene: the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 1998.

process to be adopted, there are a number of prior considerations to be taken into account. For many thermoplastic materials, the principal questions are those concerning drying and coloring.

4.1.2.1 Drying

Most thermoplastic elastomers have a low tendency to absorb water and will not normally require drying before processing. If any moisture is present, it will be as water condensed or adsorbed on the polymer surface. This can occur, for example, if the material is moved from a relatively cool store to a warm and humid environment in the processing shop. Because the effect is purely a surface one, the moisture can be easily removed by conventional dryers, but of course it is better to avoid the problem by attending to the storage conditions. Some TPEs tend to absorb moisture, and these require thorough drying (see processing details for the individual materials).

A simple hopper dryer will usually be sufficient to remove surface moisture from the granules. However, if the material is in the form of powder, the problem will be more severe, simply because of the greatly increased surface area available for adsorption. Powdered materials constitute an explosion hazard and should not be dried in conventional equipment intended for granules. Instead, the problem should be

circumvented by storing producer-dried powders in sealed containers at equable temperatures.

4.1.2.2 Coloring

Most of the TPEs are essentially colorless materials, ranging from milky white to near transparent depending on form and type. This characteristic means that it is possible to color the material to almost any desired shade by the inclusion of suitable dyes or pigments. The quality of the end result depends crucially on the even and thorough dispersion of the colorant throughout the melt, and processors have a variety of means at their disposal for achieving this. Coloring operations can be broadly divided into those that are coincidental with the forming process (in-process coloring) and those that precede it (preprocess coloring).

Preprocess coloring involves a separate coloring operation that takes place before the primary forming process. The method gives very good results but is relatively costly and adds to the heat history of the material. *In-process coloring* methods are, as the name implies, carried out during and as an integral part of the primary forming process. These processes—*injection molding*, *blow molding*, *extrusion*—involve the use of an extruder screw as a melt plasticizer, and in this case it is pressed into service for the additional duty of dispersing a colorant

additive throughout the melt. The process screws are not designed expressly for this duty and cannot be optimized for it. Instead, the machine designer has to compromise to produce a screw and barrel that will work well enough with a range of polymers, while providing a reasonable balance between the conflicting requirements of throughput, heat transfer, mixing, pressure, and cost. Process conditions, too, must be a compromise between what is best for dispersion and what is best for the physical product.

Consequently, the principal worry with in-process coloring is how to achieve widespread, uniform, and repeatable dispersion of color additives. Mixing can be improved by the addition of simple static mixers such as screen packs or flow-divider nozzles, but at the cost of greater process pressure drops and perhaps reduced throughput. On the plus side, no additional heat history is imparted to the material, and the equipment, energy, and time are effectively free. The processor also has no need to hold large inventories of bulk colored material and can respond rapidly to changing needs and specifications. The most common method of in-process coloring is the use of color concentrate and to a lesser degree liquid color and dry color.

Color-compounded polymers come to the processor already colored in standard or custom colors. A specialist compounder produces these materials either by the TPE manufacturer or more commonly the color is added in a melt process, generally a continuous process using an extruder or a screw-based mixer. Batch processes can also be performed in internal mixers or on roll mills but are less convenient and uniform for thermoplastics. The color-compounding process concludes with a pelletizing operation that results in colored pellets or granules ready for use in injection molding, extrusion, and other forming processes (for details see [Section 4.2.5.2.1](#)).

The compounding equipment can be optimized for mixing, so the colorants are uniformly and widely dispersed throughout the material. Together with the availability of specialist color formulation and color measuring equipment, this gives consistent and high quality results, but there are a number of disadvantages. Certain TPEs are prone to oxidation at melt temperatures and must be stabilized to counteract this. By imposing an extra melt operation, the color compounding process adds to the thermal strain or as it is often known, the *heat history of the material*. The additional operation also adds an extra cost, which is partially offset by the efficiency gains of a dedicated business. Standard color ranges are necessarily

limited, and the minimum order quantity for custom colors may be high.

The processor uses color-compounded materials in exactly the same way as natural grades of the TPEs. Color dispersion is already complete, so process conditions and equipment need take no account of this consideration. The color shade of the finished article can be taken for granted, provided quality checks are performed on the incoming compound. Minor process parameter adjustments may be necessary when changing from natural to color-compounded material, but this is just a function of the minor rheological and thermal effects of the color additive on the polymeric matrix.

Color concentrate or masterbatch combines some of the advantages of preprocess and in-process coloring. The color concentrate is a thermoplastic compounded in the preprocess manner with a very high loading of colorant. It is then added in a minor proportion to natural (uncolored) polymer, and the process plasticizing screw has the task of mixing and distributing the colored polymer proportion throughout the mass of natural material. This requirement is relatively unexacting because the primary task of dispersion has already been performed during manufacture of the color concentrate. Consequently, there should be no chance of color agglomerates forming, even if the process screw is a relatively inefficient mixer.

The degree of dilution, or in other words the proportion of concentrate added to the polymer to be colored, is known as the *let-down ratio*. The concentrate manufacturer will aim to get the ratio as large as possible, but it is limited by the mixing efficiency of the conversion machinery and by the practicalities of concentrate compounding. Color concentrate is now the most widely used method of coloring polypropylene. The processor requires only simple metering equipment to control the let-down ratio, and the added heat history is negligible. On the downside, the carrier polymer used in production of the color concentrate may have a minor effect on processing and on the properties of the finished part. This is because the carrier for a polypropylene color concentrate is unlikely to have exactly the same characteristics as the grade being colored. Indeed, the carrier may well be of polyethylene rather than polypropylene. These differences arise from the economic and logistical need to produce a near-universal color concentrate. The effects are usually insignificant provided the let-down ratio remains large.

4.2 Mixing and Blending

In many cases materials used to manufacture products from thermoplastics are used as received. However, some of them need to be prepared for further processing by the addition of other ingredients to attain specific processing characteristics and/or physical and mechanical properties. This process often referred to as *compounding* is essentially preparing a uniform mixture by blending and/or mixing. The method of preparing a uniform mixture depends on the nature of the components. If all components are solids, they are blended in a blender using paddles, screws, ribbons, or propellers, and the process is referred to as *dry blending*. If they are all liquids, the blending is done by simple mixing with the use of some sort of propeller. If both liquid and solid components are in the mixture, the choice of method depends on the component that is largest in volume. Although in polymer processing all the above mixing and blending methods are used, the main focus in the following sections will be on polymeric melts.

In many cases polymeric solids are melted and blended or mixed in the molten stage. Frequently, various additives, such as powders, waxes, resins, pigments, reinforcing agents, liquid or solid plasticizers, antidegradants, colorants, or other specialty chemicals are added in the mixing process. Mixing in the molten stage requires specialized equipment, such as batch mixers or continuous mixers, and consumes a large amount of energy. The finished mix is often called a *compound* or *formulation* and can be in the form of pellets, sheets, slabs, or ropes, depending on the form required for the next step in the manufacturing process.

In combining together different materials to form a mixture, there are two major concerns. One of them is to produce a homogeneous mixture. The compositional homogeneity of the mixture in a mixing process is achieved through *distributive mixing*. The second concern is to produce as fine and uniform dispersion of the ingredients as possible. The reduction of disperse phase during mixing is described as *dispersive mixing*. Another consideration regarding the mixing process is whether the substances being mixed are fully miscible, partially miscible, or totally immiscible. They can be all liquids (e.g., molten polymers) or combinations of particulates, that is, solids and liquids. If the mixtures are liquids, it is important to know the relative

viscosities (or viscosity ratios) and the interfacial tensions between the phases [4].

4.2.1 Basic Concepts Pertaining to Mixing

4.2.1.1 Melting

Melting occurs when a solid polymer turns fluid as it is heated. Many polymers have crystalline molecular structure, and therefore a distinct melting point (*crystalline melting point*, frequently denoted as T_m). Materials that are “rubbery” and without crystallinity are called *amorphous*. When these polymers melt, their transition from glassy to molten state occurs at the *glass transition temperature* (T_g). Since this transition is gradual, the exact value of the glass transition temperature may not always be well defined. Some polymers are *semicrystalline*, that is, partly crystalline and partly amorphous, and do not display a distinct melting temperature.

4.2.1.2 Rheology and Flow Pertaining to Mixing

Rheology, in general, is a scientific discipline that concerns the flow of fluids. The rheology of polymeric fluids (mainly melts) is rather complex because these materials exhibit many unusual features related mainly to their molecular structure. Polymers are usually *viscoelastic*, which means that they exhibit both *viscous* and *elastic* features. These features are apparent when a polymeric fluid is displaced slightly and then all forces acting upon it are removed. The fluid flows back slightly but not completely. *Elasticity* of a material is its ability to retract to its original dimensions. If elasticity is not exhibited, then the fluid is totally viscous.

A purely elastic material (*Hookean elastic*) behaves in such a way that its deformation is directly proportional to the applied stress, i.e., follows the Hooke’s law. If elasticity is not exhibited, then the material is totally *viscous*. Polymers are usually *viscoelastic*, which means that they exhibit both viscous and elastic features. These features are apparent when a polymeric fluid is displaced slightly and then all forces acting upon it are removed. The fluid flows back slightly but not completely.

Flow of a fluid can be imposed by either shear or elongational forces. *Shear* forces are applied when a fluid is placed between two parallel plates and one

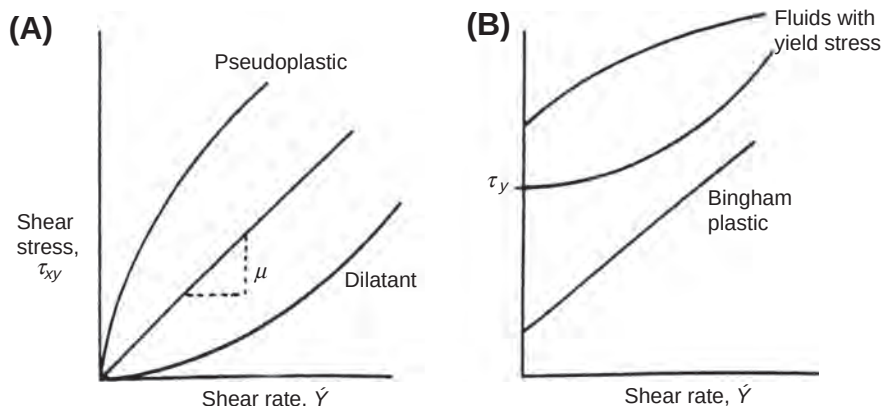


Figure 4.3 Flow curves for non-Newtonian fluids. (A) Time independent. (B) Time dependent.

of the plates is moving faster than the other. Purely *elongational* flow occurs when a fluid descends from an orifice and thins down to a smaller diameter.

The quantity providing the measure of deformation of a fluid (i.e., changes in its shape or movement) is the shear strain. *Newtonian* fluids exhibit a linear dependence of shear rate (measure of its flow) on the imposed shear stress. Thus, the plot of shear stress versus shear rate (referred to as *flow curve*) for a Newtonian fluid is a straight line passing through the origin and having a slope expressing its resistance to flow, i.e., its *viscosity*, μ (see Fig. 4.3). *Non-Newtonian* fluids are broadly classified as time-independent fluids, time-dependent fluids, and viscoelastic fluids [5].

Time-independent non-Newtonian fluids are those for which the shear rate at any point is a function of only the instantaneous shear stress (Fig. 4.3). *Time-dependent* non-Newtonian fluids are those for which shear rate depends on both the magnitude and duration of the applied shear. Such fluids also show a relationship between shear rate and the time lapse between consecutive applications of shear stress

(Fig. 4.4). *Viscoelastic* fluids display the behavior of partial plastic recovery upon the removal of a deforming shear stress.

Time-dependent non-Newtonian fluids can exhibit *yield stress*, denoted as τ_y , which can be thought of as a minimum stress value that must be exceeded for deformation to occur. Flow curves of such fluids are shown in Fig. 4.3(B). Also shown in that illustration is an idealized time-dependent fluid that is often referred to as *Bingham plastic*.

Many industrial fluid-like materials can be described as being *pseudoplastic*. The flow curve of a pseudoplastic fluid is depicted in Fig. 4.3(A). The *apparent viscosity* of a pseudoplastic fluid decreases with increasing shear rate, and such a fluid is referred to as a *shear thinning* fluid. *Dilatant* fluids are time-independent materials exhibiting an increase in apparent viscosity with increasing shear rate. The flow curve for a dilatant fluid is also shown in Fig. 4.3(A).

Time-dependent non-Newtonian fluids can be classified as thixotropic and rheopectic. *Thixotropic* fluids display a reversible decrease in shear stress with

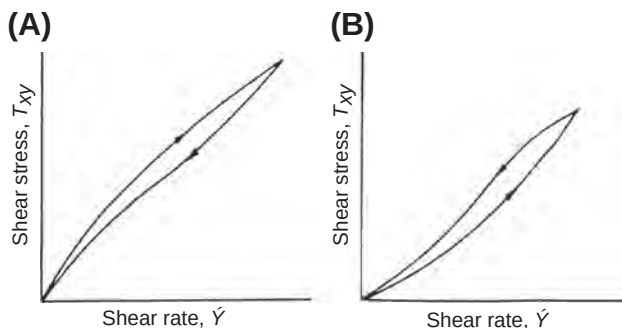


Figure 4.4 Hysteresis loops for time-dependent fluids. (A) Thixotropic hysteresis. (B) Rheopectic hysteresis.

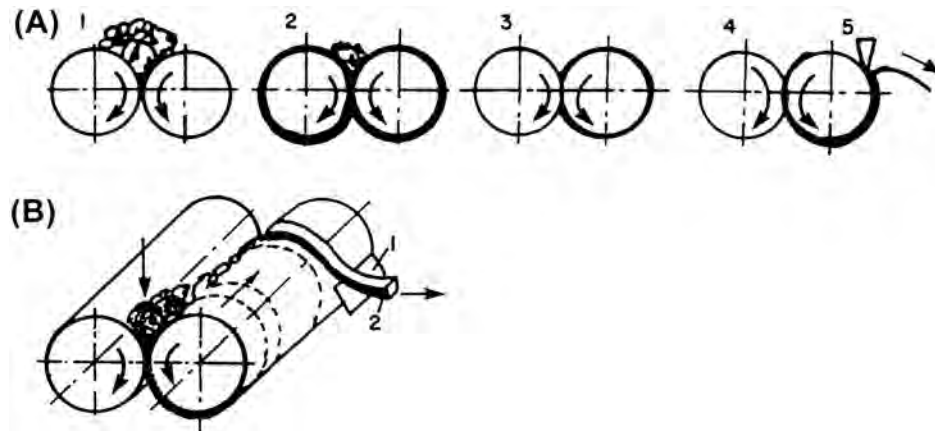


Figure 4.5 Operation of mixing rolls. (A) Batch operation ((1) loading; (2) rolling; (3) end of rolling; (4) mass shear; (5) knife). (B) Continuous operation (1—knife, 2—continuous removal of the material).

time at a constant shear rate (Fig. 4.4(A)). *Rheopectic* fluids (Fig. 4.4(B)) are sometimes called *antithixotropic* fluids because they exhibit a reversible increase in shear stress over time at a constant rate of shear under isothermal conditions [4].

Examples of non-Newtonian materials are shown in Table 4.6.

When a polymeric melt is forced through a circular opening (e.g., through an extrusion die), the emerging strand frequently has a considerably larger diameter than the opening. While a contraction may sometimes occur, most polymeric melts expand under these circumstances, sometimes as much as eight times [6]. This phenomenon is referred to as *die swell*.

Table 4.6 Examples of Non-Newtonian Fluids

Type of Fluid		Examples
1. Time-independent fluids	Fluids with a yield stress	Various plastic melts, oils, sand suspensions in water, mayonnaise, shortening, greases, toothpaste, soap, detergent slurries, paper pulp
	Pseudoplastic fluids (without yield stress)	Rubber solutions, adhesives, polymer solutions and melts, starch suspensions, cellulose acetate, mayonnaise, paints, various biological fluids
	Dilatant fluids (without yield stress)	Aqueous dispersions of titanium dioxide, corn flour/sugar solutions, gum arabic in water, wet beach sand, iron powder suspended in low-viscosity liquids
2. Time-dependent fluids	Thixotropic fluids	Melts of high-molecular-weight polymers, various greases, margarine and shortening, printing inks, paints, various food substances
	Rheopectic fluids	Bentonite clay suspensions, gypsum suspensions, various oils, dilute suspensions of ammonium oleate
	Viscoelastic fluids	Bitumen, flour dough, napalm, various jellies, polymers and polymer melts (e.g., polyamide), various polymer solutions

Ref. [5].

During the melt mixing of polymeric compounds, flow in the mixing equipment may be caused by drag (drag flow) or by positive displacement. While one or the other may predominate, a combination of the two usually takes place [5].

Drag flow can be viewed in its simplest form as one plate sliding on top of another with polymer between them [7]. If there is no pressure, the velocity profile is linear and referred to as *pure drag flow*. If pressure is forcing the melt to move in the same direction or in the opposite direction it is flowing, the velocity profile becomes curved [7].

Positive displacement occurs by mechanically enclosing and transporting a pocket of a melt. Such pockets can be formed in mixing equipment with two intermeshing screws (see Section 4.2.3.3.2). The polymer is forced along the screw axis [7].

4.2.1.3 Residence Time

Residence or dwell time is the amount of time that an arbitrarily selected, small volume element in the feed stream spends inside the mixing equipment. Frequently, for an efficient mixing the entire residence time distribution has to be known. It can be roughly estimated by dropping several black pellets into the mixer while a white material is being mixed. At first, there is no change at the exit, but after that the material blackens and eventually turns white again. If the intensity of the black color is directly proportional to the concentration of the black colorant, this intensity can be plotted as a function of time, providing the residence time distribution [8].

4.2.1.4 Specific Mechanical Energy

The amount of energy required for mixing a polymeric compound is usually dictated by the amount of mixing needed. While better mixing is desirable, there are limitations set by the amount of exposure a polymer can tolerate. Knowing how much energy is required for an optimum mixing determines the size of the mixer and drive and the energy consumption while the equipment is in operation [9].

To compare different mixing machinery and for scale-up, the concept of *specific mechanical energy* (SME) is used. It is essentially the drive energy consumption per unit weight of polymer mixed by the specific equipment. The energy consumption is usually determined by measuring the current (I) in amps through the electric motor. For direct-current

motors, the power (P) in watts is calculated using the well-known relation:

$$P = I \cdot V, \quad (4.1)$$

where I is the current in amps and V is the voltage in volts.

The SME is obtained by dividing the power by the mass flow rate $\dot{m}_r$ (in kg/h) and multiplying by the motor efficiency η :

$$\text{SME} = \eta \cdot P / \dot{m}_r = \eta \cdot V \cdot I / \dot{m}_r \quad (4.2)$$

For both direct-current (DC) and alternating-current (AC) drives, the torque is proportional to the current exerted on the drive. The power can be calculated by multiplying the torque by the rotational speed [9].

4.2.2 Polymer Blends

The development of new types of commercial polymers has decreased, with considerably more interest directed to polymer blends, where synergies of properties are exploited to meet new application needs [10]. In fact, commercial blends were developed before the use of pure polymers, because early polymers did not provide desired properties [10]. Recent statistics indicate that blends represent more than 30% of all polymers used, with an annual growth rate estimated at about 9% [11].

Only a few polymers are miscible, i.e., mutually soluble. The measure of compatibility in general is the magnitude of *interfacial tension* between the two materials. Ideally, when the interfacial tension is zero, they dissolve in each other. As the interfacial tension increases, the two materials are increasingly incompatible and immiscible with each other, in a thermodynamic sense. An example of values of interfacial tension for different polymer melt pairs is in Table 4.7. Interfacial tensions between two homopolymer melts have been found to be largely determined by the differences in polarity of the structural units. The larger the polarity difference is, the larger the interfacial tension. Thus, the greatest interfacial tension between polymer melts listed in Table 4.7 is between polyethylene and polyamide 6 [12].

When immiscible polymers are combined in the mixing process, separate phases are formed. If only two immiscible polymers are blended, droplets may form in the final product [11]. As the relative volume of each

Table 4.7 Examples of Values of Interfacial Tensions for Different Melt Pairs

Polymer Melt Pair	Melt Temperature, °C	Interfacial Tension, mN/m
Polyethylene-polypropylene	—	1.2
Polyethylene-polystyrene	180	4.1
	290	4.0–5.0
Polyethylene-polysulfone	290	6.5–7.0
Polyethylene-polyphenylene sulfide	290	7.2–7.9
Polyethylene-polymethylmethacrylate	180	9.0
Polyethylene-polyethylene terephthalate	290	9.2–9.4
Polyethylene-polycarbonate	290	12.5–13.0
Polyethylene-polyamide 6	290	12.8–13.2
Polypropylene-polystyrene	220	5.8
	250	3.7
Polystyrene-polymethylmethacrylate	180	1.2

Ref. [4].

polymer increases, a co-continuous morphology may form instead of droplets. Phase co-continuity may provide the best balance of properties in a blend of polymers. For example, a lamellar structure is preferred when barrier properties are desired [11].

In the early stages of mixing, the polymer of the minor phase is sheared into sheets that gradually disintegrate by forming cylindrical shapes or developing holes. In the next stage, the holes grow until they coalesce and the material from the original sheets forms ribbons and irregular fragments [13]. With additional flow, these fragments may turn into droplets, which may break up further into smaller droplets. These may finally combine (coalesce) into larger droplets. A dynamic interchange between drop coalescence and breakage may occur, and after a sufficient amount of time, equilibrium will be established [14].

The major factor determining the droplet size is its *surface tension*, which depends not only on the nature of the polymer within the droplet but also on the nature of the material that surrounds the droplet [15].

Interfacial tension is essentially the force that holds the droplet together. At the same time, the droplet is entrained in the melt flow inside the mixing equipment, subject to viscous forces that try to pull the droplet apart. The ratio of the two forces is called the *Weber Number*. If the droplet is in such a condition where the Weber Number is greater than some

critical value, it will break up. This critical value is related to the viscosity ratio of the dispersed phase to that of the matrix [16]. The diameter of the dispersed particles has been shown to pass through a minimum value when the viscosities are matched [16]. A reduction in the interfacial tension generally leads to a smaller particle size and better physical properties of the mixed material.

In general, the miscibility of polymers, essentially a reduction of interfacial tension, is improved by the use of *compatibilizing agents* in the mixture. Compatibilizing agents have a similar effect as surfactants in liquid systems (e.g., oil/water mixtures). These agents do not impart thermodynamic compatibility, which would cause the polymers to exist in a single molecularly blended, homogeneous phase [17]. Instead, they anchor themselves to both polymers across their interface. The molecules of compatibilizers have segments, which are soluble in each of the phases. They may have either block or graft structure [18–20]; the former is held to be more efficient; however, graft compatibilizers are used more frequently for cost reasons.

4.2.3 Mixing Equipment

Mixing machines are used to prepare materials with a minimum possible concentration gradient, i.e., with a high uniformity. In some cases this

might be accompanied by a decrease in the thermal gradient in processes involving heat generation and/or transfer.

As pointed out earlier, the design of mixing machine suitable for a given system depends on the physical properties of components to be mixed. The mixing of non-Newtonian materials is essentially done by mechanical devices that combine the ingredients and provide intensive agitation. Common devices are sigma-blade mixers, roll mills, anchor agitators, centrifugal disk-type mixers, and others. Batch mixing is in general suitable if relatively short cycles are required [21].

Heavy pastes and polymeric melts require heavy machinery to achieve satisfactory mixing. Such materials are mixed in either batch or continuous operations. A *batch* mixing process is most frequently performed in a closed volume of the mixing device. Over the course of the mixing cycle, the properties of the mixture may change considerably, and the material is completely discharged at the end of the mixing cycle.

A *continuous* mixing operation requires continuous loading and unloading of the components. There is a drastic variation in the concentration of components at the inlet. When properly performed, continuous mixing decreases these variations to the desired minimum. The main advantage of continuous mixing is that it provides a stable process. Moreover, the power consumption is both lower and more constant than in the batch process. The major disadvantage of continuous mixing is a relatively long mixing time compared to batch technology [21].

4.2.3.1 Batch Mixers

The batch mixer is the oldest and conceptually simplest mixing machine, and as pointed out earlier, the mixing occurs within a single isolated volume; the homogenization and dispersion of different phases is accomplished by rotating *agitators* or *rotors*. Certain technologies, such as mixing of rubber and certain plastics, are still carried out in mixers of this design. Batch mixers can be divided into machines open to the atmosphere (e.g., a roll mill) and machines with enclosed mixing chambers (e.g., the Banbury mixer).

4.2.3.1.1 Roll Mills

The roll mill is the simplest batch mixing equipment. The principal design consists of two horizontal rolls, usually of equal size, arranged side by side and

rotating toward each other at different speeds. The ratio of the peripheral speeds of the rolls, known as *friction ratio*, ranges from 1 to 2 but is usually around 1.2. The higher friction ratio leads to a higher heat generation in the processed material. Friction, speed, and the sizes of the rolls influence the cooling of the material mass and the intensity of its treatment. Depending on the properties of the process material and its desired temperature, the rolls may be internally cooled or heated by using circulating cooling water or a suitable heating medium.

The basic mixing operation is illustrated in Fig. 4.5. The material is charged between the rolls in the form of lumps, pellets, chunks, or powder. As a result of rotation, adhesion, and friction, the material is entrained into the gap between the rolls, and upon discharge it sticks to one of the rolls, depending on their temperature difference and velocities. Another factor is the gap between the rolls. In batch mixing the material after loading passes through the gap between the rolls several times, and the mixing action is due to the different speeds of the rolls. Both the shearing action and entrainment of the material into the gap are very important in the mixing process and transporting of the material through the unit. The gap between the rolls can be adjusted by a massive screw mechanism.

During the operation, cutting of the sheet of the material (“blanket”), folding, and rolling are carried out, which increases the uniformity of the composition. If additives, often in the powder, liquid, or paste form, are to be incorporated, they are added into a rolling “bank” formed between the rolls.

Roll mills are also used for warming up materials for calendering or extrusion. In such cases the warm material is cut into strips that are fed into the calender or extruder often continuously. Another application of roll mills is to cool materials discharged from an internal batch mixer in a form of large lumps (see Section 4.2.3.1.2). The resulting blanket is then transported in the form of strips to the calender or extruder or removed from the rolls as thick sheets.

A thorough theoretical analysis of mill mixing is in Refs [22] and [23].

Two-rotor mixers with open mixing chambers have been developed and manufactured by Werner & Pfleiderer of Germany.

4.2.3.1.2 Internal Mixers

An internal mixer consists usually of two rotors enclosed in a mixing chamber. One of the most

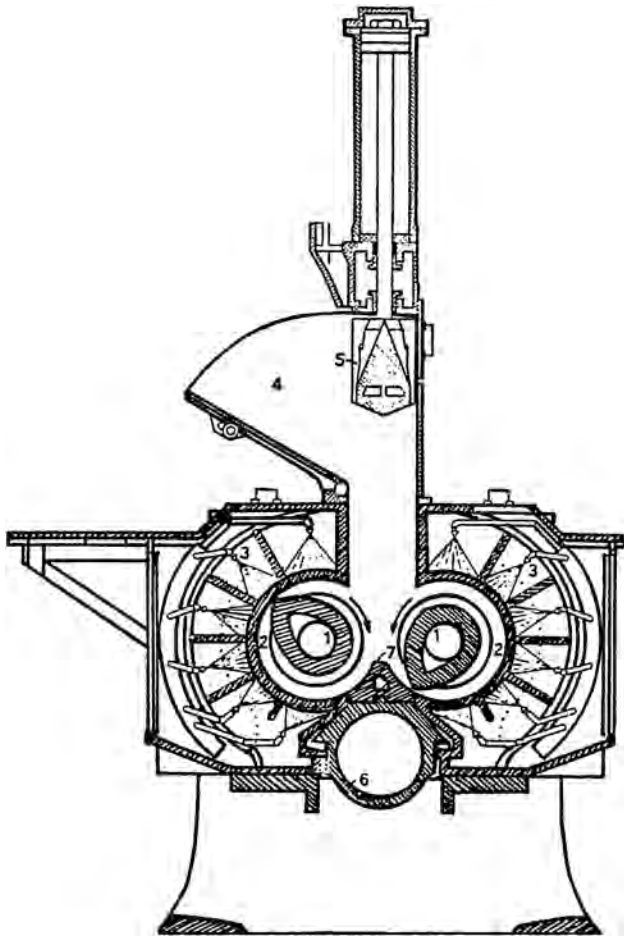


Figure 4.6 Schematic drawing of a Banbury® Mixer.
Courtesy: Farrel Corporation

widely used designs is the *Banbury® Mixer* shown in Fig. 4.6. In this design, the massive rotors (1) rotate toward each other at slightly different speeds. Each rotor has a blade that extends along the length of the rotor roughly in the form of a spiral. Each rotor is cored to permit cooling or heating by the passage of water or of an appropriate heating agent. An example of a two-wing rotor widely used in a Banbury design is shown in Fig. 4.7. The mixing chamber (2) may also be cooled or heated by means of sprays (3). The materials to be mixed are fed into the mixing chamber through the feed hopper (4). A floating weight (5) is operated by compressed air and rests on top of the feed, serving to confine the material to the mixing space and to exert pressure on it. The mixed material is discharged by a slide discharge mechanism (6) shown in this illustration. The saddle (7) between the rotors, which is attached to the sliding mechanism, slides from underneath the rotors,

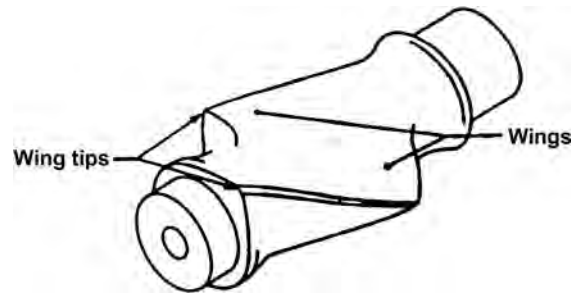


Figure 4.7 Two-wing rotor of a Banbury® Mixer.
Courtesy: Farrel Corporation

leaving an opening through which the mix discharges. Newer machines use a *drop door* for the discharge of the mixed compound, which assures a faster discharge that in turn increases the mixing capacity of the equipment by shortening the mixing cycle. The mixed batch is always dropped onto a two-roll mill or into a large single- or twin-screw extruder to partially cool it and to convert it into a desired shape for further processing, such as sheets, pellets, or chunks. Production-scale mixers of this design can process batches weighing 1000 lbs (450 kg) or more with drives 4000 hp (2985 kW) and rotor diameter 29 in (74 cm) [24]. Power draw on the motor during a mixing cycle in an internal mixer is depicted by Fig. 4.8.

Other designs of batch internal mixers include those with single mixing chambers containing single rotor or two rotors. The rotors may be separated, tangential, or intermeshing and with different directions of rotation (counter-rotating and co-rotating). These alternatives to the Banbury design are discussed in detail in Ref. [25].

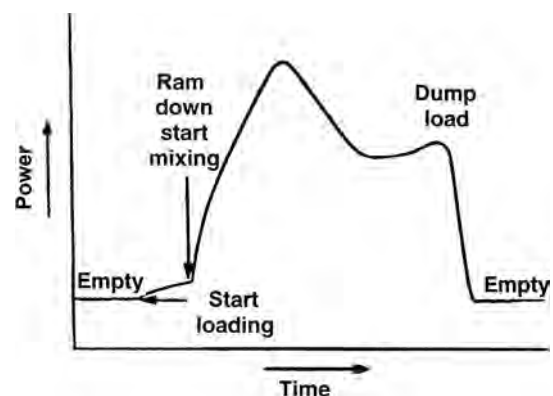


Figure 4.8 Power draw on the motor of the internal mixer during a production cycle.
Courtesy: Farrel Corporation

4.2.3.2 Continuous Mixers

There are many designs of mixing machines operating continuously. Essentially, they consist of roughly elongated cylindrical or rectangular prismatic steel chambers into which feeders monitor the addition of various ingredients. They contain one or more rotating members that are capable of pumping and mixing. Such members are often of screw or screw-like shape.

Many continuous mixers, particularly single- and twin-screw extruders, are pressurized machines with dies that extrude strands. The strands are then continuously cut into pellets. Other continuous mixing machines are not pressurized at their exits. Examples are the single screw KoKneater (or Kneader), manufactured by Buss AG, and various machines consisting of nonintermeshing, counter-rotating shafts with screw and mixing rotor sections. An example of the latter is the Farrel Continuous Mixer (FCM[®]) and similar machines manufactured by Japan Steel Works, Kobe Steel, and Techint Pomini. The molten compound is discharged through doors or other connecting members into a second pressurized screw extruder with a pelletizing die [26].

The various continuous mixers differ in their internal operation. They may contain a single rotating and pumping member with the general configuration of a screw, but with the incorporation of special mixing sections. The Buss KoKneater (Kneader) contains a screw member that rotates and reciprocates in a barrel containing pins [26]. Other designs may use co-rotating or counter-rotating modular screws, intermeshing or tangential screws.



Figure 4.9 Farrel continuous mixer.
Courtesy: Farrel Corporation

Discussion of design and operating details of these machines is beyond the scope of this book; for further information see Ref. [27].

Farrel Continuous Mixer (FCM[®]) is a non-intermeshing counter-rotating machine (Fig. 4.9). Its distinctive feature is that the clearance between the screw flights and the barrel is much less than in a twin-screw extruder. This leads to increased shearing between screw flight tips and the machine barrel [28]. A sectional view of an FCM in operation is shown in Fig. 4.10.

The Farrel Continuous Mixer was originally developed for the continuing mixing of powdered/pelletized rubber [29]. Since its commercial introduction, there have been few applications of this kind; however, it was found to be useful for postpolymerization

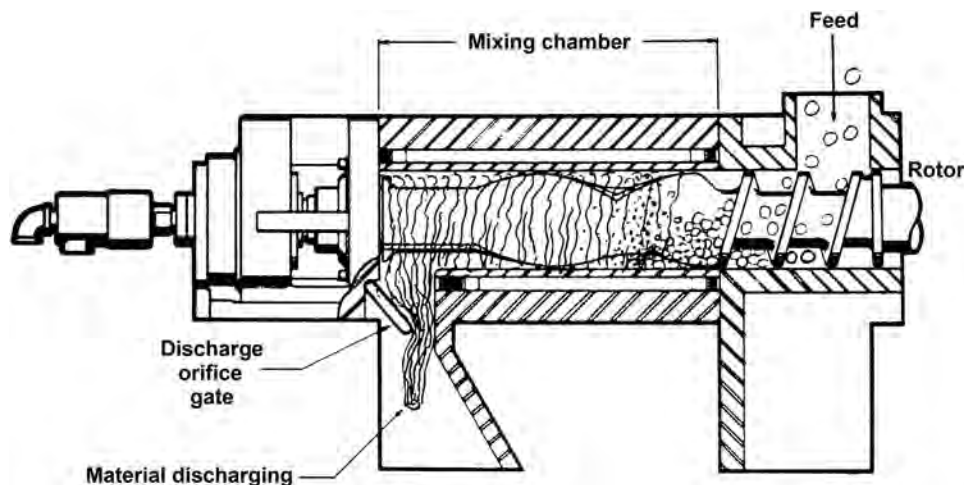


Figure 4.10 Sectional view of typical FCM in operation.
Courtesy: Farrel Corporation

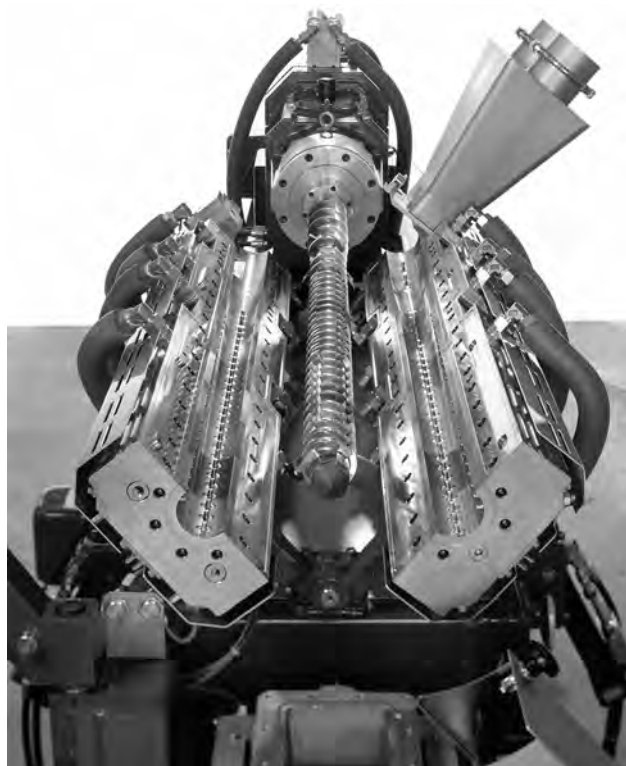


Figure 4.11 Cross-section of the Buss Kneader.
Courtesy: Buss AG

processing of polyolefins and for mixing of compounds with high content of fillers [30].

KoKneater, *Ko-Kneader*, or *Kneader* is a reciprocating single-screw mixer made by the Swiss company Buss AG. Its screw rotates and reciprocates with one complete forward and return stroke for every rotation. The reciprocating action of the screw makes it completely self-wiping in the mixing section.

In the barrel wall of the machine, there are three rows of pins running from the main feeding port to the discharge (see Fig. 4.11). The rows of the mixing pins are spaced 120° apart. These pins impart enhanced mixing to the screw but also make each pin location a possible port to the mixing chamber. The Buss Kneader is manufactured in sizes ranging from 46 mm (1.7 in) to 200 mm (7.4 in) in diameters suitable for the processing of polymeric compounds and blends [31] with typical throughputs ranging from 10 kg/h (22 lb/h) to 6000 kg/h (13,215 lb/h). It is used in applications where both dispersive and distributive mixing are required. Machines used specifically for engineering plastics are designed with electrical heating and twin-screw side feeding [32]. See Fig. 4.12 for an overall view of a typical Buss Kneader.

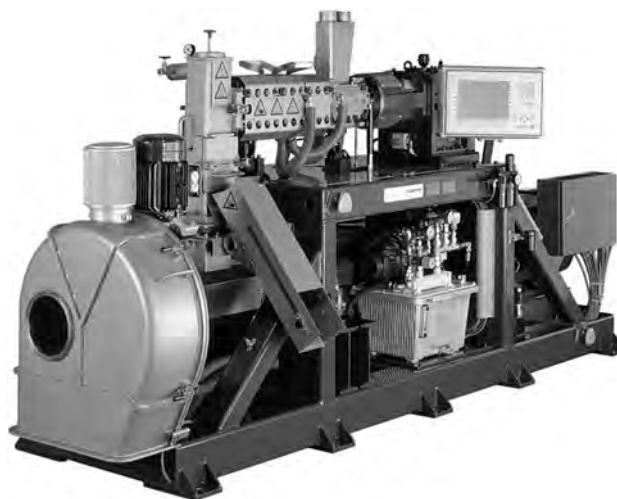


Figure 4.12 Buss Kneader, overall view.
Courtesy: Buss AG

4.2.3.3 Other Mixing Machinery

The machinery discussed in the previous sections is designated to mixing only. Other equipment that has a primary function to extrude melts into different shapes can be and at times is also used for continuous mixing. Single-screw and twin-screw extruders are pressurized machines having dies that extrude strands, which can be continuously cut into pellets if desired.

4.2.3.3.1 Single-Screw Extruders

Single-screw extruders are the most widely used polymer extrusion machines. Although their utility as mixing equipment is somewhat limited, many compounding operations have at least one [33]. Their key advantage is a relatively low cost, straightforward design, ruggedness, and favorable performance/cost ratio.

The single-screw extruder is primarily a drag pump designed to work with highly viscous fluids such as polymeric melts. The usual screw configuration has 20 or more turns with a pitch similar to the diameter, giving a long slender machine in which substantial longitudinal temperature gradients can be maintained and controlled. An appreciable residence time permitting a degree of end-to-end mixing is also provided. In addition to this *distributive* mixing, high shear stresses over flight lands give a degree of *dispersive* mixing for breaking up agglomerates such as pigments, waxes, and other similar additives [34].

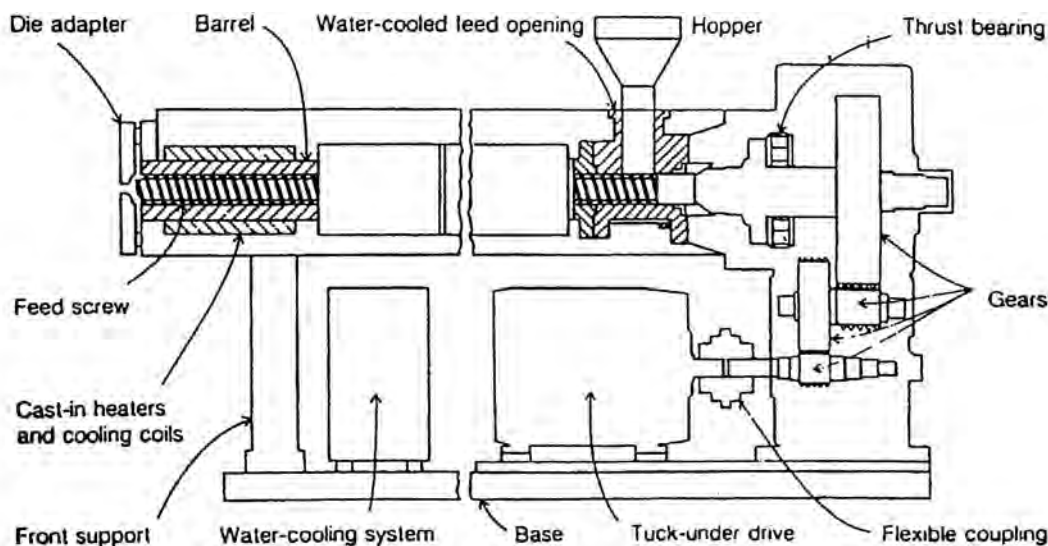


Figure 4.13 Typical single-screw extruder.
With permission

A typical single-screw extruder is shown in Fig. 4.13. Its main components are:

- Barrel and feed section
- Barrel heating and cooling mechanism
- Barrel and die temperature control systems
- Motor and drive
- Gearbox
- Thrust bearing
- Feed screw

The barrel houses the feed screw and provides a transfer medium for heating, cooling, and venting; it is made from special bimetallic hardened liners to withstand wear and high pressures occurring during the operation of the extruder.

Inside diameter of the barrel (D) and barrel length (L)-to-barrel diameter ratio (L/D) are the principal dimensions used to express the size of the extruder. The (L/D) measurement is arrived at by dividing the barrel length from the downstream edge of the feed throat to the end of barrel by the barrel diameter. The (L/D) ratio has an important relation to available barrel surface area and residence time of the material within the extruder [35].

The feed opening is located at the end of the barrel, near the gearbox. The material to be processed is usually fed from a hopper that is bolted over the feed opening. In general, the opening is round and of

the same diameter as the screw [36]. The material flows in most cases by gravity from the feed hopper down into the barrel and into the annular space formed between the extruder screw and barrel.

Most extruder screws have a single metal ridge (flight) wrapped like a large screw thread around a cylindrical root. The screw nomenclature is shown in Fig. 4.14 and the specific geometrical attributes in Fig. 4.15. The majority of single-screw extruders have single-flighted screws, which means that the screw has a single-helical flight. Some screws are of multi-flight design, that is, they have more than one helical flight, typically two or three. The screw flights may be *right-handed* or *left-handed* when the screw rotation is in the clockwise direction, as viewed from the end

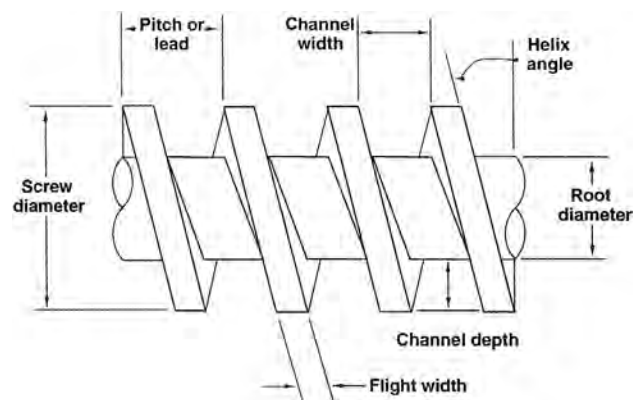


Figure 4.14 Feed screw nomenclature.
Copyright: Spirex Corporation, 1979–2006

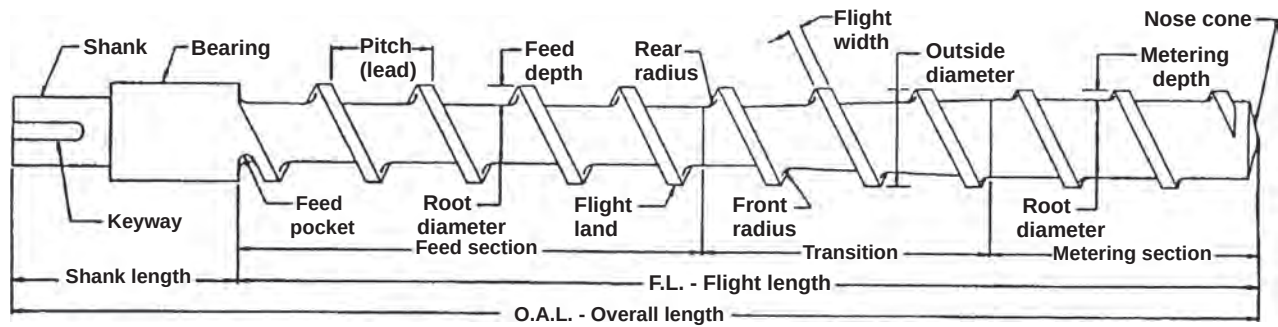


Figure 4.15 Geometrical attributes of a screw.

With permission

of the screw (see Fig. 4.16). Almost all single-screw extruders have righthanded screw threads and rotate in the clockwise direction when viewed from the end of the screw [37].

The barrel is stationary and the screw is turning. The result is that the frictional forces act on the material and cause a forward movement. The output rate is controlled by the intake capacity of the feed screw. The flights in the feed section are full in most cases. This case is referred to as *flood feeding*. As the material moves forward, it heats up as a result of the heat generated by and conducted from the barrel heaters. When the material exceeds its melting point, a melt film forms at the barrel surface. During the forward movement, the amount of melted component increases, and at one point all of it is melted. In the last part of the extruder, the *pumping section*, the polymer melt is pressurized and pumped into the die.

Although a single-screw extruder provides a degree of end-to-end mixing, the residence time of

the melt is of the order of only 10 s. On the other hand, it is quite effective, especially at high back pressure, as a distributive mixer on a small scale, thus forming a useful compounding device when fed with a blend containing masterbatch (a premix) or following an intensive high-speed mixer for powders [38].

Feed screw mixing devices, such as *mixing pins*, *Dulmage section*, *Dray Mixer*, and *Maddock Mixer*, have been developed to overcome problems inherent in the design of single-screw extruders [38]. They mostly represent different modifications of the screw. Examples of such local screw modifications are in Fig. 4.17.

4.2.3.3.2 Twin-Screw Extruders

There are many different designs of twin-screw extruders being used in mixing of thermoplastic

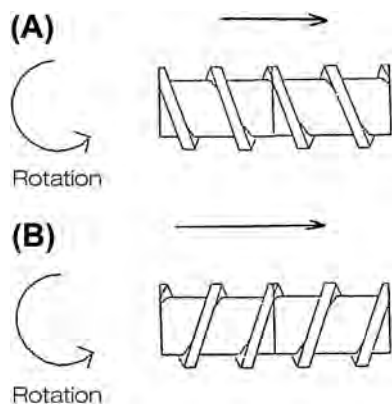


Figure 4.16 (A) Right-handed screw. (B) Left-handed screw.

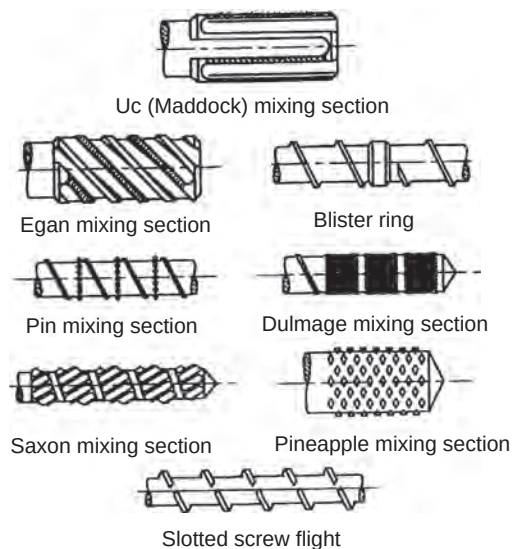


Figure 4.17 Various local screw modifications to enhance mixing.

and elastomeric materials. Essentially, they can be grouped into two basic designs, namely *modular co-rotating* twin-screw extruders and *modular counter-rotating* twin-screw extruders.

4.2.3.3.2.1 Modular Co-rotating Twin-Screw Extruders

Modular co-rotating twin-screw extruders have become the most important commercial machine for continuous mixing of compounds based on thermoplastics. They also are the most studied and understood of the equipment developed in the period after World War II [39].

The machine contains two shafts mounted with various screw and mixing element modules each having a specific function. These are usually right-handed and left-handed screw elements, kneading disc blocks, distributive mixing elements, rotor and polygonal elements, and valves.

Modular co-rotating twin-screw extruders are widely used for blending of polymers and incorporation of fillers, pigments, oils, and other additives into the polymeric base. Moreover, they are used for removal of liquids (devolatilization), for reactive extrusion, polymerization, and grafting [40].

Modular co-rotating twin-screw extruders are suitable mixing equipment for TPO, TPV, and SEBS compounds. Each compound requires specific process conditions. Typically, TPV requires high torque and long residence time. Low bulk density materials in highly filled TPO and SEBS-based formulations require improving feed intake, such as feed enhanced technology (FET). This high-torque extrusion technology increases the feed intake/feed zone throughput capacity for difficult-to-feed materials by improving the conveying efficiency through an increase in the coefficient of friction between the feedstock and barrel wall. This design of twin-screw extruder is also capable of providing good homogenization of the reactants and sufficiently large free volume for precise adjustment of residence time as needed for the reaction [41].

4.2.3.3.2.2 Modular Counter-Rotating Twin-Screw Extruders

Modular counter-rotating twin-screw machines with modular construction are used for mixing, blending, devolatilization, and reactive extrusion. Two classes of these machines have been

commercialized, namely *tangential screw* and *intermeshing screw* machines [42]. The intermeshing screw machines have been used for difficult mixing problems involving pigments, fillers, and lubricants that are difficult to disperse. The machines with tangential screws provide the processed material with a milder stress history and consequently are much less able to break up difficult particle agglomerates than the intermeshing screw machines. Therefore, they found their major applications in devolatilization and reactive extrusion [43].

4.2.4 Material Feeding and Feeders

Bulk raw materials are most frequently stored in large storage bins or tanks. Some liquids, such as highly viscous oils, require heating in order to facilitate their flow into the feeding system. Other raw materials, such as waxes and certain chemicals, have to be melted before being introduced into the mixer and are often stored in heated tanks.

All mixing machines must have some device or system to feed the material into the process. Their design depends on the type of machine and the type of materials processed, their physical properties, and flow behavior. Such devices or systems are referred to as *feeders*.

There are many types of feeders, such as single- and twin-screw feeders, rotary feeders, belt feeders, and vibratory feeders. They can discharge the raw materials by volume (volumetric feeders) or by weight (gravimetric feeders). The latter require weighing system and accurate and dependable controls.

Feeding systems for batch mixing are relatively simple. They may include scales, simple conveyor belts, or weigh belts. Liquids can be introduced directly into the mixing chamber from a volumetric or gravimetric feeder. Feeding systems for continuous mixers are considerably more sophisticated, often with complex controls.

The subject of feeding and feeders is covered in a great detail in Ref. [44].

4.2.5 Finishing Operations

The mixed compound is often not in a form to be delivered to the user. Thermoplastic materials are most widely reduced in size to be suitable for the manufacture into semifinished or finished products.

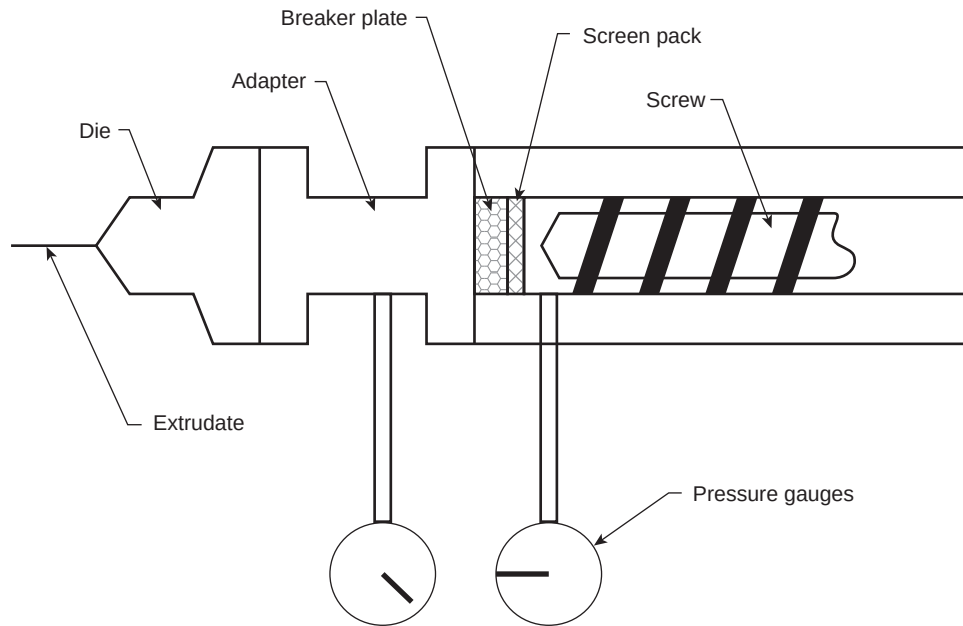


Figure 4.18 Location of screen pack and breaker plate in an extruder.

4.2.5.1 Filtration

For certain applications the compounds must be clean, without solid contaminants, such as particulates, gels, unconverted polymers, carbonized polymers, agglomerated additives, and debris such as metal particles, dirt, or dust. These must be subjected to melt filtration. Machines with mixing screws almost always have a built-in filter, consisting of a breaker plate and a screen pack (see Fig. 4.18). In order to maintain continuous melt flow, *screen changers* of various designs are used. An example of a screen changer is in Fig. 4.19.

Compounds mixed by batch mixing equipment must be cleaned in downstream equipment, which

can be a simple single-screw extruder with a filtering device as described above or a specialized strainer with a screen changer.

4.2.5.2 Size Reduction

In general, mixed compounds can emerge from the mixing equipment as lumps, strips, and slabs. In some cases the shapes and dimension are not suitable for use in manufacturing equipment, such as injection molding machines, extruders, blow molding, and rotomolding equipment. In order to prepare the mixed compounds for the next manufacturing step, they have to be reduced in size. The size reduction methods include pelletizing, dicing, and granulation. The

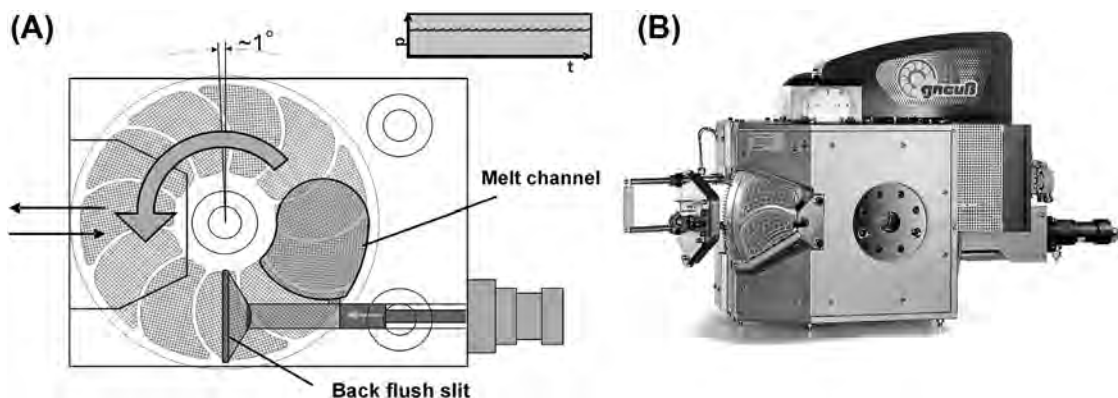


Figure 4.19 An example of a screen changer. (A) Schematic diagram; (B) Overall view.

Courtesy: Gneuß Kunststofftechnik, GmbH

Table 4.8 Processes and Equipment Used for Pelletizing and Dicing

Quenching, Solidifying and Cutting	Cutting, Quenching and Solidifying
Dicers	Die face pelletizers
Strand pelletizers	Dry face pelletizers
	Wet ring pelletizers
	Underwater pelletizers
	Rotary knife pelletizers
	Centrifugal pelletizers

processes and equipment used for pelletizing and dicing are listed in Table 4.8.

Below is a description of the most common processes and machines used for the production of reduced sizes of thermoplastic compounds after they are mixed or prepared for recycling.

4.2.5.2.1 Pelletizing

Pelletizing is the most widely used process for the size reduction of many thermoplastic materials, including raw polymers and mixed compounds. The process involves extrusion through a die. The extrudate is cooled to solidification and then cut into pellets, or the molten extrudate is cut as it emerges from the extrusion die and the pellets are subsequently cooled. In the latter case, both cutting and cooling can be done in air or water, or cutting may be done in air, followed by quenching in water [45]. Cutting thermoplastics as a melt rather than as a solid generates fewer fines and less knife wear [46].

The pelletizing device, which converts the product into pellets of different shapes and sizes, is frequently attached to an extruder or a gear pump. The pellet form offers several processing advantages over other forms. It can be easily weighed, uses simple feeding systems with fewer feeders, and allows homogeneous and uniform free-flowing feed for the subsequent end uses.

The product viscosity, heat history, uniformity, required throughput, and other factors will generally determine the cutting method that can be successfully employed. Following are the most widely used pelletizing machines used for thermoplastics.

Strand pelletizers have been the most widely used machinery for pelletizing thermoplastic polymers and compounds [47] in the past, but the current trend is to

use the underwater machines. The strands emerging from the die of an extruder or a gear pump are conveyed through a cooling water bath with grooved rollers that keep them separate until they solidify. Then they are air dried and fed into nip rolls to a multiknife-blade rotor operating against fixed blades. The cross-section of the pellets can be round, oval, or nearly square [48], with typical diameter of 2–4 mm (0.08–0.16 in) and length of 1–5 mm (0.04–0.2 in). There are several methods of cooling and drying the pellets; these are discussed in some detail in Ref. [49]. A schematic diagram of a strand pelletizer is in Fig. 4.20.

Die-face pelletizers produce pellets by the use of knives rotating rapidly across a multiple-hole die plate. The pellets are quenched in air alone with a water mist or by subsequent immersion into a water bath [50]. A schematic diagram of a hot die-face pelletizer is in Fig. 4.21.

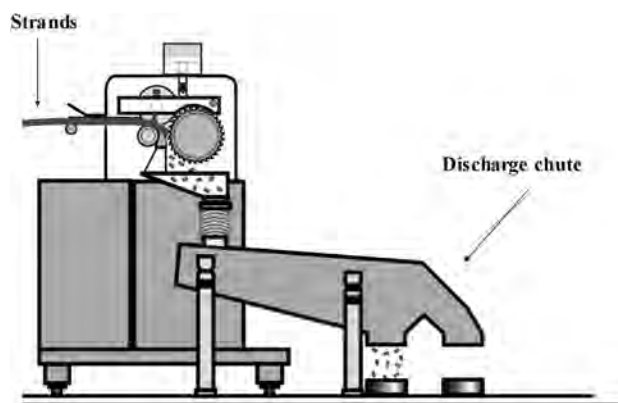


Figure 4.20 Schematic drawing of a strand pelletizer.

Courtesy: Rieter-Automatik

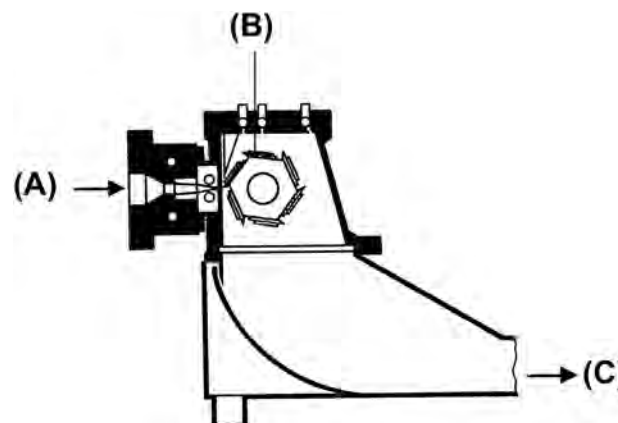


Figure 4.21 Schematic diagram of a hot die-face pelletizer. (A) Polymer melt; (B) Rotary knife; (C) Discharge chute.

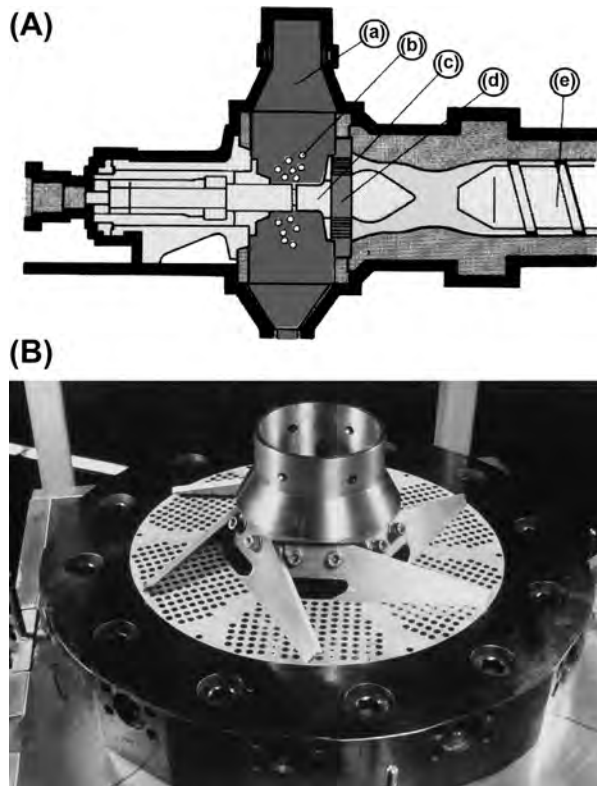


Figure 4.22 (A) Schematic drawing of an under-water pelletizing head. (a) Water chamber; (b) Pellets; (c) Knife holder; (d) Die plate; (e) Extruder feed screw. (B) Detail of the cutting head of an under-water pelletizer.

Courtesy: Pomini; Davis-Standard LLC, Black Clawson Converting Machinery

Dry-cut eccentric pelletizers have an eccentrically mounted cutter with multiple arms rotating at speeds up to 2500 rpm.

Underwater pelletizers are probably the most versatile equipment for a wide viscosity range, higher outputs, and pellet size capability. They operate with the die face and rotating cutter fully immersed in water. The produced pellets are carried away as slurry in water for further cooling in transit, to the dewatering, screening, and drying equipment [51]. An example of an underwater pelletizing head is in Fig. 4.22(A), and the detail of cutting knives is shown in Fig. 4.22(B).

In the *water ring pelletizer* the molten strands emerging from the die are cut with a centrally mounted cutter. The freshly cut pellets are thrown into spirally rotated water, about 20 mm (0.8 in) deep. The pellets are cooled down in the water, then screened and dried. A schematic of this type of pelletizer is in

Fig. 4.23(A), and an example of the arrangement of die knives in such a device is in Fig. 4.23(B).

In *centrifugal pelletizers* the melt is fed into a rotating die chamber at atmospheric pressure. The pressure to extrude the polymer through the die holes is generated by the centrifugal force within the die rather than by an extruder or gear pump. The emerging strands are cut by a single stationary knife [51]. This type of machine was offered at one time but is no longer being made.

Rotary knife pelletizers operate with a die similar to the strand die, but with the rotary cutter operating in close proximity to the emerging strands. The cutter is completely enclosed [52].

Thermoplastic elastomers can be processed essentially by any of these machines; the selection depends mainly on the apparent viscosity of the melt of the given material. The layout of a typical pelletizing system for most thermoplastic elastomers is in Fig. 4.23(C).

4.2.5.2.2 Dicing

Dicers are used to produce square, rectangular, parallelogram, or octahedral pellets [53]. The strip from an extruder or a sheet from a calender or a roll mill is quenched before entering the dicer and is then fed at a constant rate through nip rolls into the rotating knives operating against a stationary-bed knife. The configuration of the knives, the strip feed rate, rotor speed, and the number of rotating knives determine the pellet size, configuration, and output.

4.2.5.2.3 Granulation

Although granulation is mostly used for reclaiming and recycling of thermoplastics, granulators can be useful for short runs or for compounds that are difficult to pelletize. They have two or more rotary knives inside a chamber, where stationary knives are mounted. Granulators are used in very limited applications to pelletize hot melt directly from the extrusion die; cooling for solidification is achieved in the granulator [54]. A schematic of a granulator is in Fig. 4.24.

4.3 Extrusion

Extrusion is one of the widely used processes for fabricating parts from thermoplastic elastomers.

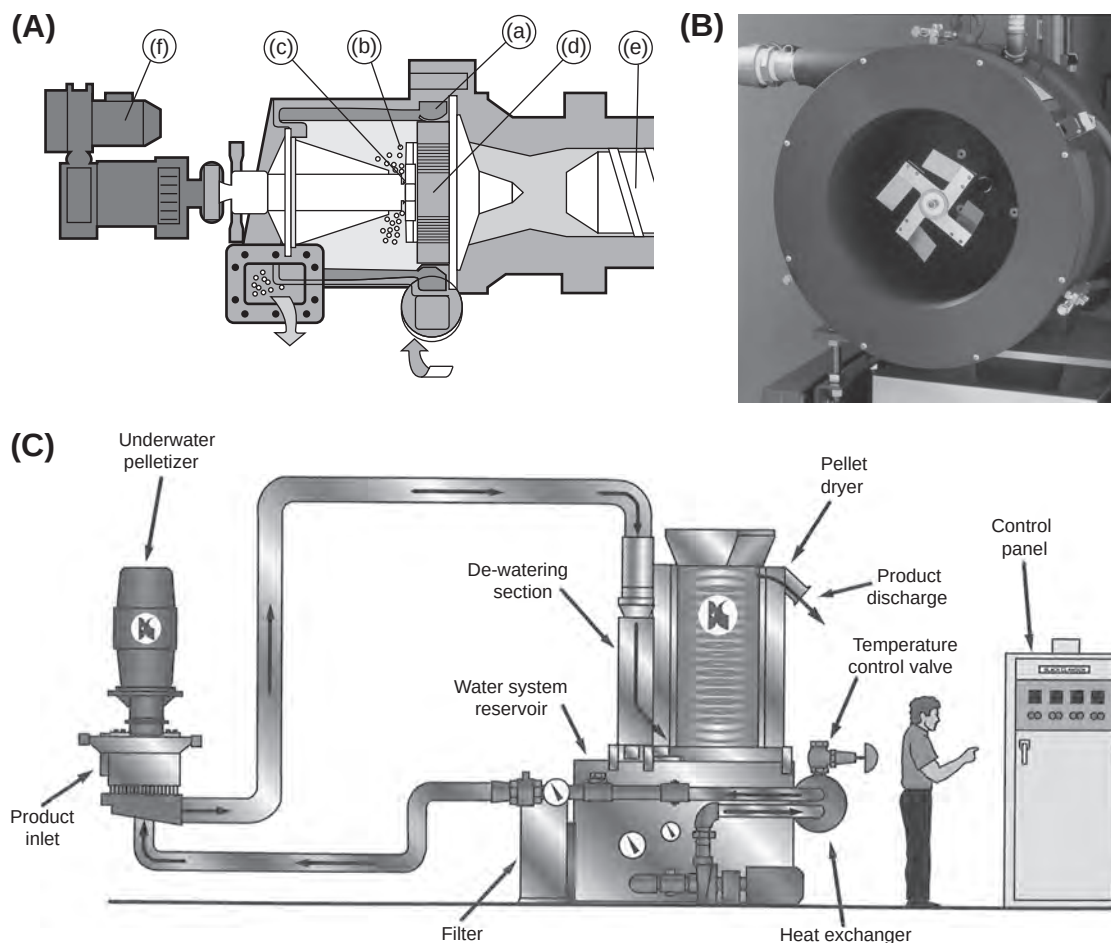


Figure 4.23 (A) Schematic drawing of a water-ring pelletizer. (a) Water ring chamber; (b) Pellets; (c) Knife holder; (d) Die plate; (e) Extruder feed screw; (f) Motor. (B) Detail of the cutting head of a water ring pelletizer. (C) Typical layout of a system for pelletization of thermoplastic elastomers.

Courtesy: Pomini; Xaloy Extrusion; Davis-Standard LLC, Black Clawson Converting Machinery

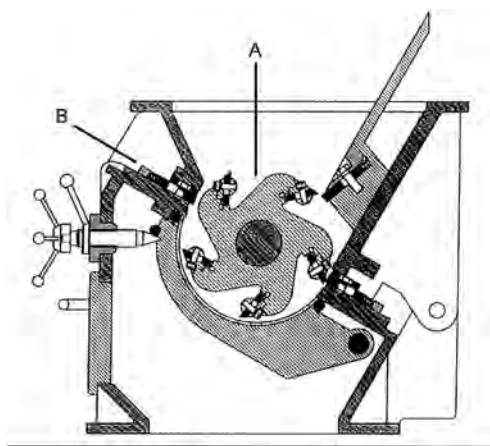


Figure 4.24 Schematic drawing of a granulator.

Courtesy: Neue Herbold GmbH

Unlike injection molding (Section 4.4), extrusion usually results in a semifinished or intermediate article that needs further processing to arrive at an end product. The principal end products made by extrusion are wire insulation, tubing, profiles, film, and sheets.

The flow behavior of the molten polymer is of critical importance in the extrusion of most thermoplastics. TPEs, and generally thermoplastic materials, must be processed below the velocity at which *melt fracture* occurs, referred to as the *critical shear rate*. Melt fracture in molten plastics takes place when the velocity of the resin inflow exceeds the critical velocity, the point where the melt strength of the polymer is surpassed by internal stresses. Parts extruded in a process that exceeds the critical shear rate have poor quality. Typical symptoms of melt

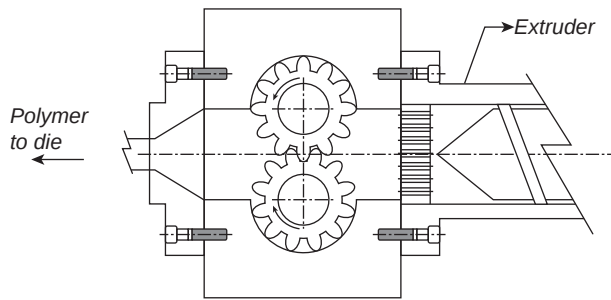


Figure 4.25 Schematic diagram of a melt pump.

fracture include a rough surface (*shark skinning*), and frosty or cloudy surface.

4.3.1 Fundamentals of Extrusion Processes

Extrusion is a continuous process that involves forming a product (*extrudate*) in two dimensions. These x - y dimensions determine the cross-sectional form of the extrudate, and this can be almost unlimited in scope, ranging from a simple tube to a very complex extruded profile. The third (z) dimension is the length of the extrudate. In principle it can be infinite. In fact, it is limited by practical considerations governing winding, reeling, storage, and transport. The essential point is that extrusion always produces an object of constant cross-section.

The product cross-section is formed in a die; the extrusion process consists of heating a thermoplastic above its melt temperature and forcing it through the die. The heating and pressurizing device involves one or more screws operating in a heated barrel and is known as an *extruder*. Downstream of the die, the extrudate is calibrated, cooled, and packaged by an array of ancillary devices including vacuum calibrators, air cooling chamber, water tanks, cooling

rolls, haul-offs, cutters, and winders. Upstream of the die, a melt pump (Fig. 4.25) may be interposed between the extruder and the die [55]. The exact selection and arrangement of these components of an extrusion system will depend on the end product. The specific processes for production of different extruded products will be discussed in detail later in this chapter. The principle of extrusion is common to all these processes and will be discussed first.

4.3.2 The Extruder

The function of the extruder is to heat the plastics material to a homogeneous melt and to pump it through the extrusion die at a constant rate. Because the extrusion of plastics is a continuous process, the melt preparation device must be capable of a constant output. Thermoplastic extrusion depends almost entirely on the rotating screw as a melt delivery device. Thermoplastics are generally characterized by low thermal conductivity, high specific heat, and high melt viscosity, so the preparation of a uniform melt and its delivery at adequate pressure and a constant rate pose considerable challenges. These have been countered by the introduction of various types of extruders.

The principal variants are the single-screw and the twin-screw types. Of these, the single-screw extruder (Fig. 4.26) is by far the most popular. The twin-screw extruder may have parallel or conical screws, and these screws may rotate in the same direction (*co-rotating*) or in opposite directions (*counter-rotating*) (see Fig. 4.27). Extruders with more than two screws are known, for example, the quad-screw extruder, but are not widely used [55]. Twin-screw extruders are normally used when mixing and homogenization of the melt is very important, and in particular where

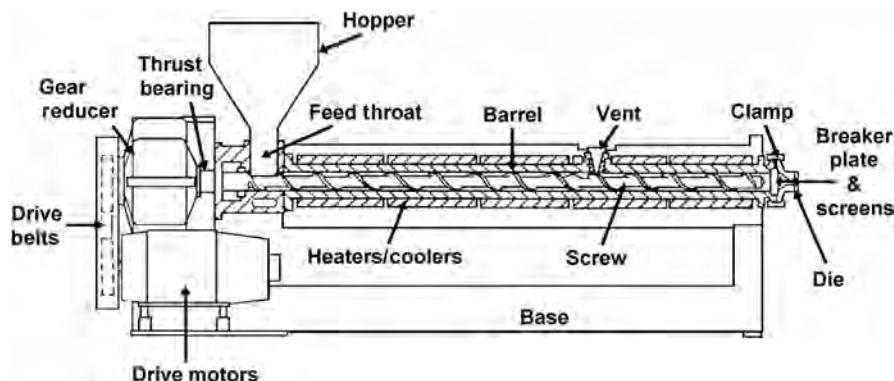


Figure 4.26 Typical single-screw extruder with a vented barrel.

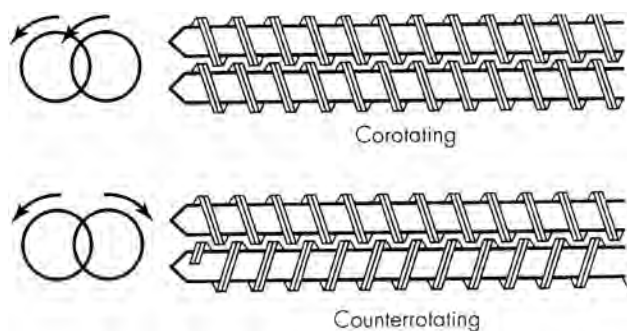


Figure 4.27 Co-rotating and counter-rotating twin screws.

additives are to be incorporated. Thermoplastic elastomers are normally extruded using a single-screw machine.

The single-screw extruder consists essentially of a screw that rotates in an axially fixed position within the close-fitting bore of a barrel. The screw is motor driven through a gear reduction train and is supported by a thrust bearing that opposes the force exerted on the plastic melts. A helical flight on the screw provides the drag-induced conveying motion that develops this force. The barrel is equipped with both heating and cooling means, and its downstream end is provided with an attachment device for a shaping die that determines the cross-section of the extruded product. The upstream or inlet end of the barrel is equipped with a feed throat or an aperture in the barrel wall where a plastics material is input, generally in the form of granules or pellets. During its passage along the helical screw flight, this material is heated by a combination of conducted heat received from the barrel and mechanical shear heat derived from the mixing and kneading action of the screw. The output rate of the extruder is a function of screw speed, screw geometry, and melt viscosity. The pressure developed in the extruder system is a function of melt viscosity, screw design, and barrel and die resistance. Extrusion pressures are lower than those encountered in injection molding and are typically less than 35 MPa (5000 psi) [56].

The key determinant of extruder performance is the screw. The screw has three functions to perform: feeding and conveying the solid thermoplastic feed (most frequently pellets); melting, compressing, and homogenizing the material; and metering or pumping the melt to the die. The typical extruder screw (Fig. 4.28) takes the form of a single constant-pitch flight that decreases in depth from the input end to the output end. The pitch is usually equal to the screw

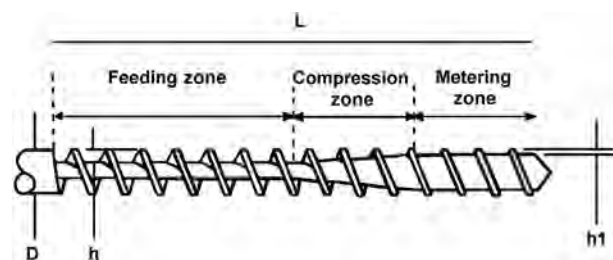


Figure 4.28 Features of a typical extrusion screw L = screw length; D = diameter; h = initial length; h_1 = final flight depth; h/h_1 = compression ratio.

diameter. This is sometimes known as a square pitch screw; the resulting helix angle is 17.8° . The screw features three sequential zones, corresponding to the three functions of feeding, compression, and metering.

Flight depth is usually constant in the feeding and metering zones, and decreases at a constant rate over the compression zone. The feed zone occupies about 50% of the screw length, the compression zone takes up 25–30%, and the metering zone accounts for the balance. The ratio of the flight depths in the feeding and metering zones is known as the compression ratio, and it affects the mixing and shear-heating characteristic of the screw. The ratio of the screw length to its diameter is known as the L/D ratio; this has a bearing on mixing and uniformity of output. Most conventional screw designs perform satisfactorily for thermoplastic elastomers. Extrusion screws for wire insulation should have an L/D ratio in the range of 24:1 to 30:1. A screw with a long feed section with approximately a 3:1 compression ratio (core progressive profiles that do not subject the resin to excessive shear) is preferable.

The mixing performance of a single screw can be improved by the addition of mixing elements in the metering zone as shown earlier in Fig. 4.17. These are sometimes teamed with or replaced by static elements such as pins in the barrel. Attention to the barrel can also improve the material conveying performance at the inlet, stepping up the output rate. A series of axial grooves in the barrel wall (Fig. 4.29), extending for at least three screw diameters, is effective.

Variants on the single screw include the *barrier* or *melt extraction screw* (Fig. 4.30) and the *vented screw*. Barrier screws have separate input and output flights that overlap in the midsection of the screw where the plastics material is only partially melted. The barrier flights are slightly smaller in diameter than the main flights. Molten material passes through this clearance and proceeds to the metering zone,

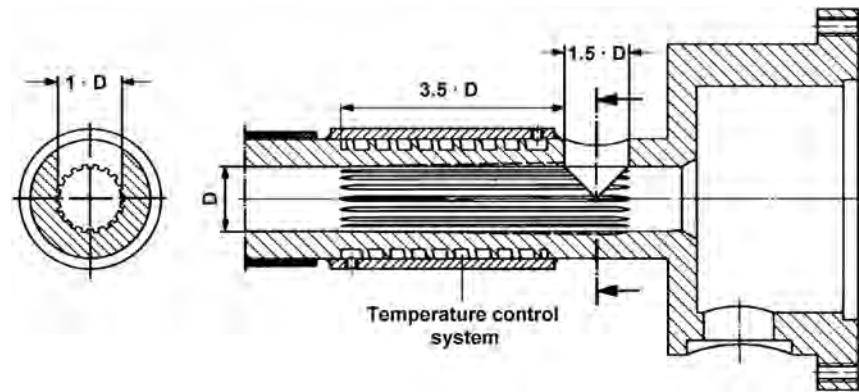


Figure 4.29 Grooved feed section of barrel.

while solids are retained for further heating. The barrier screw offers the potential for lower melt temperatures or higher output rates, but is difficult to design and optimize. Vented screws, sometimes known as decompression screws or two-stage screws, are effectively two screws placed in series, with the second or downstream screw having a higher transport rate than the first. The upstream end of the screw is provided with conventional feeding, compression, and metering zones, but these are followed by a sudden increase in flight depth, and then by further compression and metering zones. The mid-screw increase in flight depth causes a sudden pressure drop in the molten plastic, and this allows any dissolved volatile matter to boil out. The lack of compression at this point, coupled with the differential transport rates of the two screw sections, makes it possible to extract the volatile material through a port in the extruder barrel without the plastics melt emerging at the same time. Vented screws typically have an L/D ratio of greater than 30:1 and suffer from some instability in pumping output. Operating conditions are also constrained by the need to ensure that the vent does not plug with plastics melt. For these reasons, the use of vented screws is usually confined to materials likely to contain moisture, volatile matter, or entrained air. TPEs are not usually prone to these problems, so vented screws are not normally used in their processing.



Figure 4.30 Section of a barrier screw.

4.3.2.1 Extrusion Methods

Depending on the intended use, the corresponding extrusion method is used. Each method requires specific tooling and process conditions. Often the method and the polymer grade have to be matched to assure a satisfactory product. The most common extrusion methods are film and sheet extrusion, pipe and tube extrusion, and wire coating and profile extrusion.

4.3.2.1.1 Film and Sheet Extrusion

Films from thermoplastics can be produced either by extrusion casting or extrusion blowing processes. Each has its advantages and disadvantages. These basic processes result in film with a molecular orientation predominantly in the machine direction. Regardless of process, film production lines include common downstream equipment such as haul-off, tensioning, and reeling stations. A high purity melt, free of inclusions, is essential for film production. This is achieved by filtering the melt through a *screenpack* located upstream of the die.

4.3.2.1.1.1 Cast Film Extrusion

Cast film is produced by extruding the melt from a slit die and cooling it either by contact with a *chill roll* or by quenching in a *water bath*. Both processes are characterized by relatively high melt temperatures and rapid rates of film cooling. This results in films with low haze, good clarity, and high gloss. Cast film grades typically have a melt flow index in the range 5.0–12.0 g per 10 min.

In the *chill roll cast film process*, a plastics web is extruded from a slit die (Fig. 4.31) against the surface

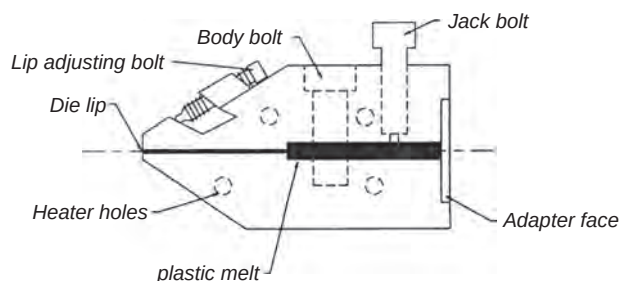


Figure 4.31 Typical slit die for cast film.

of a water-cooled chill roll. The die is arranged to extrude vertically or obliquely downward so the film web is delivered approximately tangentially to the roll surface. The die is similar in principle to a sheet die but will usually not include a restrictor bar. Film thickness is partially regulated by the gap between the die lips but also by the rotational speed of the chill roll, which is arranged so as to draw down and thin the melt web. Consequently, the die gap is set in excess of the desired film thickness. Typical die gap settings for most thermoplastics are 0.4 mm for films up to 0.25 mm (0.01 in) thick and 0.75 mm (0.03 in) for film gauges in the range 0.25–0.6 mm (0.01–0.024 in). Die lip adjusters should allow the die gap to be varied at each adjustment point across the die width in order to allow control of the transverse film thickness. Film reel quality will suffer if the transverse thickness tolerance exceeds $\pm 5\%$ of target thickness. A constant temperature should be maintained across the die so that film drawdown rates and physical properties remain constant across the film web. Attempts to control film thickness by varying the temperature profile across the die will disturb these factors and reduce film quality. When the process is correctly regulated, the thickness uniformity of chill roll cast film is substantially superior to blown film.

The die is maintained in close proximity (typically 40–80 mm or 1.6–3.2 in) to the chill roll so that the low-strength melt web remains unsupported for a minimal distance and time (Fig. 4.32). If the die is too close, there is insufficient space for thickness drawdown and widthwise neck-in to take place in a stable manner. The web flows onto the water-cooled chill roll with a wraparound of 240° or more before passing to a second chill roll and then proceeding to edge trimming, tensioning, and windup stations. The first chill roll is critical to process quality. The cooling capacity must be sufficient to chill the film at high output rates, and the temperature gradient across the width of the roll should not exceed

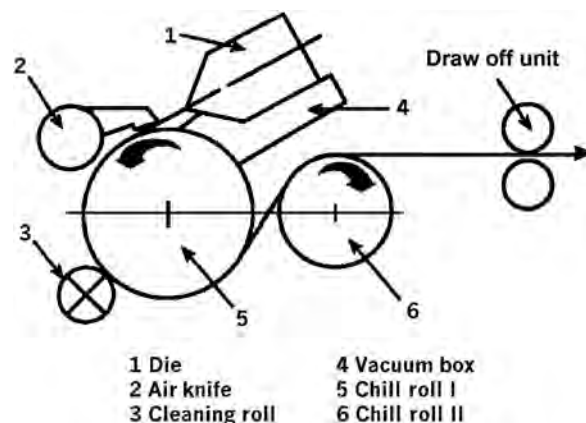


Figure 4.32 Detail of chill roll process.

$\pm 1^\circ\text{C}$ (1.8°F). The actual roll temperature depends on film gauge, line speed, and roll diameter. The chill roll drive speeds must be very precisely regulated to control film drawdown and finished thickness.

At line speeds greater than 30 m per minute (98 ft per minute), there is a tendency for a thin cushion of air to become trapped between the film and the chill roll. This results in slow and uneven cooling, affecting the appearance and properties of the film. Two measures are adopted to counteract the problem (Fig. 4.32). An air knife delivers a streamline jet of filtered air that impinges on the film just beyond the point of first contact with the chill roll and presses it against the roll. The air is supplied through a narrow slit of about 1.5 mm (0.06 in) gap and is controlled at a low differential above atmospheric pressure. An optimum air knife setting improves film clarity and gloss, but excessive pressure induces melt vibration and mars the film surface. The second measure is the provision of a vacuum box, associated with the die, and operating close to the chill roll surface just ahead of the extruded melt web. The vacuum box removes any condensates that have been deposited on the roll by the film and tends to draw air out of the interface between film and roll.

The film temperature should be close to ambient at the film windup station; otherwise the reel will continue to shrink after cooling, causing stretch marks and corrugations, and accentuating any variations in thickness. Winding tension should be sufficient to ensure the integrity of the reel but otherwise be kept low to allow for a small amount of postwinding shrinkage that will tighten the reel. A typical line for chill roll cast film is in Fig. 4.33.

As in other plastic processes, the cast film process depends on many interactive variables, so any defect

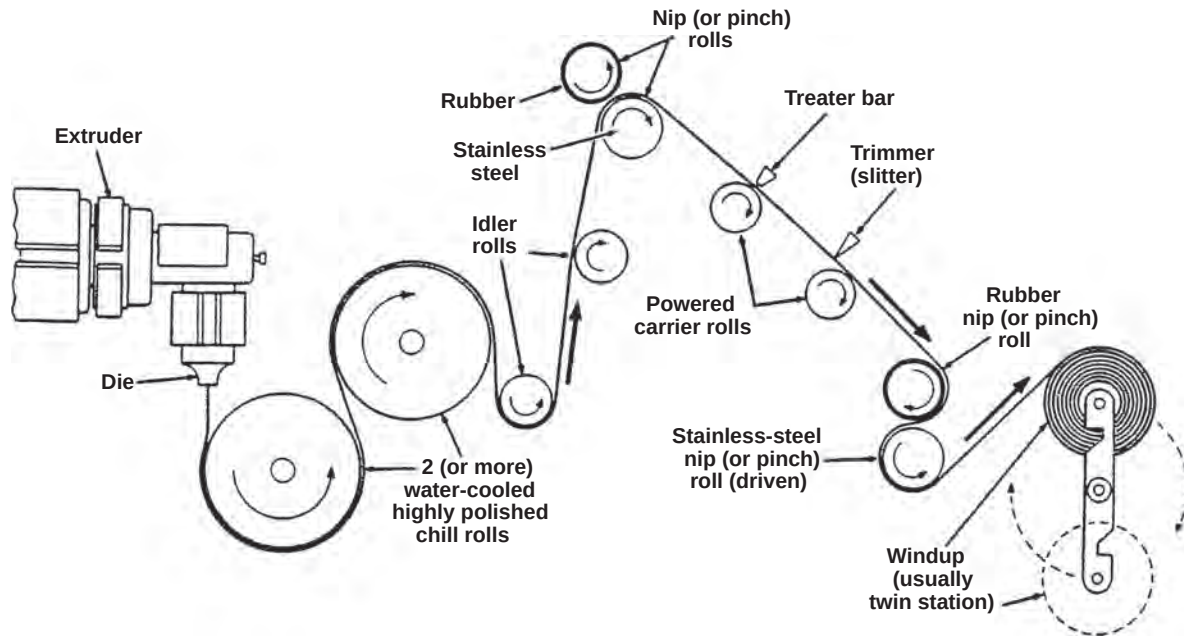


Figure 4.33 Typical line for chill roll cast film.

may have one of several causes. A remedy for one defect may introduce another, so process problem solving is not straightforward. With these provisos, the troubleshooting chart (Table 4.9) provides a useful guide for problem solving.

The *water quench cast film process* (Fig. 4.34) is similar in concept to the chill roll process and uses similar downstream equipment. A water bath takes the place of the chill roll for film cooling, and by cooling both sides of the film equally, it produces

a film with slightly different properties compared to chill roll cast film. The extruder's slit die is arranged vertically and extrudes a melt web directly into the water bath at close range. The film passes under a pair of idler rollers in the bath and, for any given rate of extrusion, it is the rate of downstream haul-off that regulates film drawdown and finished thickness.

The speed of the process is limited by the tendency of the film to carry over water from the quench bath.

Table 4.9 Chill Roll Troubleshooting Chart

Problem	Possible Cause	Suggested Remedy
Poor clarity	Cooling rate too low	Increase melt temperature
		Reposition air knife
		Increase air knife pressure
		Reduce chill roll temperature
Variable optical properties	Temperature gradient across the chill roll	Adjust chill roll coolant supply
		Check chill roll cooling circuits
Pleatout	Poor chill roll contact	Increase chill roll wraparound
		Adjust air knife
Flow defects	Melt temperature too low	Increase die and adapter temperatures
Brittle and fibrous heat seals	Melt temperature too high	Decrease die and adapter temperatures

Maier C, Calafut T. *Polypropylene, the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 1998.

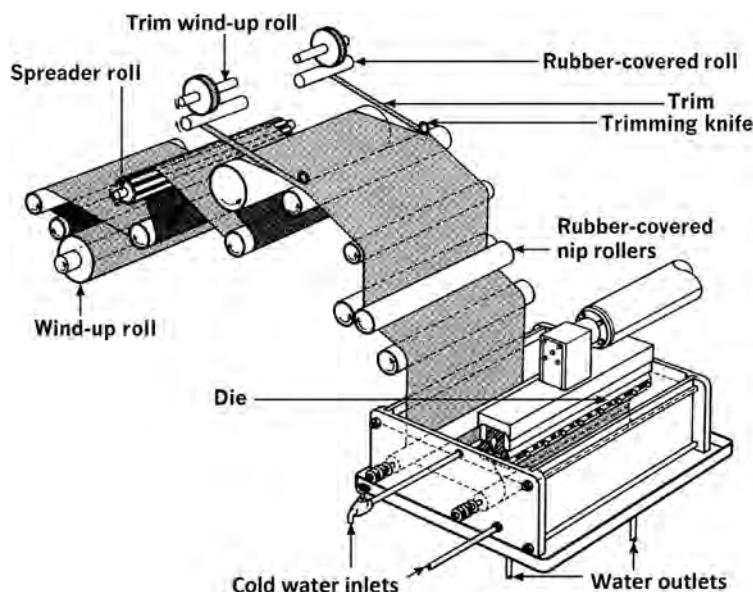


Figure 4.34 Typical water quench film line.

Surface defects can also arise from rippling in the water bath. The very rapid quenching induced by the water bath reduces crystallinity and produces a tough film.

4.3.2.1.1.2 Blown Film

The blown film process involves extruding a relatively thick tube, which is then expanded or blown by internal air pressure to produce a relatively thin film. The air-cooled blown film process is in very widespread use mainly for polyolefin films. The process needs a melt strength greater than that required by cast film processes, so lower melt temperatures are used.

The die should be designed for constant output rates and thickness at every point around the annular die gap. This requires streamlined internal melt flow paths and precise multipoint means of centering the mandrel within the die ring. The die gap is typically about 0.4 mm (0.015 in), with a short land length and a die entry angle of about 10°. Close thickness tolerances are difficult to achieve with the blown film process; variations around the bubble can be limited to perhaps $\pm 10\%$ of the target film thickness. To distribute these variations evenly, blown film lines may include rotating or oscillating motions applied either to the die, the extruder, or the haul-off.

As it emerges from the die, the tube passes through an air ring that lays a large volume of low velocity cooling air over the external surface. At the same time,

the tube is pressurized internally by air supplied through the die mandrel. The air is confined by downstream nip rollers, so it inflates the still soft tube to form an enlarged bubble. The amount that the bubble is extended is called the *blow-up ratio* (BUR) and is typically in the range 2:1 to 4:1. The distance that the tube travels upward before its diameter increases is called the *stalk height*. Most materials are blown with a short stalk, with the bubble diameter being increased to the final size shortly after leaving the die lips [57].

The line speed is effectively limited by the bubble length available for cooling. Downstream equipment includes bubble calibration, a collapsing frame, and haul-off, tensioning, and reeling stations. Film thickness and process control is a balance between cooling rate, bubble length, blow-up ratio, and film tension.

After the bubble is cooled and collapsed into a flat shape, the product (*layflat*) is rolled up on a high-speed winder. In some cases the layflat is slit to form two separate sheets and wound onto individual rolls, requiring two independent winding shafts (Fig. 4.35).

The *water-quench blown-film* process is also known as the tubular water-quench process, and uses a tube die that is arranged to extrude vertically downward (Fig. 4.36). The bubble size is limited and calibrated by an annular water-cooling weir that covers the outer bubble surface with a stream of cooling water. The water contact is directed and controlled by an annular flexible skirt [56]. The rapid

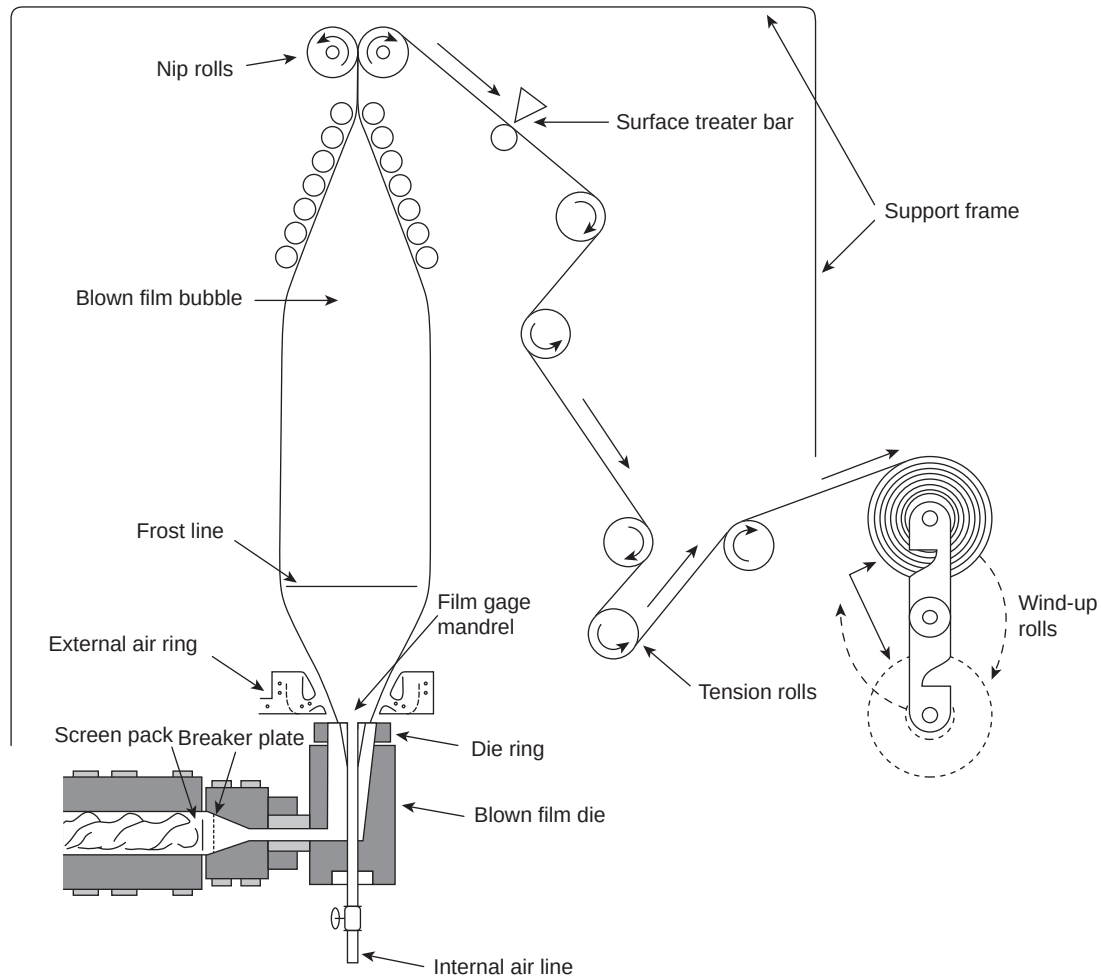


Figure 4.35 Air-cooled blown film process.

bubble cooling induced by the water stream limits crystallinity and produces a clearer film than is possible by the air-cooled blown process.

After cooling, the film passes through a collapsing frame and proceeds through de-watering, haul-off, and winding stations.

4.3.2.1.1.3 Sheet Extrusion

A *sheet* is usually defined as thicker than 0.25 mm (0.01 in); anything thinner is classified as *film*. Many thermoplastic sheets are extruded up to 30 mm (1.18 in) thick and in widths up to 2500 mm (100 in). The sheet material can be thermoformed, or fabricated by blanking, punching, machining, and welding.

Extruded sheet is produced with a die having a wide slit-like outlet. The internal flow geometry is designed to transform the cylindrical melt flow

received from the extruder to this slit form, while at the same time ensuring that the melt flow velocity at the slit exit is constant at all points across the slit width. This is difficult to achieve, particularly in wide sheet dies, and a number of solutions have been devised to deal with the problem. The usual approach is known as the *coat hanger* die, so called because the internal flow passage tapers from the die center to the edges (Fig. 4.37) [58]. By offering a greater resistance to flow in the die center, this tends to equalize flow rates across the die. Most sheet dies include two other regulating devices. An internal adjustable dam known as a *restrictor bar* or *choker bar* is positioned in the flow path of the die exit and acts as a coarse regulator. Fine regulation is achieved by adjustment of the *die lips* at the die exit slot. The gap is formed by two flat metal plates and is called the *land area*. The upper die lip includes a thin section that can be flexed elastically by the action of manual or

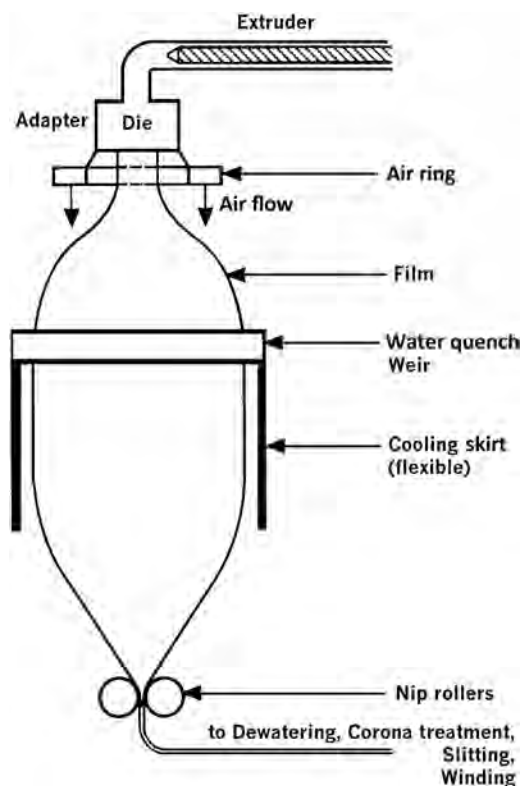


Figure 4.36 Water-quench process for blown film.

automatic adjuster bolts, so that the die exit gap can be varied across the die width [59]. The die gap should be set in the range of 0–10% greater than the desired sheet thickness.

From the die, the sheet passes immediately to a cooling and finishing device in the form of a roll cooling stack. The usual configuration is a three-roll vertical stack with the sheet entering at the nip between the upper two rolls. Variations include up-stack working where the sheet enters between the

lower two rolls, a horizontal roll stack used with a vertical die for low viscosity melts, and a two-roll stack for thinner sheet gauges. The function of the stack is to cool and polish the sheet. Alternatively, an embossed roll may be used to impart a texture to the sheet surface. Close temperature control of the rolls is critical; the temperature variation across the roll should be no more than 1.5 °C (2.7 °F). Roll temperatures depend on sheet thickness and production rate, and on whether a gloss surface is required. If so, the appropriate sheet surface must be maintained at least at 110 °C (230 °F) until it contacts the polishing roll. Table 4.10 summarizes the effect of die and roll variables on sheet characteristics.

4.3.2.2 Coextrusion

Coextrusion is the process of forming an extrudate composed of more than one thermoplastic melt stream. The process came about because some service demands, particularly from the packaging industry, could not be satisfied by a single polymer although they could be met by a combination of polymers. Coextrusion was first practiced in the production of cast film and is now also used in blown film and sheet extrusion. The intention is normally to produce a laminar structure in which each layer contributes a key property to the overall product performance. Coextruded films may be very complex structures composed of many different functional layers, including tie layers whose purpose is to bond neighboring layers of limited compatibility. Five layers is not uncommon. However, side-by-side coextrusion is also possible.

Separate extruders are required for each distinct material in the coextrusion. The process has two

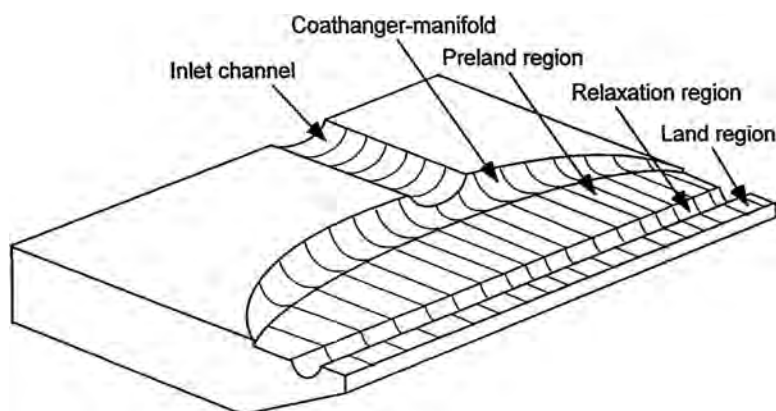
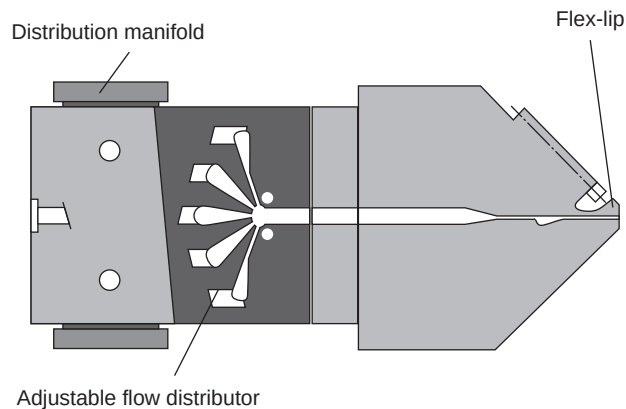


Figure 4.37 Coat hanger die.
With permission

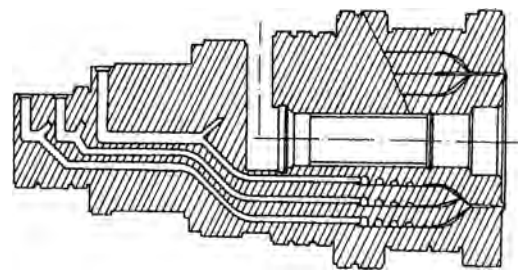
Table 4.10 Influence of Die and Roll Stack Variables on Sheet Characteristics

Variable	Orientation	Transparency	Gloss	Stiffness	Impact Resistance
Die gap	>	—	—	—	—
Melt temperature	<	—	>	—	—
Roll temperatures	—	<	>	>	<
Roll speeds	>	<	>	>	<

Ebnesajjad S. *Fluoroplastics, volume 2: Melt processible fluoropolymers, the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 2003.

**Figure 4.38** Schematic of coextrusion feedblock.

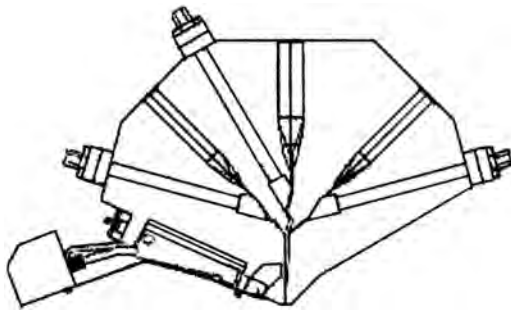
variations, depending on the point at which the separate melt streams are brought together. In feed block coextrusion, the streams are merged into a single laminar melt flow in a feedblock (Fig. 4.38), which is positioned immediately upstream of the extrusion die. The process depends on the high viscosity of plastics melts to prevent intermingling of the layers as they pass through the extrusion die. The flow rate of each component layer can be controlled by valves in the feedblock, and the capital cost is relatively low. The alternative, die coextrusion, uses a complex die construction in

**Figure 4.40** Three-layer coextrusion die for blown film.

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which separate melt path manifolds are arranged to merge at a point close to the die exit (Fig. 4.39). The thickness and flow rate of individual layers can be independently controlled, and it is also possible to handle polymers with substantially differing viscosities and melt temperatures. The capital and maintenance costs of such multi-manifold coextrusion dies are high.

Coextrusion of blown film is accomplished by multi-manifold dies. The distribution of melt along the circumference of these dies is accomplished by a spiral mandrel [58]. An example of a die for the coextrusion of a three-layer film is in Fig. 4.40, and an arrangement for the coextrusion of a nine-layer blown film is in Fig. 4.41.

**Figure 4.39** Three-layer multi-manifold coextrusion die.

4.3.2.3 Wire Coating

The process of coating wire and cable by extrusion has been around for quite some time. Molten plastic is extruded into a crosshead die through which the wire being coated is passed. After leaving the die, the coated wire is cooled in an air and/or water bath while it is continuously tested for spark and *concentricity* (roundness of the coating). In this process, *primary insulation* is defined as a metal wire

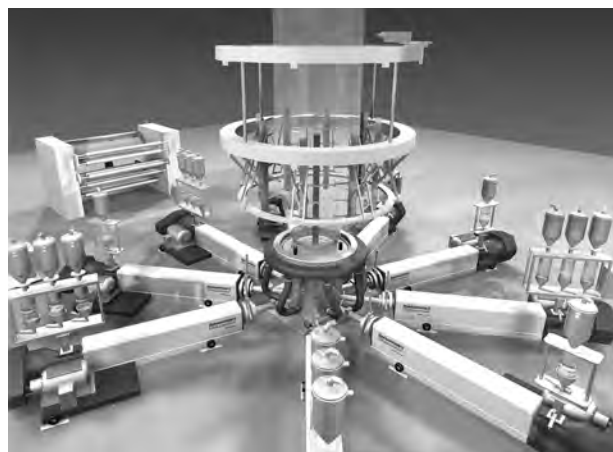


Figure 4.41 Equipment for coextrusion of nine-layer blown film.

Courtesy: Battenfeld Gloucester Engineering Company

directly coated with a plastic to isolate the metal electrically. *Jacketing* (or *sheathing*) is referred to covering one wire or a group of wires with a plastic coating or jacket for nonelectrical protection. Jackets are usually put on primary wires.

Typical wire coating line has several pieces of equipment as summarized in Table 4.11. A standard thermoplastic extruder design, built using special materials of construction, with a length-to-diameter (L/D) ratio of 20:1 to 30:1, can be used to extrude most TPEs. High L/D machines are required to obtain sufficient contact surface area for heat transfer to melt the resin. Lower L/D results in a lower output, and barrel temperatures would have to be raised, which can lead to an increase in the polymer

Table 4.12 Relationship Between Extruder Output and Motor Size

Extruder Diameter	Output, kg/h	Motor Size, kW
30	15	3.7–7.5
50	45	11.1–18.6
65	75	26.1–37.3

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degradation. Table 4.12 shows the relationship between diameter, output, and motor size for different extruders. Restriction of flow imposed by the sizing die usually reduces the extruder capacity.

Moisture should be avoided during the extrusion because it can form bubbles in the insulation, which can form points of dielectric breakdown failure. Most TPEs are hydrophobic but can pick moisture due to condensation (pigments in color concentrates can be hygroscopic). The best way to dry the resin is to blow warm air into the feed hopper in a concurrent manner to the flow of the pellets. Blowing air at a temperature in the range of 120–160 °C (248–320 °F) for 1–2 h at a velocity of <1 cm/s is sufficient for drying the resin [11]. It is also possible to dry the resin in an oven prior to charging it to the hopper. More details on drying are found in sections on the processing of individual thermoplastic elastomers.

Polymer melt travels from the extruder to the head through an adapter. The internal design of the adapter should be streamlined to allow smooth flow. Conical

Table 4.11 Wire Insulation Line Equipment and Components

Equipment/Component	Function
Hopper (feed of material)	Dry and feed resin to the extruder
Unwind	Feed uncoated wire to the crosshead die
Tension control device	Regulates tension in the feed wire
Preheater	Heats up the uncoated wire
Extruder	Melts, heats up the resin, and feeds the crosshead die
Crosshead die	Redirects the molten resin 90° to coat the wire
Cooling trough	Quenches the coated wire
Capstan	Drives the wire to the line speed
Spark tester	Detects faults in the coated wire
Take-up	Winds up the coated wire

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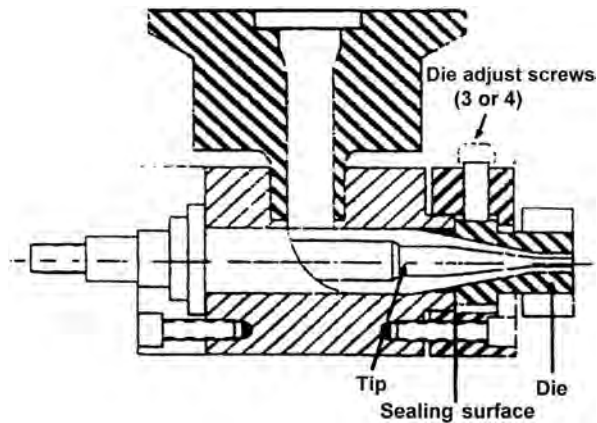


Figure 4.42 A conventional crosshead design.

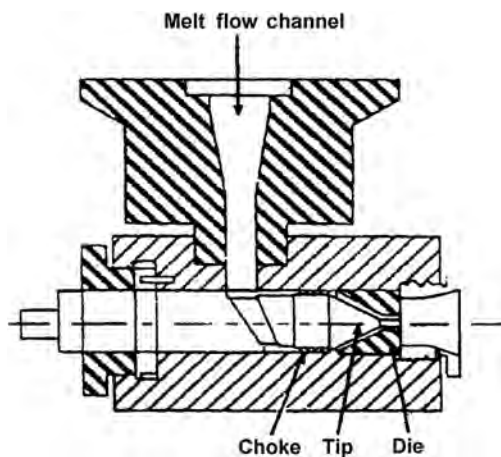


Figure 4.43 A self-centered die crosshead design.

reductions should, thus, be made at a maximum angle of 30° . The adapter should be equipped with a heater band to prevent cooling of the melt and also alleviate the need for overheating the melt in the extruder. Melt viscosity is a strong function of the melt temperature. Extrusion rate (the volume of the resin extruded per unit time) varies with viscosity, so any variation in melt viscosity will be reflected in the extrusion rate. It is important to preheat the adapter by using the heater band to prevent solidification of the initial melt on its interior surface, which can result in excessive pressure buildup.

A crosshead die is the transition piece that usually alters the direction of the melt flow by 90° to coat the wire. Design of the crosshead should be streamlined with minimum melt residence time. Figures 4.42 and 4.43 show two designs of crosshead dies. In one design (Fig. 4.42), the die is manually adjusted for concentricity, while in the other design the die is fixed and concentricity adjusts automatically. The

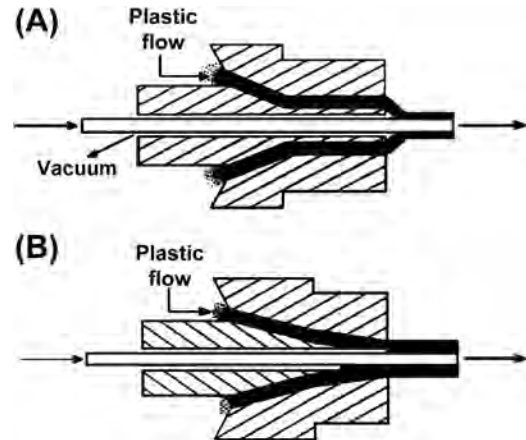


Figure 4.44 Schematic diagrams of (A) tube and (B) pressure die.

most common type of die for thermoplastic extrusion is a tube die (Fig. 4.44(A)) that extrudes a thin wall tube around the wire. The tube is drawn by vacuum onto the wire after it leaves the die. The vacuum is pulled through the clearance between the conductor and its passageway through the crosshead. Another type is a pressure die in which the melt comes in contact with the wire prior to leaving the die while the melt is under pressure (Fig. 4.44(B)).

4.3.2.4 Extrusion of Pipe and Tubing

Dies for pipe and tubing production consist essentially of a female die ring that shapes the pipe outside diameter and a male mandrel that shapes the inside diameter. The difficulty is to support the mandrel in rigid and accurate alignment with the die ring without compromising the product. The spider type (Fig. 4.45) uses three or four spider legs (ribs) to support the mandrel, but these legs cause axial weld lines as the melt flows around them [56]. An alternative is the breaker plate design in which the mandrel is supported by a disc pierced by a multitude of small holes. A better solution, particularly for larger pipe dies, is the spiral mandrel. Here the mandrel is rigidly supported, and the melt flow is directed around it in an initially helical pattern, which is converted to axial flow by the geometry of the flow channels and lands. Weld lines are eliminated, but the difficulty is to ensure an even flow rate at all points of the die outlet [56].

As the melt exits the die, it swells slightly. Therefore, it requires a size adjustment, namely *calibration*. The outside diameter of a pipe or tube may be calibrated either by an internal air pressure of

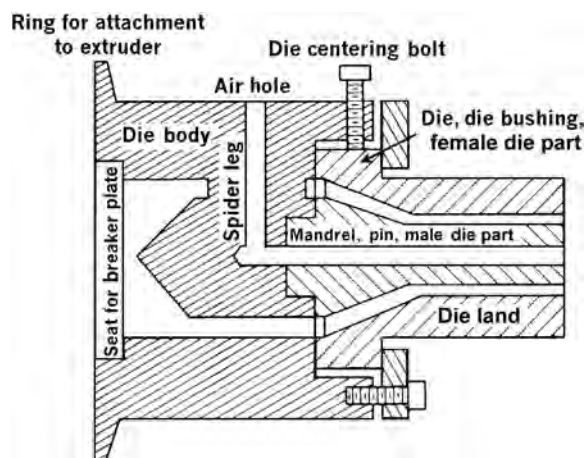


Figure 4.45 Typical spider-type tube die for pipe and tube extrusion.

1.3–2.0 bar (19–29 psi), or by external calibration in a vacuum sizing tank (Fig. 4.46) operating at a pressure of 0.3–0.5 bar (4.5–7 psi). For calibration by internal pressure, the diameter of the die ring is made approximately equal to the internal diameter of the finished pipe. For vacuum tank calibration, the die ring is made up to 25% larger, and the haul-off is set for a wall thickness drawdown of up to 30%. Below is a more detailed description of the pipe and tube sizing methods.

Thermoplastics tube and pipe size is set by one of four techniques: the vacuum trough, the extended (internal) mandrel, the sizing sleeve, and the sizing plates (Fig. 4.47). Vacuum trough and extended mandrel are the more common techniques for holding the size of the tubes and pipes in a quench bath. These

two methods are described in detail below. In the sizing sleeve method, the outside diameter of the tube is fixed as it comes in contact with a water-cooled metal sleeve (usually brass). This contact takes place by air pressure inside the tube or by drawing a vacuum through the perforated internal surface of the sleeve. The sizing-plate method predates the vacuum trough technique. In this method, the tube takes its size as it is pulled through a series of brass or stainless steel plates, similar to the way that metal wire is drawn from a metal rod. The tube is forced through the plates by a positive internal air pressure.

In the *vacuum trough method* illustrated in Fig. 4.47(A), the tube (or pipe) enters into one end of a closed long trough and is extruded out of the other end. The trough is filled with water, which directly contacts and surrounds the tube, providing efficient cooling. Inside the trough, vacuum is drawn over the water, reducing the pressure in the trough, thus allowing the soft tube to expand against the collars or rings at the entrance and exit. This mechanism prevents tube collapse and ensures well-rounded sizing of the outside of the tube. The pressure difference between the outside (under vacuum) and the inside of the tube that is open to the atmosphere generates the expansion force. The tube moves through fixed metal collars or rings, which give it its size. The first collar at the trough entrance is the most important one. A small stream of water is directed at the pipe just before the entrance as a lubricant. The number and positions of the rings and sleeves are usually adjustable. They become slightly smaller as the pipe passes through the trough, taking into account shrinkage that results from cooling and crystallization of the polymer.

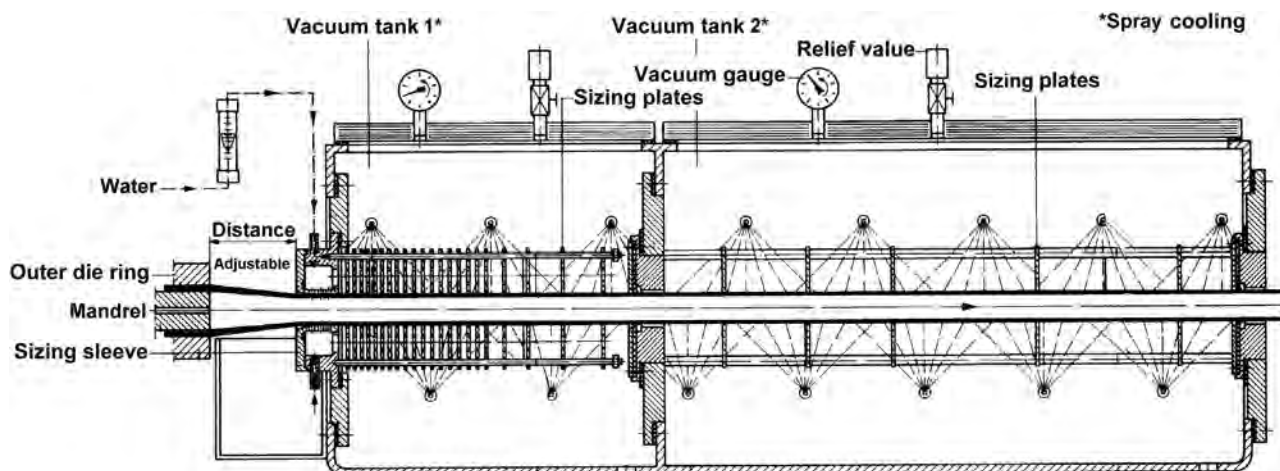


Figure 4.46 Vacuum sizing tank used for pipe and tube extrusion.

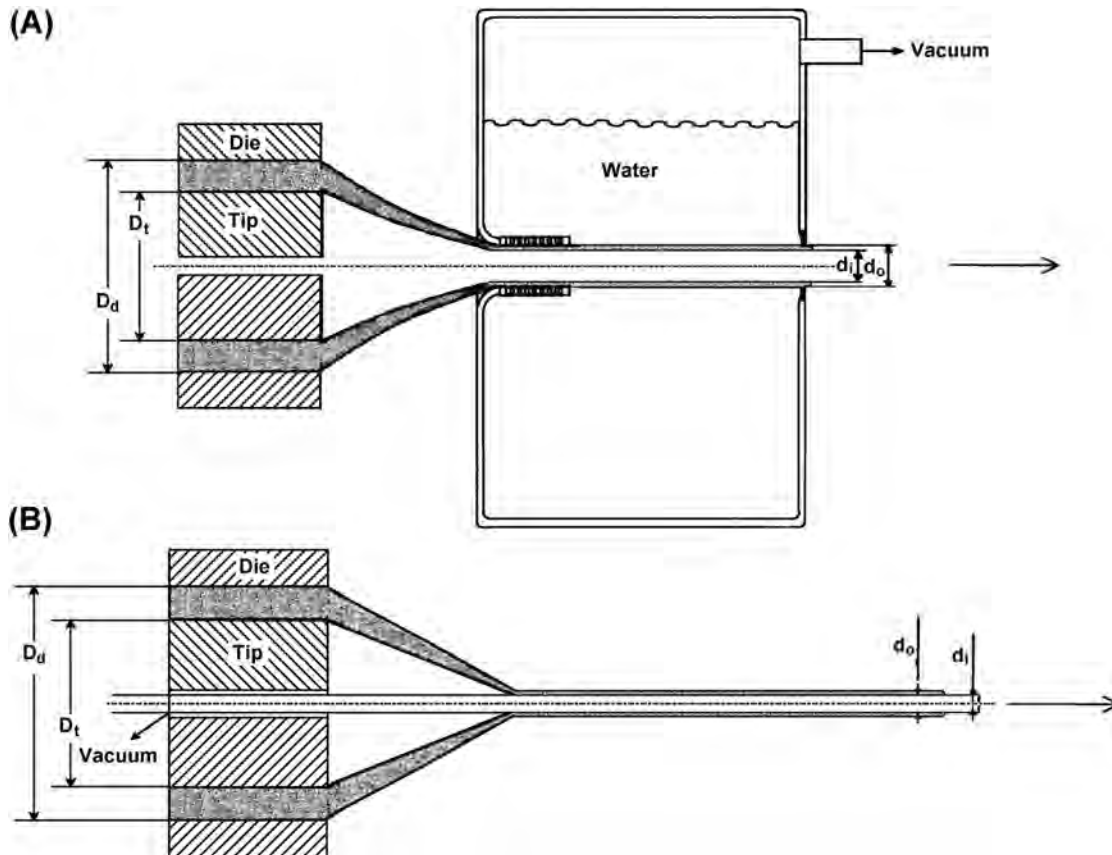


Figure 4.47 Methods for pipe and tube sizing: (A) Vacuum trough; (B) Extended mandrel method.

The vacuum trough method provides excellent cooling with little frictional drag acting against the tube. There are no theoretical limitations to the production rate. The trough has to be longer for higher output rates, which has a bearing on the available space. Large pipes (>100 mm or 4 in outside diameter) are hard to keep submerged under the water without distorting them or marring their surface. On these occasions, the trough is not filled, but water is sprayed and cascaded all around the pipe while it is passing through. The entire inside space of the trough is maintained under vacuum. Smaller pipes and tubing (OD 12.5 mm or 0.5 in) are usually sized without the use of vacuum [57].

The *extended mandrel technique*, illustrated in Fig. 4.47(B), provides internal cooling and support to the tube. The shrinkage of the plastic as a result of cooling causes a tight contact between the tube and the metal mandrel that can extend up to 30 cm (12 in) beyond the die. Longer mandrels have been difficult to use due to mechanical difficulties [56]. The mandrel is tapered with the larger end closer to the die. The diameter difference between the large and small ends is

a function of the polymer type in addition to the variables related to the tube type and size. The end of the mandrel is slightly larger than the final pipe size to allow additional shrinkage. There is a passage for cooling water inside the mandrel. To ensure a constant temperature, the passage must be uniform. Water cascades accomplish additional cooling over the tube. A small split ring is placed around the tube just as it leaves the die to prevent oscillation of the water, which could otherwise cause water marking. Water cascades further cool the tube after it leaves the mandrel. It finally enters a water trough equipped with sizing plates.

Pipe and tubing can also be made by extrusion through a crosshead die, similar to that used for wire and cable coating, described in Section 4.3.3.3 [57].

4.3.2.5 Extrusion of Profiles

Profile shapes, from simple tubing or rods to complex custom shapes, can be readily produced by extrusion. Methods of cooling and shaping of the final products vary with the type of profile. It may be a simple water trough to a complex vacuum sizing

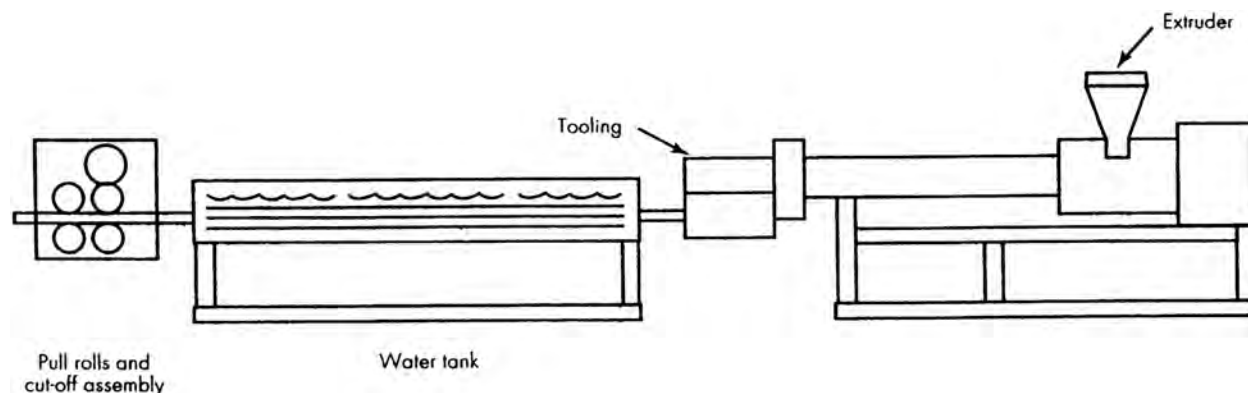


Figure 4.48 Schematic drawing of a profile extrusion line.

equipment that holds the outer surface fixed during the melt solidification. The melt temperatures for profile extrusion are lower than those for the extrusion of films and sheets, where lower melt viscosities aid in forming the product [57]. A schematic of a simple profile extrusion line is in Fig. 4.48.

4.3.2.6 Extrusion Coating

The extrusion of melt through a flat sheet die also can be used to produce a thin film coating on paper, fabric, foils, or other substrates. The substrate to be coated is unwound off a feeder roll and passed through the first nip of the roll stack (Fig. 4.49). Sometimes the substrate is treated prior to coating for enhanced adhesion [57].

4.3.3 Process Control in Extrusion

It is important to equip the extrusion line with sufficient instrumentation to produce a high quality product. Process variables that are routinely controlled and/or monitored are various temperatures, melt pressure inside the extruder, and motor drive speed. Table 4.13 contains a list of process variables, the location of each variable, the impact of each variable, and the methods of its control.

Temperature control is critical because of the sensitivity of viscosity to temperature. Thermowells (encasements to place a thermocouple) can be built into the barrel wall to measure the temperature. Melt temperature should be measured directly to avoid dependence on the barrel temperature, which

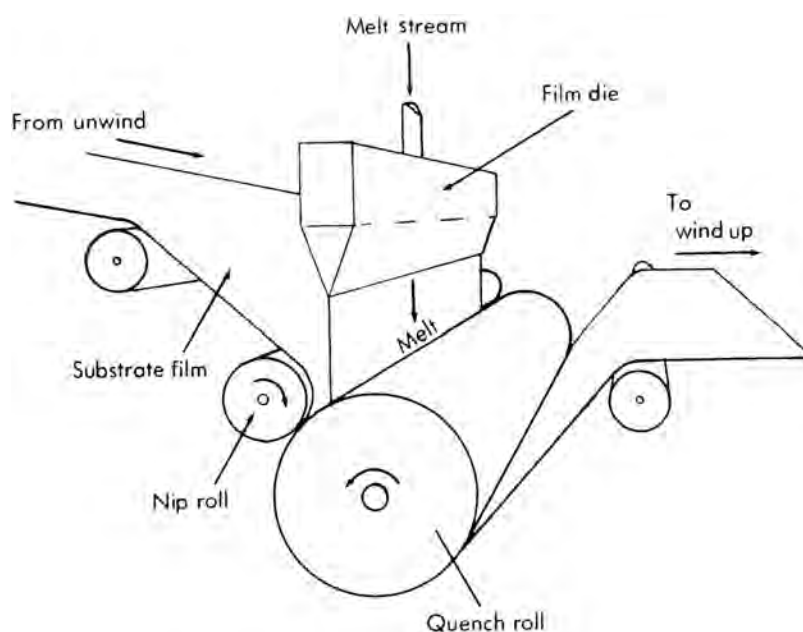


Figure 4.49 Schematic of the extrusion coating process.

Table 4.13 Extrusion Process Control Variables

Variable	Location	Impact	Control Method
Temperature	1. Extruder barrel; 3–4 zones 2. Heater bands	Melt viscosity Resin degradation	1. PID ^a control of the barrel zones 2. On-Off control is less desirable
Pressure	Inside the barrel	Consistent flow requires consistent pressure	1. Melt temperature 2. Screw speed 3. Breaker plate 4. A rupture disk relieves overpressure
Motor drive	1. Extruder 2. Take-up capstan	1. Extruder output 2. Line tension	1. Solid state controllers 2. Electronic controllers

^aPID is abbreviation for Proportional-Integral-Differential controller.

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could significantly differ from the melt. A thermocouple is placed in the barrel in a manner that its tip is immersed in the melt, extending to the middle of the flow channel. Temperature controllers should be equipped with limit switches or other mechanisms to detect the failure of thermocouples, the heater, or the controller itself. An ammeter can detect a full-on failure that could lead to degradation of the resin. In cases where multiple band heaters are controlled by a controller, all units should have the same power flux.

Pressure measurement is important both to the quality of the product and safety of the extrusion process. The most preferred sensor is a pressure transducer. High backpressure can damage the equipment, particularly when screenpacks or high-pressure drops are present. Similar to the melt thermocouple, pressure transducers should also be constructed from corrosion-resistant materials.

A variety of AC and DC drives are available for extruders. DC motors with solid-state controllers and power supplies provide the most flexible scenario for control. A speed-control feedback loop on the drive will minimize variation in the extruder output.

4.4 Injection Molding

A significant portion of thermoplastic elastomer consumption is processed by means of injection molding. The process produces a complex finished part in a single rapid and automatic operation. This distinguishes plastics injection molding from most other

manufacturing processes, although there are parallels with metal casting, particularly with die casting. Generally speaking, a whole series of forming, joining, and finishing operations would be needed to replicate an injection-molded article in other materials using different manufacturing methods. It is the single operation that makes injection molding economically viable despite the high cost of machinery and molds. Injection molding machines and molds are very costly because of the high pressures required when injecting most TPE melts (thermoplastics, in general) and the complexity of the process controls. The ability to produce a completely finished part at high speed balances the equation with high machine and mold costs and makes injection-molded articles highly cost-effective.

4.4.1 General Considerations

As mentioned earlier, several factors affect any type of the processing of thermoplastics including injection molding. They include viscosity, heat, temperature, thermal stability, thermal conductivity, crystallinity, and moisture.

Viscosity is a measure of flow of a plastic, that is, how fast a given mass of the plastic will flow as a result of applying a force to it. Flow of plastics is inversely proportional to viscosity. Viscosity decreases with an increase in temperature. Lower viscosity is helpful to injection molding in that it reduces the flow time of the plastic, resulting in higher production rates and good geometric definition. Temperature must be increased

beyond the melting point of the material to allow flow of the plastic. Above the melting point, viscosity reduction should be balanced against thermal degradation of the plastic. In practice, viscosity is replaced by the melt flow rate of the polymer, which is measured under standard conditions. The lower the melt flow rate, the higher the viscosity of the polymer.

Heat has to be delivered to the plastic to increase its temperature and melt it. The molding equipment should be able to deliver sufficient heat to melt the polymer being processed. *Thermal conductivity*, the speed by which heat is transferred through a material, of the plastic is usually the controlling step for the delivery of heat to the material.

Crystallinity is an important consideration in injection molding because of the impact of a part's crystalline content on its properties and appearance. Most polymers are *semicrystalline*, meaning that there is a relatively large volume increase as the polymer melts and becomes entirely amorphous. After a part has been molded, the rate at which it is cooled (the speed of cooling the part) will determine the extent of its recrystallization. For example, flex fatigue life and transparency increase when crystallinity decreases. Mechanical strength and various moduli increase with higher crystallinity.

Finally, the polymer should be free of moisture before molding begins; it should be dried before charging the machine. Moisture evaporates during the melting process and forms defects in the part. It appears as bubbles if it is trapped or as voids if it escapes from the part. Both types of defects are unacceptable quality problems.

4.4.2 Basic Technology

Injection molding is one of the most important processes for mass production of objects from thermoplastics, usually without additional finishing being required. Today, most injection molding machines are the universal types, which can accept all types of molds, within limits. The economics of this process is excellent for articles with complex geometry, giving this process an advantage over other techniques. Cost per molding improves with scale, despite the sizable initial cost of injection molding machines.

The principle of injection molding is very simple. The plastic material is heated until it becomes a viscous melt. It is then forced into a closed mold that defines the shape of the article to be produced. There the material is cooled until it reverts to a solid,

then the mold is opened and the finished part is extracted. Although the principle may be simple, the practice of injection molding is anything but simple. This is a consequence of the complex behavior of plastics melts and the ability of the process to encompass complicated products. The essential mechanisms of injection molding are heat transfer and pressure flow. The essential equipment is an injection molding machine, sometimes known as a *press*, and a mold that may also be referred to as a *tool* or sometimes a *die*. The product of the process is a *molded part* or *molding*, which confusingly and inaccurately is sometimes called a mold.

Injection molding is a process in which a thermoplastic polymer is heated above its melting point, resulting in the conversion of the solid polymer to a molten fluid with a reasonably low viscosity. This melt is mechanically forced, i.e., *injected*, into a mold in the shape of the desired final object. The low viscosity of the molten polymer allows complete filling of the mold where the article resides until it is cooled below the freezing point of the polymer. In the case of semicrystalline polymers, the crystallinity of the object (which governs its mechanical and appearance properties) is usually controlled by in-mold cooling of the object at a defined cooling rate. In the last step, the mold is opened and the part is ejected and recovered.

4.4.3 The Process

An injection molding machine (Fig. 4.50) can be divided into five components: plasticating/injection section, clamping unit, mold including the runner system, control system, and tempering devices for the mold [60]. The most important part of the process is the mold, which is made of at least two parts to allow ejection (demolding) of the molded part. The injection molding process can be divided into six steps. Table 4.14 presents the main function of each step.

4.4.4 Injection Molding Machinery

There are many varieties of injection molding machines, but they all perform the same essential functions. They include melting or plasticating the plastic, injecting it into the mold, holding the mold closed, and cooling the injected material. It is convenient to think of an injection molding machine as consisting of two units. The plastication and injection requirements are combined in the *injection unit*, while the mold handling is performed by the

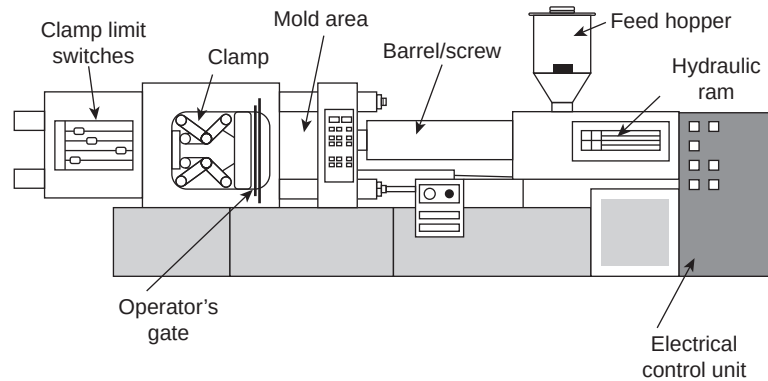


Figure 4.50 Typical injection molding machine.

Table 4.14 Processing Steps in Injection Molding

Step	Function
1. Beginning of plastification	Screw transports the melt to the reservoir where it is heated
2. End of plastification	The screw is switched off after the reservoir is filled
3. Closing the mold	Clamping unit actuates closure of the mold
4. Beginning of injection	Forward axial motion of the screw starts the flow of the melt into the mold until it is filled
5. Mold cooling and end of injection	The mold begins to cool, and additional melt is injected to compensate for the part shrinkage
6. Ejection of the molded part	The part is ejected, and the screw retracts for a new cycle

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clamp unit. The two units are mounted on a common machine base and are integrated by power and control systems. The convention is that the injection unit shall be on the right of the operator, with the clamp unit on the left (Fig. 4.50).

4.4.4.1 Clamp Unit

The function of the clamp unit is to open and close the mold halves and particularly to hold the mold closed during injection of the plastic melts. High injection pressures are necessary, due to the high viscosity of plastic melts, so the force needed to hold the mold closed is very great. The melt pressure inside the mold is exerted over the entire area of cavities and feed systems at the mold parting line. The significant figure is the extent of this area when projected onto a plane perpendicular to the opening axis of the clamp system. This is known as the *projected area* of the mold. The clamp force needed to hold the mold shut during injection is a function of the injection pressure and the

projected area, but this is not a simple function. The injection pressure varies throughout the cavities and feed systems and is also a complex function of process parameters such as melt and mold temperature, and injection rate. The cavity pressure is also a function of part thickness, which is completely independent of the projected area, so attempts to determine clamp force on the basis of the projected area by itself are going to be inaccurate. This means that the old rule-of-thumb method of allotting x units of clamp force per unit of projected area should be seen as a last resort. It is one that is likely to lead to underutilization of machines due to the need for a large safety factor to cover the deficiencies of the method. The rule-of-thumb clamp figure for fluoropolymer is 0.79 tons per square centimeter of projected area should be sufficient for all polymers in this group.

The force requirements ensure that the clamp unit must be engineered very robustly, but this conflicts with the need to open and close the mold rapidly to minimize production time. A variety of clamp

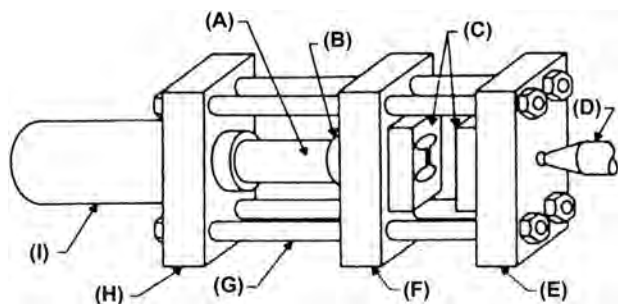


Figure 4.51 Typical direct hydraulic clamp unit. (A) Actuating plunger; (B) Removable spacer; (C) Mold; (D) Injection nozzle; (E) Fixed platen; (F) Movable platen; (G) Tie bar; (H) Cylinder base plate; (I) Clamping cylinder.

mechanisms has evolved in the search for a suitable compromise. The two most common types are the direct hydraulic clamp (Fig. 4.51) and the toggle clamp (Fig. 4.52). Other variants include hybrid toggle/hydraulic types, lock-and-block systems, and electromechanical systems.

Whatever the variation, the clamp unit always features a stationary or fixed platen and a moving platen on which the mold halves are bolted or otherwise attached. The fixed platen is mounted rigidly on the machine base and is positioned adjacent to the nozzle of the injection unit. The injection half of the mold is attached to the fixed platen, while the moving platen carries the ejection half of the mold. These terms may, in the case of some sophisticated molds, cease to be literally true, and the expressions *fixed* and *moving* mold halves are often used instead.

The clamp also includes a tailstock platen or equivalent unit that the pressure means reacts against in order to clamp the mold halves together between

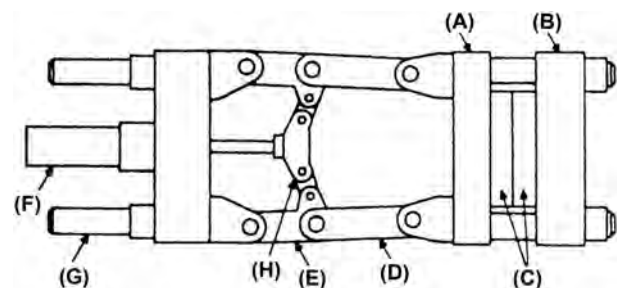


Figure 4.52 Typical toggle clamp unit. (A) Movable platen; (B) Fixed platen; (C) Mold; (D) Front link; (E) Rear link; (F) Actuating cylinder; (G) Tie bar; (H) Crosshead link.

the moving and fixed platens. For this purpose, the fixed and tailstock platens are united by tiebars (tie rods) that also serve as guides for the moving platen. The tiebars are stretched elastically when the clamp unit locks the mold shut under pressure. Since the tiebars limit access to the mold area and impede mold changing, tiebarless machines have been intensively developed in recent years. The tiebarless machine uses the same clamp concepts but employs a greatly strengthened machine base to tie the fixed and tailstock platens together. The result is a completely unencumbered mold area with free access for automation, ancillaries, and mold-changing operations. Under clamp pressure, the machine frame and platens flex elastically. Tiebarless machines use a variety of means to counteract this tendency and keep the platens parallel. However, the effect limits the clamp force that can be designed into tiebarless machines, although the figure is gradually being pushed upwards.

Another development, particularly in large injection molding machines, is a move toward two-platen clamp systems. These systems do away with the tailstock platen and use a variety of mechanisms to lock the tiebars to the moving platen in the closed position. The advantage of a two-platen clamp is a considerable saving of up to 35% in floor space.

Clamp units are rated according to the maximum closing force they can apply to the mold. The figure may be expressed as kilonewtons (kN), metric tonnes (tonne), or US tons (ton) [61].

4.4.4.2 Injection Unit

The function of the injection unit is to heat the plastics material to a uniform and homogeneous melt and to inject it into the mold under controlled conditions of pressure and flow rate. Given the low thermal conductivity, high specific heat, and high melt viscosity of thermoplastic elastomers, these are exacting tasks. Once again, many variants have been devised to solve the difficult problems involved. The variants can be grouped roughly into four principal injection unit concepts:

- Single-stage ram or plunger
- Two-stage ram
- Single-stage screw
- Two-stage screw/ram

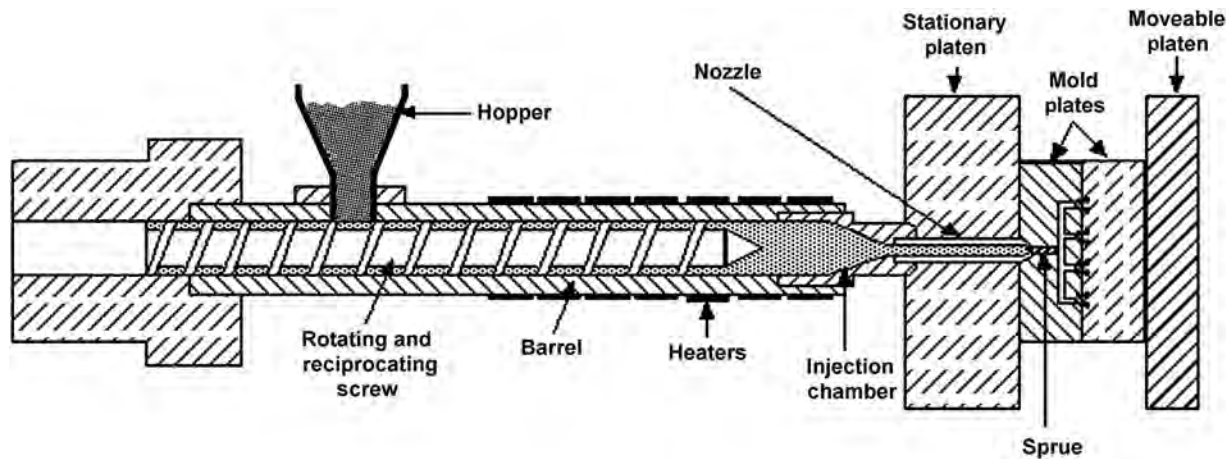


Figure 4.53 Typical reciprocating screw injection unit.

The single-stage ram unit is inefficient in heating, mixing, and pressure transmission and is largely obsolete, although the form survives in very small machines and some specialized equipment. It has the merit of simplicity and low cost. The two-stage ram is also all but obsolete. It was an attempt to improve on the single-stage ram by separating the functions of heating and pressure flow, but the ram remains an inefficient mixer and heater. The two-stage screw/ram unit also separates the functions of heat and flow, using a screw for heating and mixing, and a ram for injection. Both are relatively efficient devices for their respective duties, so the concept is attractive. However, the unit cost is higher, and it is difficult to devise an ideal melt flow path between the stages. The single-stage screw concept is by far the dominant form. A screw capable of both rotational and axial movement combines heating and mixing function with the function of injection. For this reason, the form is frequently referred to as a *reciprocating screw injection unit* (Fig. 4.53).

The extruder-like screw operates within a heated barrel and has axial zones that are concerned successively with feeding, melting, and metering the plastic material. Many different screw forms have been designed in the search for the best compromise between plastification and throughput, particularly since CNC machining has made it possible to cut shapes that were previously impractical. The design process has been accelerated by extrusion simulation software that makes it possible to predict how a screw design will perform. Ideally, the screw should be optimized for use with a particular fluoropolymer, but this can only happen if it is known that the injection

molding machine will be dedicated throughout its life to a narrow range of uses. Instead, virtually all injection molding machines are supplied with a screw that is designed as a compromise between the requirements for the majority of thermoplastics. This is known as a general-purpose screw. It is usual for a machine to be offered with additional screw options. Other options may include a vented screw, which includes a decompression zone and an associated exhaust port for the removal of water vapor or other volatile species.

Most general-purpose screws take the form of a single constant-pitch flight that decreases in depth from the input or upstream end to the output or downstream end (see Fig. 4.54). The flight pitch is usually equal to the screw diameter, giving a helix angle of 17.8° . Flight depth is usually substantially constant in the feed and metering zones and decreases at a constant rate over the compression zone. The feed zone typically occupies half the screw length, with the compression and metering zones each making up a quarter of the length. The key parameters of such a screw are the ratio of length to diameter (the L/D ratio) and the compression ratio. The L/D ratio affects mixing and melts uniformity, higher values giving better results. An L/D ratio of 20:1 is regarded as a minimum for injection molding. Long screws with the L/D ratio as high as 28:1 are offered by some manufacturers. The compression ratio has a bearing on mixing and shear heating. Typical values range from 2:1 to 3:1 or greater. The real difference is between semicrystalline and amorphous polymers. On heating to melt temperature, semicrystalline materials undergo a greater

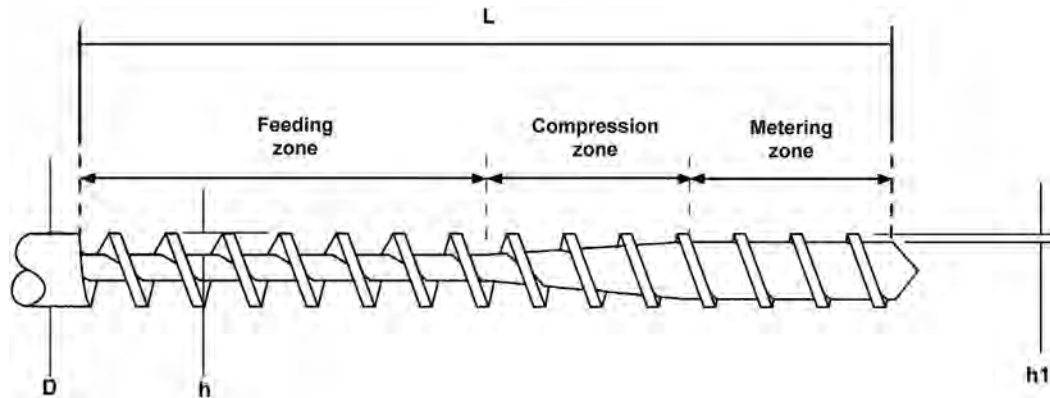


Figure 4.54 An example of a screw design for the injection molding of thermoplastics.

volume increase than amorphous materials and so require a lower compression ratio.

The basic sequence of events in the injection unit is:

- The screw rotates, thereby heating and melting the material, which is conveyed along the screw flights to the downstream end of the screw. The barrel nozzle is closed by means of a thermal or mechanical valve, or by the presence of a previous molding. The accumulating melt presses the still-rotating screw back against a controlled resistance (the back pressure) until sufficient melt has accumulated to make the next molding. At this point, screw rotation stops. This is the melt preparation phase.
- The barrel nozzle is opened, and the screw performs the action of a ram by moving forward in the axial direction without rotating. This forces (injects) the melt that has accumulated ahead of the downstream end of the screw through the nozzle and into the mold. The downstream end of the screw may be equipped with a valve arrangement to prevent melt flowing back down the screw flights. This is the mold filling or injection phase.
- After the mold is filled, screw pressure is maintained for a short period to compensate for volumetric shrinkage of the cooling melt contained in the mold. This is the packing or holding phase.
- At the conclusion of the holding phase, and while the mold remains closed for the molding to cool to ejection temperature, the injection unit cycle recommences with the resumption of screw rotation and melt preparation.

Injection units are rated in terms of the maximum injection pressure and injection volume available. Injection pressure is the theoretical maximum available at the downstream end of the screw. This is a function of the screw diameter and the force acting on it. It should not be confused, as it often is, with the hydraulic line pressure acting on the injection cylinder that supplies the force to the screw, nor should it be taken as the pressure available to fill the mold cavities. This is much less because of pressure losses in the nozzle and mold feed systems. Injection pressures are normally quoted in megapascals (MPa), atmospheric pressures (bar), or pounds per square inch (psi) [60].

The maximum injection volume or swept volume is the product of the screw diameter and its maximum retraction stroke during plastification. The value is expressed in cubic centimeters (cm^3), cubic inches (in^3), and sometimes as the weight in ounces (oz) or grams (g) of plastic material that can be injected. The weight rating is a less accurate measure and is relative to the density of the plastic material in question. The figure used to make the conversion should be the density in the melted state rather than in the solid state.

In principle, the entire theoretical shot volume is available for injection. In practice, the volume is limited by the concept of *residence time*. This is the time that an element of plastic material takes to pass through the screw and barrel system. It is a function of cycle time and injection stroke. The significance of residence time rests on the fact that a plastic material may begin to degrade if exposed too long to process temperatures normally regarded as safe. Residence time itself is independent of material, but the sensitivity of materials to residence time varies and is at its

greatest with materials that are processed at a point close to the degradation temperature. It is especially unwise to expose such polymers to lengthy residence times in the injection unit. Small shots produced from big machines are likely to lead to trouble, especially if the cycle time is long.

Figure 4.55 shows residence times for a range of cycle times. Injection strokes are expressed in terms of D , the screw diameter. If, for example, we wish to limit residence time to 5 min, this means that the injection stroke should not be less than about $1D$ for a 50-s cycle, or not less than about $0.6D$ for a 30-s cycle. The two values equate to about 25% and 15% of maximum shot volume, respectively. The maximum injection stroke for a typical injection molding screw is about $4D$. The preferred shot volume is in the range of $1D$ to $3D$, or 25–75% of the maximum available.

Allowable residence times for TPEs depend on the material temperature. Temperature should be decreased as residence time is increased.

The European Committee of Machinery Manufacturers for the Plastics & Rubber Industries has developed a standard classification for injection

molding machines. This is known as the Euromap international size classification and consists of two numbers in the format xxx/xxx. The first number indicates the clamp force in kilonewtons (kN). The second number is an injection unit rating derived by multiplying the maximum injection pressure (bar) by the shot volume (cm^3) and dividing by 1000. This figure is useful for classifying injection molding machines that are supplied, as most are, with a choice of screw diameters. The maximum injection force exerted by the machine on the screw remains constant because only the screw and barrel assembly is interchanged. This means that shot volume is proportional to screw diameter, but the maximum injection pressure is inversely proportional. The Euromap injection unit rating is unaffected by screw diameter. In other words, it returns the same figure for each of the alternative screw and barrel assemblies for a particular machine and so simplifies the task of classification. This rating is not much help in specifying an injection molding machine; maximum shot volume and injection pressure figures are indispensable for that purpose [61].

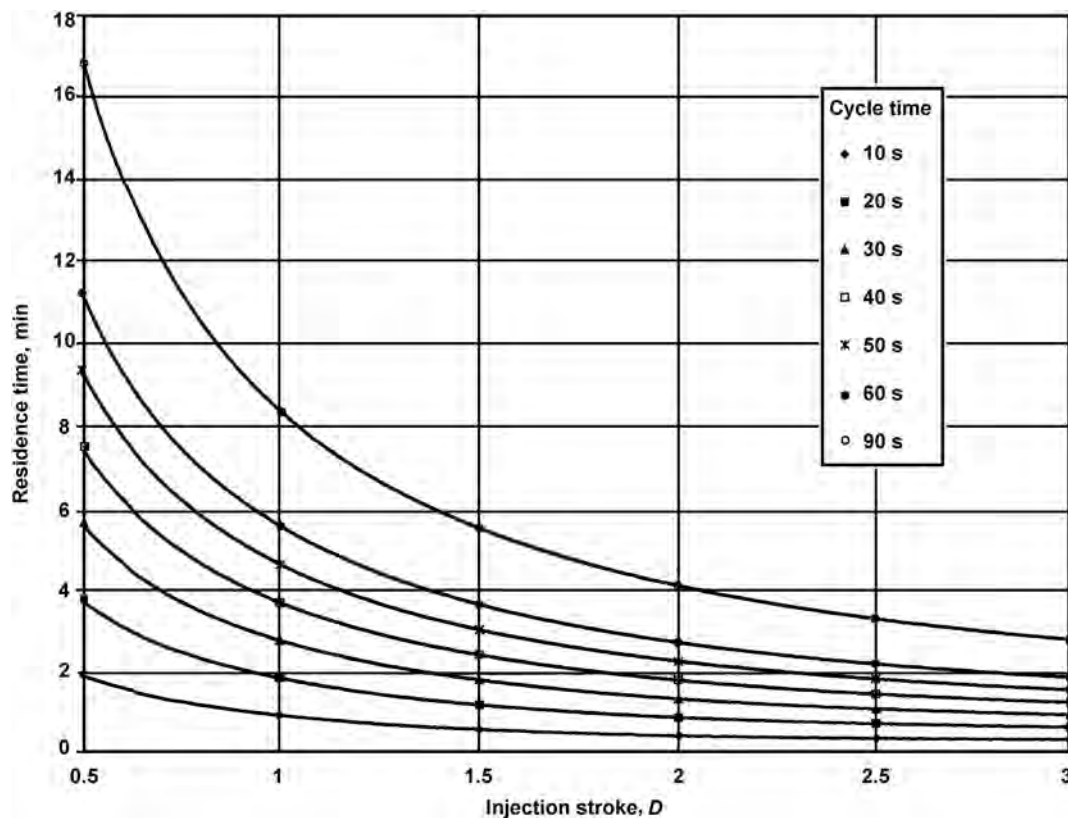


Figure 4.55 Material residence times.

Major pressure drops occur in forcing the plastic melt through the injection nozzle and hence through the mold feed system and cavities. These pressure losses cannot be quantified by simple rules. They are a function of the physical form of the flow path, the condition of the plastic melts, the rate of heat exchange, the type of polymer, and the rate and pressure of injection. Specific figures can be calculated with adequate accuracy by computer simulations of the molding process [62].

4.4.4.3 Power Systems

Injection molding machines perform a wide range of mechanical movements with differing characteristics. Mold opening is a low-force, high-speed movement; mold closing is a high-force, low-speed movement. Plastification involves high torque and low rotational speed, while injection requires high force and medium speed. The modern injection molding machine is virtually always a self-contained unit incorporating its own power source. Early machine frequency ran from a centralized source serving an entire shop or factory. In this respect, injection molding machines have undergone the same metamorphosis as machine tools.

Oil hydraulics has become firmly established as the drive system for the vast majority of injection molding machines, and until recently was almost unchallenged as the power source. Put at its simplest, the injection molding machine contains a reservoir of hydraulic oil that is pumped by an electrically driven pump at high pressure, typically at up to 14 MPa (2030 psi), to actuating cylinders and motors. High and low pressure linear movements are performed by hydraulic cylinders, and rotary movements for screw drive and other purposes are achieved by hydraulic motors. Hybrid machines, in which the screw is driven by electric motor while the linear movements remain hydraulically powered, are not uncommon.

In recent years, the supremacy of the hydraulic machine has been challenged by all-electric machines. These use new brushless servo motor technology to power the various machine movements. The capital cost of all-electric machines is higher than that of conventional machines, but the energy consumption in production is much lower. This is because the electric motors run only on demand, and there are no losses due to energy conversion, pipelines, or throttling. The elimination

of hydraulic oil makes the all-electric machines inherently cleaner, so these machines are attractive for sterile or clean room use. There is also evidence that all-electric machine movements can be resolved with a higher degree of precision and repeatability than hydraulic systems.

4.4.4.4 Control Systems

The full sequence of operations and necessary options in a modern injection molding machine is very complex (Fig. 4.56). So too, is the range of parameters and adjustments needed to control the process accurately and automatically (Table 4.15). Control is ultimately exercised by valves, regulators, and switches, but it is rare now for these to be under individual manual control. The norm now is electronic control of varying degrees of sophistication ranging from simple partial control by programmable logic controller up to fully centralized computer control. It is usual for an injection molding machine to be offered with a choice of control options to suit a variety of end uses and budgets.

The precision and repeatability of injection molding machines has been much improved by the introduction of closed-loop control to critical features like the injection screw sequence. The closed-loop principle uses sensors to measure an important parameter—speed, position, pressure—of the element to be controlled. The readings are processed by the control system, which generates control signals to a servo valve that regulates the element. The process is often known as *feedback*. In effect, the system monitors itself to check whether it is performing as instructed and, if not, it makes an adjustment based on the discrepancy.

4.4.5 The Injection Mold

The injection mold performs two vital functions: it defines the shape of the molded part, and it acts as a heat exchanger to cool the plastic material from melt temperature to ejection temperature. It must be very robustly engineered to withstand injection and clamping forces, it must operate automatically at high speed, and it must be built to very high standards of precision and finish. The mold also has other less obvious influences on the finished part. The dimensions and properties of the molding are greatly affected by shear rates, shear stresses, flow patterns, and cooling rates. Some of these are affected by both mold and machine; others are almost exclusively

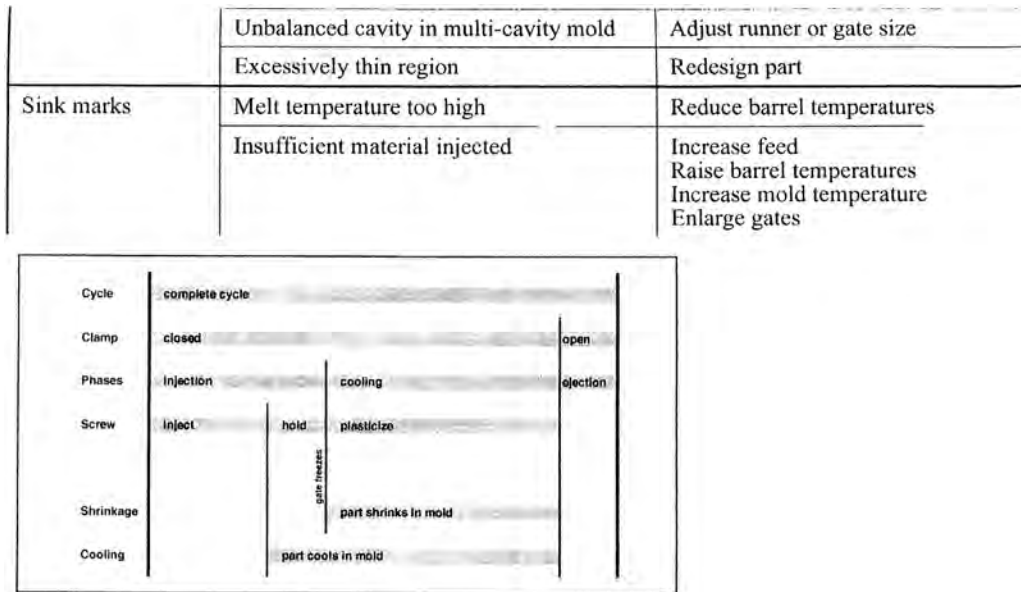


Figure 4.56 Principal elements of the injection molding cycle.

a function of the mold. These factors combine to make the injection mold a costly item. Modern technologies in the form of concurrent engineering, computer-aided analysis of flow and cooling, and high-speed and computer-controlled machining can help to keep the costs down. So too can the use of standard mold components that enjoy economies of scale and specialization. Even so, mold costs frequently dismay purchasers of moldings, and there

can be pressure to cut costs by reducing mold quality. This is a false economy and will almost always result in a more expensive molding. There is no substitute for a quality mold [63].

4.4.5.1 Injection Mold Components

Figure 4.57 illustrates the principal components used in the construction of an injection mold.

Table 4.15 Some Injection Molding Process Factors

Temperature	Time	Distance	Speed	Pressure or Force	Profile
Melt	Hold changeover	Hold changeover	Screw rotation	Hold changeover	Injection pressure
Mold	Open	Fast open	Injection stroke	Injection	Injection speed
Nozzle	Carriage forward delay	Slow open	Carriage	Peak	Holding pressure
Barrel zones	Hold	Eject	Slow break	Holding	
Feed throat	Carriage back delay	Sprue break	Fast open	Back	
Pellets	Screw start delay	Suck back	Slow open	Nozzle hold-on	
	Cooling	Shot	Eject	Clamp close	
	Eject	Cushion		Clamp open	
	Cycle delay				

Maier C, Calafut T. *Polypropylene, the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 1998.

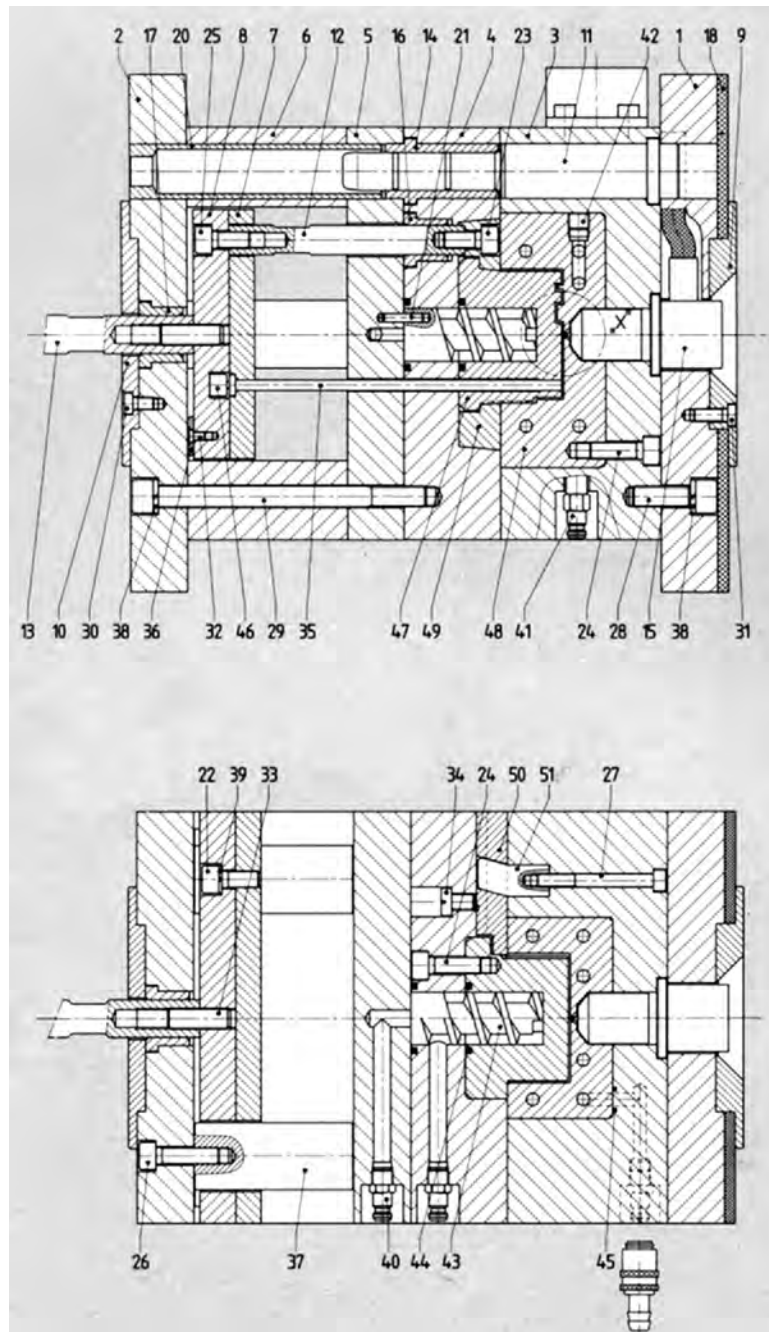


Figure 4.57 Example of an injection mold, illustrating principal component parts.

The sequence of operations (Fig. 4.58) for a typical mold is:

- Plastics material is injected into the closed mold.
- The mold remains closed while the molding cools. The mold temperature is controlled by a coolant fluid (generally water or oil), which is pumped through cooling channels. Even if the mold is heated relative to ambient temperature, it is still cool in relation to the plastics melt temperature.
- The mold opens, leaving the molding attached by shrinkage to the core. During opening, the side action is retracted by a cam to release an undercut on the molding.

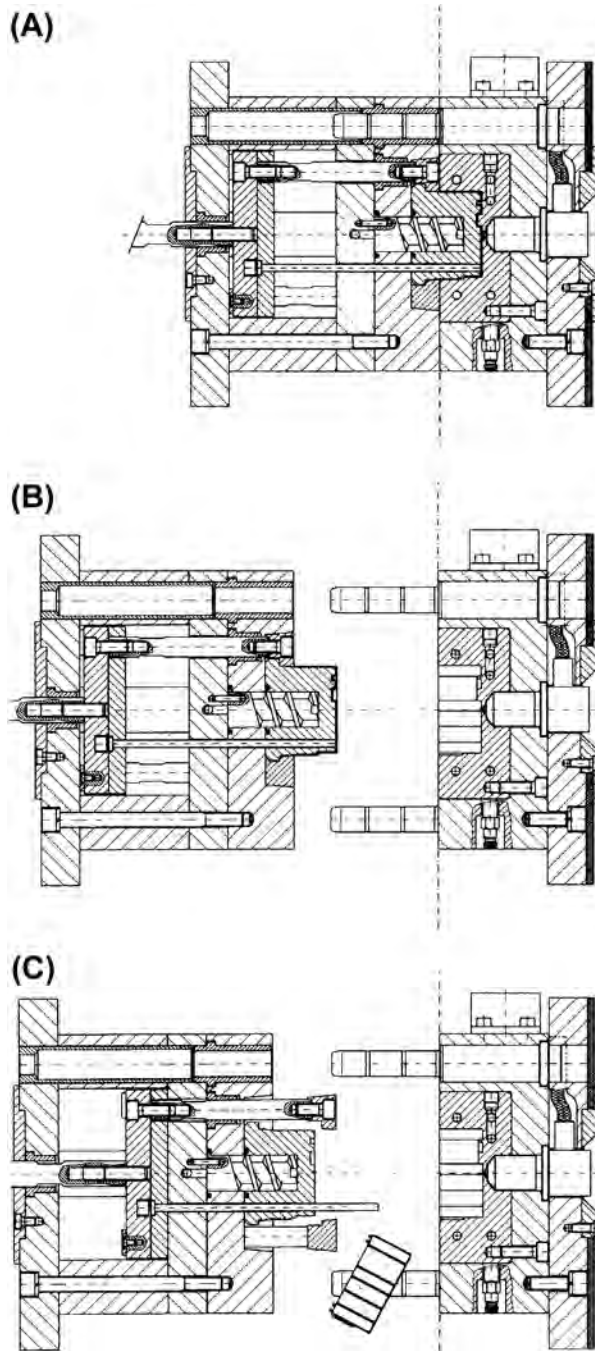


Figure 4.58 Sequence of mold operation. (A) Plastic material is injected into the closed mold, (B) the mold opens, leaving the molding attached by shrinkage to the core, (C) the ejector plate is moved forward, causing ejector pins and stripper bars to push the molding off the core.

- The ejector plate is moved forward, causing ejector pins and stripper bars to push the molding off the core.

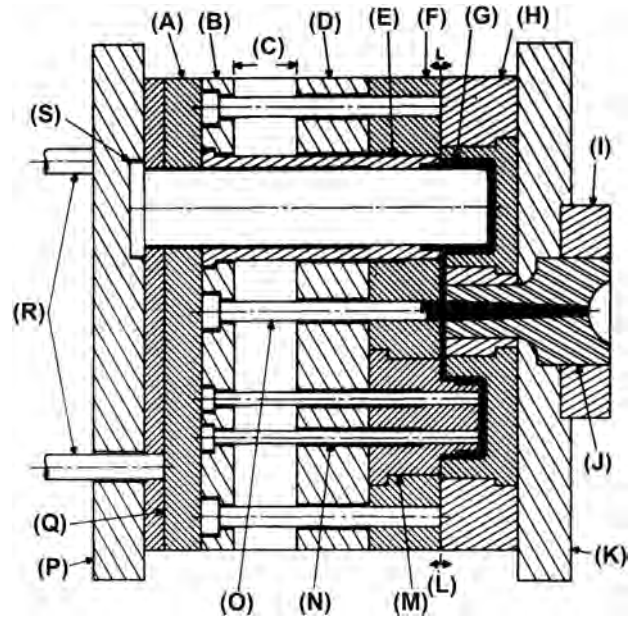


Figure 4.59 Schematic drawing of a two-plate mold. (A) Knockout plate; (B) Ejector retainer plate; (C) Ejector travel; (D) Support plate; (E) Sleeve-type ejector; (F) Rear cavity plate; (G) Cavity; (H) Front cavity plate; (I) Locating ring; (J) Sprue bushing; (K) Clamping plate; (L) Parting line; (M) Core or force; (N) Ejector pin; (O) Sprue puller; (P) Clamping plate; (Q) Retainer plate; (R) Knockout pins; (S) Core or force pin.

- The ejector plate returns and the mold closes, ready for the next cycle.

4.4.5.2 Injection Mold Types

Every molded part is different, and so every mold is unique. Nevertheless, it is possible to distinguish some standard features and types. All are generally suitable for use with thermoplastic elastomers. The principal types are two-plate, three-plate, and stack molds. A further distinction concerns the feed system, which can be either the cold or hot type. These classifications overlap. A three-plate mold will have a cold runner feed system, and a stack mold will have a hot runner system. Two-plate molds can have either feed system [60].

4.4.5.2.1 Two-Plate Molds

The two-plate mold has more than two plates in its construction. The description means that the mold opens or splits into two principal parts (Fig. 4.59).

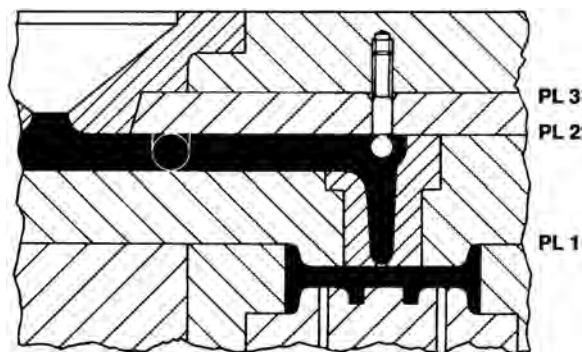


Figure 4.60 Schematic drawing of a three-plate mold (PL-Plate).

These are known as the *fixed* or *injection half*, which is attached to the machine's fixed platen, and the *moving* or *ejection half*, which is attached to the moving platen. This is the simplest type of injection mold and can be adapted to almost any type of molding. The cavities and cores that define the shape of the molding—these are sometimes known as the *impressions*—are so arranged that when the mold opens, the molding remains on the ejection half of the mold. In the simplest case, this is determined by shrinkage that causes the molding to grip on the core. Sometimes it may be necessary to adopt positive measures such as undercut features or cavity air blast to ensure that the molding remains in the ejection half of the mold.

4.4.5.2.2 Three-Plate Molds

The three-plate mold is so called because it splits into three principal linked parts when the machine clamp opens (Fig. 4.60). As well as the fixed and moving parts equating to the two-plate mold, there is an intermediate floating cavity plate. The feed system is housed between the fixed injection half and the floating cavity plate. When the mold opens, it is extracted from the first daylight formed by these plates parting. The cavity and core is housed between the other side of the floating cavity plate and the moving ejection part of the mold. Moldings are extracted from the second daylight when these plates part. The mold needs separate ejection systems for the feed system and the moldings. Motive power for the feed system ejector and the movement of the floating cavity plate is derived from the clamp-opening stroke by a variety of linkage devices. The molding ejection system is powered normally by the injection machine ejection system.

The three-plate mold is normally used when it is necessary to inject multiple cavities in central rather than edge positions. This is done for flow reasons: to avoid gas traps, ovality caused by differential shrinkage, or core deflection caused by unbalanced flow. This type of mold also has the advantage of automatically removing (degating) the feed system from the molding. The disadvantages are that the volume of the feed system is greater than that of a two-plate mold for the same component, and that the mold construction is more complicated and costly.

4.4.5.2.3 Stack Molds

The stack mold also features two or more daylights in the open position. Two daylights are normal (Fig. 4.61), but up to four are known. The purpose of the stack mold is to increase the number of cavities in the mold without increasing the projected area and hence the clamp force required from the injection molding machine. This is done by providing cavities and cores between each of the daylight. Provided the projected area at each daylight is the same, opposed components of opening thrust from each daylight cancel out, leaving the total mold opening force no greater than that developed in a single daylight. The cavities are fed by a hot runner system deployed in the floating cavity plate. Separate ejection systems are required for each daylight. The mold engineering and hot runner control systems are complicated and become much more so when there are more than two daylights present. Stack molds are normally used for high volume production of relatively small and shallow components such as closures for packaging applications.

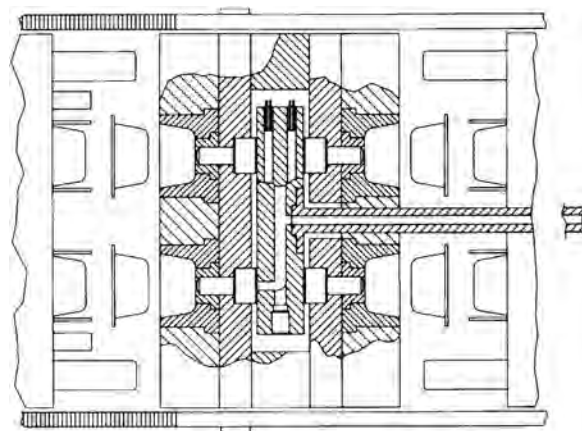


Figure 4.61 Schematic drawing of a stack mold.

4.4.6 Injection Mold Feed Systems

The feed system is the name given to the flow melt passage in the mold, between the nozzle of the injection molding machine and the mold cavities. This apparently utilitarian feature has a considerable effect on both the quality and economy of the molding process. The feed system must conduct the plastics melt to the cavity at the right temperature, must not impose an excessive pressure drop or shear input, and should not result in nonuniform conditions at the cavities of multi-impression molds. The feed system is an unwanted by-product of the molding process, so a further requirement is to keep the mass of the feed system at a minimum to reduce the amount of plastic material used.

This last consideration is a major point of difference between cold and hot runner systems. The cold runner feed system is maintained at the same temperature as the rest of the mold. In other words, it is cold with respect to the melt temperature. The cold runner solidifies along with the molding and is ejected with it as a waste product in every cycle. The hot runner system is maintained at melt temperature as a separate thermal system within the cool mold. Plastic material within the hot runner system remains as a melt throughout the cycle and is eventually used on the next or subsequent cycles. Consequently, there is little or no feed system waste with a hot runner system. Effectively, a hot runner system moves the interface between the machine plasticizing system and the mold to a point at or near the cavities. In a cold runner system, the interface is at the outside surface of the mold, at a point between the machine nozzle and the sprue bush [63].

4.4.6.1 Cold Runners

Cold runner feed systems include three principal components: sprue, runner, and gate. The *sprue* is a tapered bore in line with the axis of the injection unit that conducts the melt to the parting line of the mold. The *runner* is a channel cut in a parting face of the mold to conduct melt from the sprue to a point very close to the cavity. The *gate* is a relatively small and short channel that connects the runner to the cavity. The gate is the entry point of the melt into the molding cavity [62].

Runners are produced in a variety of cross-sectional configurations (Fig. 4.62), but not all of them perform equally well. The best shape for the runner itself is a full-round section, cut in both halves

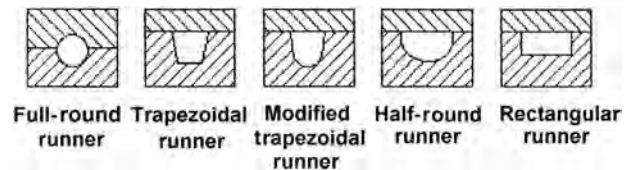


Figure 4.62 Common runner configurations.

of the mold. This is the most efficient form for melt flow without premature cooling. There are some instances when it is desirable to cut the runner only in one half of the mold, either to reduce the machining cost or where it is mechanically necessary over moving splits. In this case, the preferred runner sections are trapezoidal or modified trapezoidal. The half-round runner provides only a restricted flow channel combined with a large surface area for cooling and consequently is not recommended.

The concept of the hydraulic diameter (D_H) provides a quantitative means of ranking the flow resistance of the various runner configurations [64]. The hydraulic diameter is calculated from an expression chosen to give a full-round runner a value of $1D$, where D is the runner diameter, A = cross-sectional area, and P = perimeter:

$$D_H = 4A/P \quad (4.3)$$

The resulting values for equivalent hydraulic diameters (Fig. 4.63) clearly demonstrate the superiority of the full-round design for runners cut in both halves of the mold and the modified trapezoidal design for runners cut in one half of the mold.

Runner layouts should be designed to deliver the plastic melt at the same time and at the same temperature, pressure, and velocity to each cavity of a multicavity mold. Such a layout is known as a *balanced runner* (Fig. 4.64). A balanced runner will usually consume more material than an unbalanced type, but this disadvantage is outweighed by the improvement in the uniformity and quality of the moldings. Balance in a multicavity mold with dissimilar cavities (known as a family mold) can be achieved by careful variation of runner diameter in order to produce equal pressure drops in each flow path. Such balancing can only be achieved efficiently by the use of computer flow simulations, and this method really should now be the norm for injection mold design.

If flow simulation software is used, runner dimensions will be calculated precisely and can then optionally be adjusted to a standard cutter size.

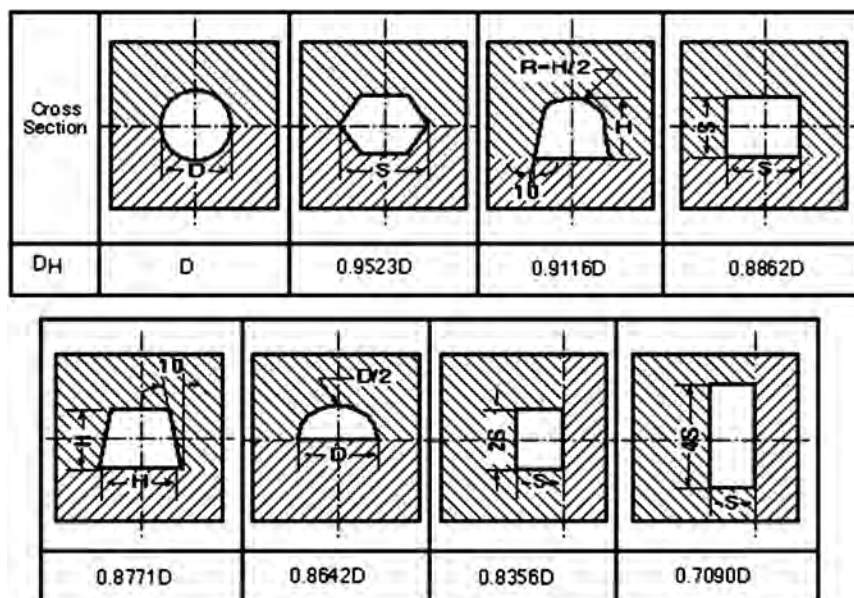


Figure 4.63 Equivalent hydraulic diameters for common runner configurations.

4.4.6.2 Sprues

The sprue is often the thickest part in an injection molding shot and in extreme cases may influence the cycle time. Since the sprue is a waste part, this should not be allowed to happen. The reason that it sometimes does is that there is little control over the dimensions of the sprue. The length is fixed by the thickness of the fixed mold half, while the diameter is

largely a function of the machine nozzle bore and the necessary release taper. Sometimes the sprue can serve a useful function as a gripping point for an automated shot handling system, but the answer in most cases is to eliminate the cold sprue (Fig. 4.65) by means of a heated sprue bush (Fig. 4.66) that serves as a limited hot runner device. In this case, the material in the bush remains as a melt while the cold runner system is injected through a vestigial sprue.

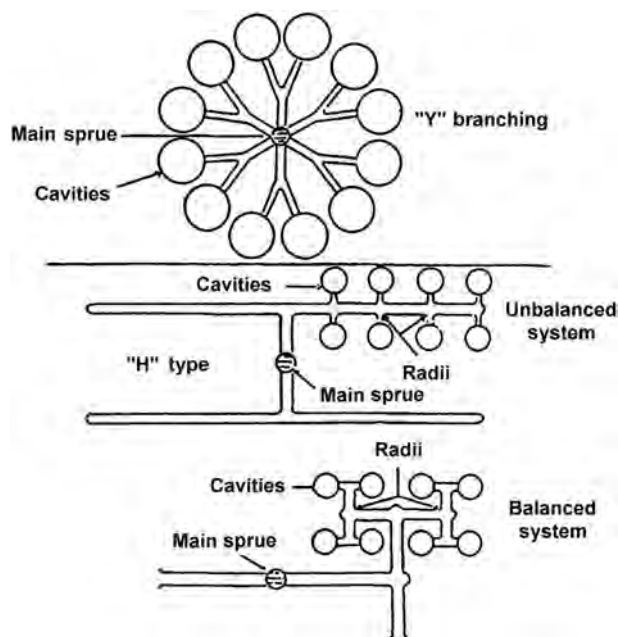


Figure 4.64 Balanced and unbalanced runner layouts.

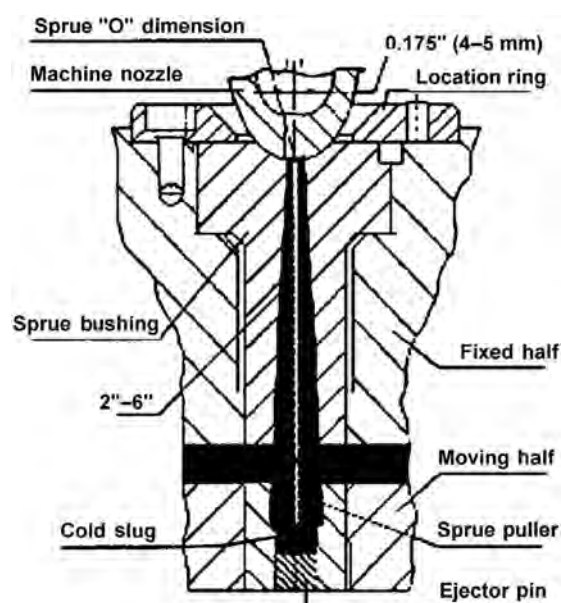


Figure 4.65 Typical cold sprue design.

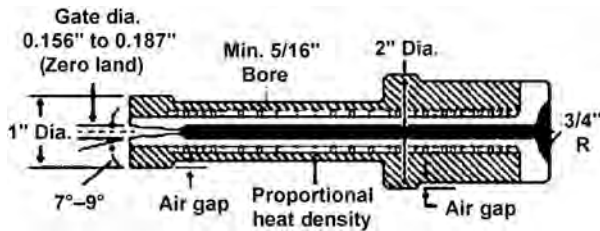


Figure 4.66 Example of heated sprue bushing.

Elimination of the sprue typically saves a few grams of material waste per cycle.

4.4.6.3 Gates

The gate is the region of the feed system between the runner and the cavity. It is the entry point by which the plastics melt enters the cavity and is an important element of the mold. Its position and dimensions have a considerable influence on the finished molding. The position of the gate or gates directly influences flow paths in the cavity and so has a major bearing on issues such as filling pressure, weld line quality, and gas traps. Gate positions must be judged individually for each molding case. An experienced practitioner can usually assess the best gate position for relatively simple part geometry, but for complex parts, computer-aided flow analysis is preferred for gate positioning. Gate positions should be chosen with these general recommendations in mind:

- Gate near a thick section to ensure that it can be packed out
- Position the gate where the gate scar or witness mark will not be cosmetically objectionable
- Position the gate where it can be easily removed with cutting tools
- Position the gate for flow symmetry in symmetrical parts
- Gate to minimize gas traps and weld lines
- Gate so that unbalanced flow does not take place around cores
- Do not place the gate at a point where high stresses or high packing could cause problems
- Position the gate so that flow impinges on a mold surface rather than jets into a void
- Position the gate to minimize shrinkage differentials

The gate is usually small in relation both to the molding and the upstream feed system. There are two principal reasons for this. The gate acts as a thermal valve that seals the filled mold cavity from the feed system. When the gate freezes, no more flow can take place. A very heavy gate would be slow to freeze and would possibly allow compressed melt to flow back out of the cavity and into the feed system, so one aim of gate design is to find a size that will remain open during the injection-packing phase and freeze off immediately thereafter. The other reason for a small gate is so that the feed system can be easily removed from the molding, leaving little trace of its presence.

Flow conditions in the gate are extremely severe. The melt is accelerated to a high velocity and is subjected to a high shear rate. This is the main reason for keeping gates short. The gate length is often referred to as the *land length*. If the gate land is very short, there will be a weak section in the mold between the runner and cavity, and there will be insufficient clearance to use cutters for gate removal. During the passage of the melt through the gate, frictional heating is likely to occur and indeed is sometimes exploited in the design of feed systems for heat-sensitive materials. Here the strategy is to keep barrel temperatures low and generate additional heat at the last moment in the feed system.

Many different gate types (Fig. 4.67) have evolved to deal with a variety of molding needs. Some of these are associated with a particular geometry. For example, diaphragm and ring gates are usually employed for parts with a cylindrical form. The pinpoint gate is normally used in three-plate molding. The most common gate type is the edge gate. The edge gate is usually square or rectangular in cross-section and is cut in just one parting face of the mold. Circular section gates are also used but must be cut equally in both parting faces. Semicircular section gates are not recommended. Gate dimensions depend on product geometry and are frequently adjusted by trial and error during the testing of a new mold. The only practical way to do this is to start with a small gate and gradually enlarge it.

Simple large area parts in single-cavity molds may be gated by running the sprue directly into the cavity. This is known as *sprue-gating* or *direct sprue-gating*. The gate must be removed in a subsequent machining operation that leaves a witness mark. The sprue gate is perhaps the least sophisticated way of dealing with this type of molding. Fan gates are preferred for thin-walled parts of a relatively large area. The flash gate,

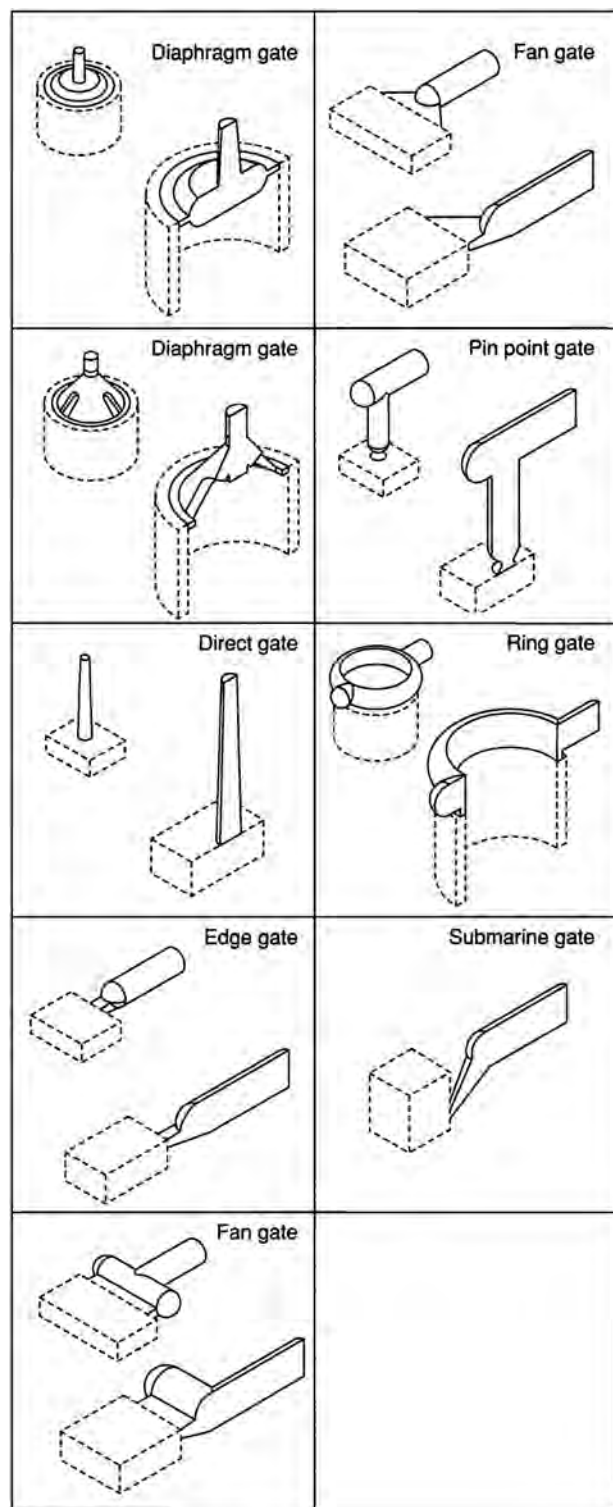


Figure 4.67 Examples of various gate types.

a variant of the fan gate, is used for thin-walled parts that would be difficult to fill from individual gates at any point. The flash gate is very wide and shallow so that a large flow area is combined with a short freeze

time. Ring and diaphragm gates are similar in concept to the flash gate. They are normally used to obtain cylindrical parts free of weld lines and core shift caused by unbalanced flow.

The submarine gate, also known as the tunnel gate, is cut into the one half of the mold rather than on a parting face. This constitutes an undercut, which is freed on ejection by the runner and gate flexing. The advantage of the submarine gate is that the feed system is automatically separated from the mold by the act of ejection that shears the gate off. The winkle or cashew gate is a variant in which the gate is machined in a curved form and is suitable only for flexible grades. A further gate type known as the tab gate is used to prevent jetting into an open cavity or when some defect is expected close to the gate. The tab is a small extension on the molding, which is fed at right angles to its axis by an edge gate; the tab is later removed from the finished part.

4.4.6.4 Hot Runners

Hot runner systems maintain the feed channels in a permanently molten state and eliminate the waste associated with a solidified cold feed system. Another advantage is that the pressure drop through the feed system is less than that of a comparable cold runner arrangement [62]. The principal disadvantage is the need to maintain two very different temperature regimes within the mold. This results in difficult problems of temperature control and differential expansion. The cost of a hot runner mold is also much greater than that of the cold runner equivalent. However, the important point is not the cost of the mold but that of the molding, and here hot runner molds have the advantage. Unless order quantities are low or frequent color changes are required, there are grounds to prefer the hot runner mold. Processors are still often deterred by control and engineering fears associated with hot runners, but there has been great progress in this area, and very sophisticated and reliable designs are now available as stock components. Most manufacturers of hot runner components now offer completely engineered systems that free the molder and mold builder from design responsibility. Traditionally, cold runner molds have been the norm and hot runners the exception, but progress has been such that the project concept really should now start from the opposite premise.

The heart of a hot runner system (Fig. 4.68) is the manifold. This is a distribution block containing flow

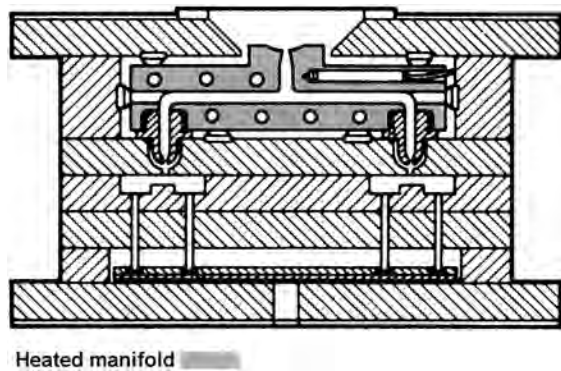


Figure 4.68 Schematic of hot runner mold.

channels maintained at melt temperature. The channels distribute the melt from the single entry point at the sprue to multiple outlets at nozzles that feed individual cavities in a multicavity mold or serve as multiple gates in a single large cavity. The latter case is one of the most important applications of hot runners; multiple gates allow the flow lengths in a large part to be brought within easily manageable proportions. The same strategy also limits the necessary clamp force.

Contact between the hot manifold and the remainder of the cool mold must be kept to a minimum to prevent heat flow. This is normally achieved by the use of air gaps that also allow for expansion, but care must be taken in the design to ensure that the mechanical strength of the mold remains adequate to deal with molding and clamping forces. The heat transfer problem is reduced with internally heated hot runners, but the disadvantage is the relative inefficiency of the annular flow channel. These channels have higher pressure drops than unobstructed channels and are also prone to “slow

flow” areas where material may stagnate and decompose.

A primitive variant of the hot runner is known as an insulated runner. This employs an unheated manifold with very large runners of 20–35 mm diameter and relies on the poor thermal conductivity of plastics to ensure that a flow channel in the center of the large runner always remains molten. The insulated runner mold is not capable of precise and consistent control and is now rarely seen.

The connection between the hot runner manifold and the cavity is made by means of a hot nozzle that may operate in conjunction with a surrounding bushing. A wide variety of nozzle types allow for many gating options (Figs 4.69 and 4.70), with or without witness marks. Hot runner nozzles may be provided with shut-off valves for precise control of flow. Fig. 4.71 shows the velocity profile in internally and externally heated hot runners. In recent years, great progress has been made in the design of hot runner nozzles for small and closely spaced cavities. These designs allow one nozzle to feed a number of cavities and also permit gating options that are almost undetectable on the finished part.

Flow channels should be streamlined to prevent slow or stagnant flow. Corners should be radiused by contoured end plugs. Manifold support pads should have minimal surface contact and should be furnished in materials of relatively low thermal conductivity such as stainless steel or titanium. Precise temperature control is necessary for consistent results. The temperature of the manifold block should be uniform throughout. Each nozzle should be provided with individual closed-loop control.

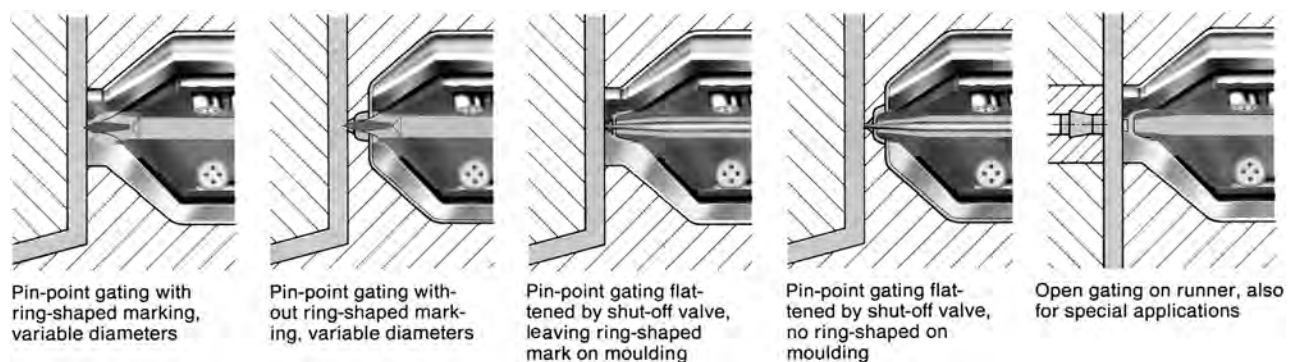


Figure 4.69 Some types of direct hot runner gates.

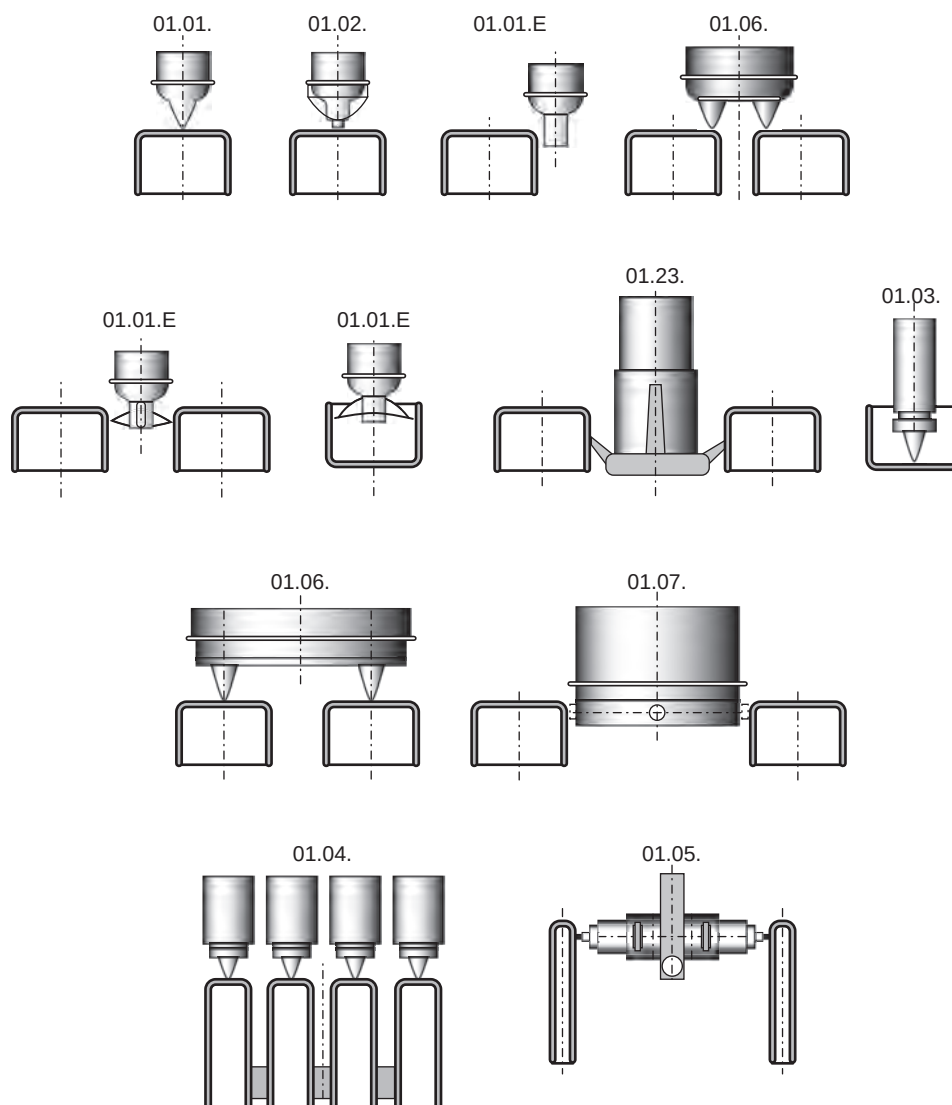


Figure 4.70 Advanced hot runner gates.

4.4.7 Injection Mold Features

4.4.7.1 Materials

Injection molds are subject to rigorous requirements that have a direct bearing on the materials of construction. Mold materials must withstand high injection pressures and clamp forces. They must be good thermal conductors, easy to machine, and capable of reproducing fine detail and taking a high polish. They must be resistant to corrosion, abrasion, and wear. Specific materials required for construction of molds and other parts of injection molding machines for TPE processing are discussed individually for each group.

4.4.7.2 Cooling

It is a fundamental requirement of the injection mold to extract heat from the molding. With each cycle, the mold acts as a heat exchanger to cool the injected material from melt temperature to at least ejection temperature. The efficiency with which this is done has a direct bearing on the speed of production. Heat is removed from the injection mold by circulating a fluid coolant through channels cut through the mold plates and particularly through the cavities and cores (Fig. 4.72). The coolant is usually water but may be an oil if the mold is to be cooled at temperatures near or above the boiling point of water. Such a mold appears hot in relation

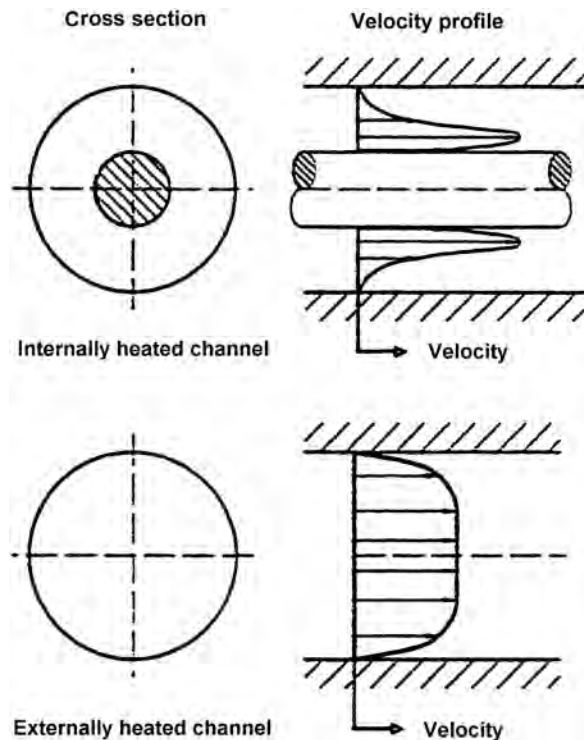


Figure 4.71 Velocity profiles in hot runners.

to the ambient temperature, but it is still cold compared to the plastic melt. If the mold is to be chilled at low temperatures, it is usual to circulate a mixture of water and ethylene glycol. Occasionally the coolant may be air, but this is an inefficient means of heat transfer and should be regarded as a last resort.

Cooling channels represent a real difficulty in mold design. Core and cavity inserts, ejector pins, fasteners, and other essential mechanical features all act as constraints on the positioning of cooling channels, and all seem to take precedence over cooling. However, uniform and efficient cooling is crucial to the quality and economy of the molding, so channel positioning must take a high priority in mold design.

Cooling channel design is inevitably a compromise between what is thermally ideal, what is physically possible, and what is structurally sound (Fig. 4.73). The thermal ideal would be flood cooling over the entire area of the molding, but the pressurized mold cavity would be unsupported, and mechanical details like ejectors could not be accommodated. Support could be provided by interrupting the flood-cooling chamber with supporting ribs, but the mold construction is complicated by the

need to fabricate and seal the cooling chamber. The reasonable and practical compromise provides the cooling channels in the form of easily machined through-bores that may be linked either inside or outside the mold to form a complete cooling circuit.

The correct placement of the channels is important. If they are too widely spaced, the result is a wide temperature fluctuation over the cavity or core surface (Fig. 4.74). If the channels are too closely spaced or too close to the cavity surface, the mold becomes structurally weak.

Another important consideration in cooling channel design is to ensure that the coolant circulates in turbulent rather than laminar (streamline) flow. The coefficient of heat transfer of the cooling system is drastically reduced in laminar flow.

For a channel of circular cross-section, turbulent flow occurs when the Reynolds number is greater than 2300. The coefficient of heat transfer of the cooling system continues to increase as turbulence increases, so the design limit of the Reynolds number for cooling channels should be at least 5000 and preferably 10,000. If the volume flow rate of the coolant remains constant, then the Reynolds number can be increased by reducing the size of the channel. This runs counter to the natural impulse to imagine that a larger channel must always result in better cooling. It is harder to achieve turbulent flow with oils or antifreeze solutions because of their greater viscosities compared with water.

The significance of wall temperature is second to the wall thickness in its impact on cooling time [64]. Wall temperature differences could cause warping of the part. Thermoplastic molds are cooled with water and oil if higher temperatures are required because water-tempering equipment is limited to 140 °C (285 °F).

4.4.7.3 Venting

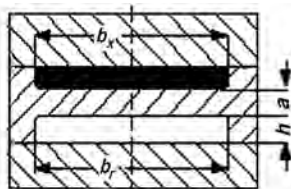
When an injection mold fills, the incoming high-velocity melt stream is resisted by, and must displace, the air in the feed system and cavities. Molders often rely on incidental air gaps between the parting faces and between the assembled parts of the core and cavity to provide a leakage path for air, but this is no substitute for properly engineered venting, which should be designed into all molds. Provided the vent is machined to the correct depth, the injected material will not flash through the air gap. More than one vent may be used; if necessary, up to 60% of the

Core Diameter Core Width d , mm	Description	Design
≥ 3	Heat elimination by air with open mold	
≥ 5	Copper or thermally conductive pipe to conduct heat to the heating/cooling medium	
≥ 8	Long slender heating/cooling channel (with spiral)	
≥ 40	Spiral heating/cooling channel Pipe core	
Pipe core $s \geq 4$	Heating/cooling for pipe core with a double flighted spiral	

Figure 4.72 Cooling arrangements for cores of various sizes.

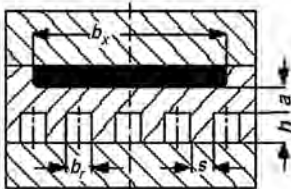
1. Ideal shape in physical terms

- Width of article b_r =
- Width of heating/cooling channel b_x



2. Ideal shape in technical terms

- Condition:
- Heating/cooling with a sufficiently rigid mold cavity to withstand the injection pressure.
 - Interruption of physical shape by means of crosspieces.



3. Easily implemented shape in technical terms

- Conditions as under (2), but with a circular shape, a smaller surface for heating/cooling if $d_r = b_r$

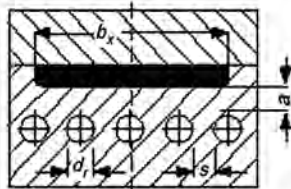
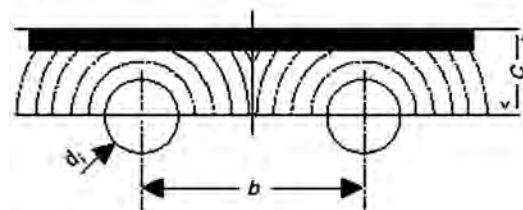


Figure 4.73 Cooling channel considerations.

1. Uneven heat elimination



2. Largely uniform heat elimination

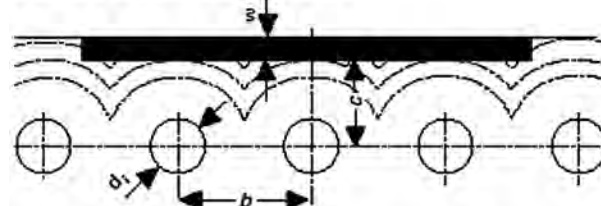


Figure 4.74 Good and bad channel layouts.

peripheral dimension can be vented. The width of individual vents should not exceed 6 mm (0.25 in).

Venting can also be used to prevent or minimize gas traps. A gas trap occurs when the flow of injected plastics melt surrounds and isolates an area in the cavity, so trapping air, which is rapidly compressed and heated. Burned or charred material is often associated with gas traps. The best remedy is to redesign flow to do away with the gas trap but, if this is not possible, venting will help provided the vent is positioned in the correct spot. Most gas traps cannot be vented through the parting faces of the mold. Instead, the vent is machined in inserted pins or plugs. Such vents are prone to blocking unless one of the parts is in motion. For this reason, an ejector pin is often used for venting. An alternative method is to use an insert of porous steel.

4.4.7.4 Ejection

Ejection is the name given both to the process of removing the molding from the mold and to the means by which it is done. Ejectors inevitably leave witness marks on the molding, and this alone may determine the disposition of the part in the mold. Once that basic choice has been made, there is usually not much further freedom to position ejectors in cosmetically acceptable positions. The choices are much constrained by other features in the mold and the need to put ejectors where they are most needed to overcome the resistance of the molded part.

Ejection may be by means of pins or a stripper plate, or a combination of both. The stripper plate acts on the entire peripheral wall thickness of the part and so distributes the ejection force. This is the

preferred method for thin-walled parts, but the method is difficult to apply to anything other than a circular periphery. A variant on this theme is the stripper bar, which works on part of the periphery. Most ejection is performed by pins, usually cylindrical in form. Rectangular pins may be used in constricted areas; these are often referred to as blade ejectors. Hollow ejector pins known as sleeve ejectors are commonly used to push the molding off small core pins. Ejection of deep-drawn or thin-walled parts is often assisted by an air valve that breaks the vacuum between the molding and the mold core.

4.4.8 Materials of Construction

Products of the degradation of molten thermoplastic elastomers are in general not corrosive, thus it is not necessary to construct the parts of the machine that come in contact with molten polymers from corrosion-resistant metals, which are significantly more expensive than lower grades of steel. However, there are cases where it is necessary to use corrosion-resistant metals (see chapters describing the individual TPEs). Corrosion of process surfaces can result in the contamination of the finished product and deterioration of its physical properties. [Table 4.16](#) lists the metals and suppliers recommended for the construction of various parts of the injection molding machine.

For injection molding machines used for the processing of thermoplastics producing corrosive decomposition products, materials like Xaloy 309 and Bernex C240 can be used for construction of barrels and Hastelloy C-276 for the screw, adapter, and nozzles. The corrosion rate of the mold surface

Table 4.16 Some Corrosion-Resistant Metal Alloys and Their Suppliers

Metal	Supplier	Parts
Hastelloy C	Stellite Division, Cabot Corporation, Nokomo, Indiana, USA	Screw, adapter, and nozzle
Hastelloy C-276	Stellite Division, Cabot Corporation, Nokomo, Indiana, USA	Screw, adapter, and nozzle
Duranickel	International Nickel Co., Huntington, West Virginia, USA	Screw, adapter, and nozzle
Monel	Sales@espi-metals.com	Screw, adapter, and nozzle
Xaloy 309	Xaloy, Inc., New Brunswick, New Jersey, USA	Barrel and barrel lining
Brux	Brookes (Oldbury), Ltd, Oldbury, Warely, Worcestershire, UK	Barrel and barrel lining
Reiloy	Reiloy Metal GmbH, Köln, Germany	Barrel and barrel lining
Bernex C240	Berna AG, Olten, Switzerland	Barrel and barrel lining

Ebnesajjad S. Fluoroplastics, volume 2: Melt processible fluoropolymers, the definitive user's guide and databook. Norwich (NY): William Andrew Publishing; 2003.

Table 4.17 Shrinkage as a Function of Thickness

Part Thickness, mm	Shrinkage	
	mm/m	%
3.2	35–40	3.5–4.0
6	40–45	4.0–4.5
12.7	45–50	4.5–5.0
19.1	50–60	5.0–6.0

Ebnesajjad S. *Fluoroplastics, volume 2: Melt processible fluoropolymers, the definitive user's guide and databook*. Norwich (NY): William Andrew Publishing; 2003.

will be lower than that of the other parts of the machine because its temperature will be lower than the melting point of the polymer. For short production runs, unplated molds of hardened tool steel or high quality or chrome and nickel plating of the injection mold cavities normally provide sufficient protection. For longer runs, more corrosion-resistant materials of construction may be required.

4.4.9 Dimensional Stability of Parts

Close tolerances can be achieved provided that operating variables of the process are tightly controlled. Mold design is, however, the other critical factor in obtaining high precision molded parts. As tolerances become smaller, cost of manufacturing and complexity of the process grow. Almost every variable in the molding process affects the part dimensions. Shrinkage during the molding process is a critical factor in determining the final dimensions of the part.

Shrinkage increases with part thickness (Table 4.17) and mold temperature because in both cases cooling rate decreases. Consequently, crystallinity increases and internal stresses decrease. A number of plastics exhibit direction-dependent shrinkage (Figs 4.75 and 4.76). The least amount of shrinkage takes place in the direction of flow due to the highest degree of orientation in this direction. The rule of thumb that is useful to the design of molds is that the straighter the path, the lower the shrinkage. Table 4.18 shows the effect of various parameters on shrinkage of injection-molded parts. Annealing a molded part, that is, heating and holding it above its performance temperature, can prevent further shrinkage during its use.

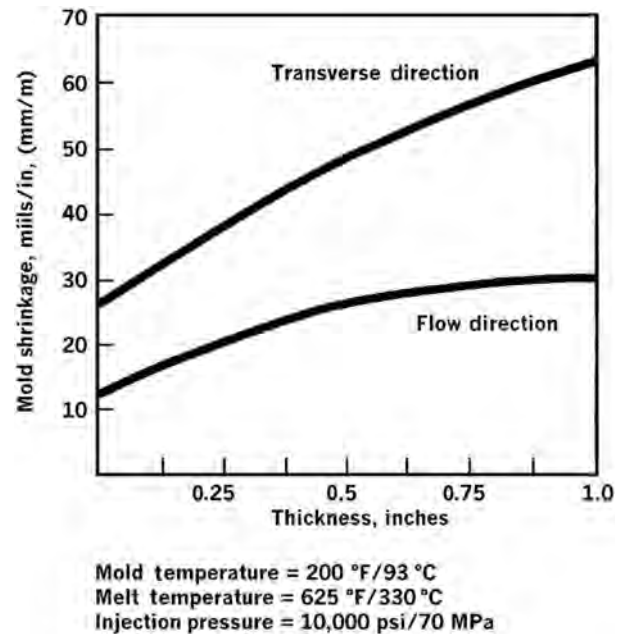


Figure 4.75 Example of shrinkage vs thickness in flow and cross directions.

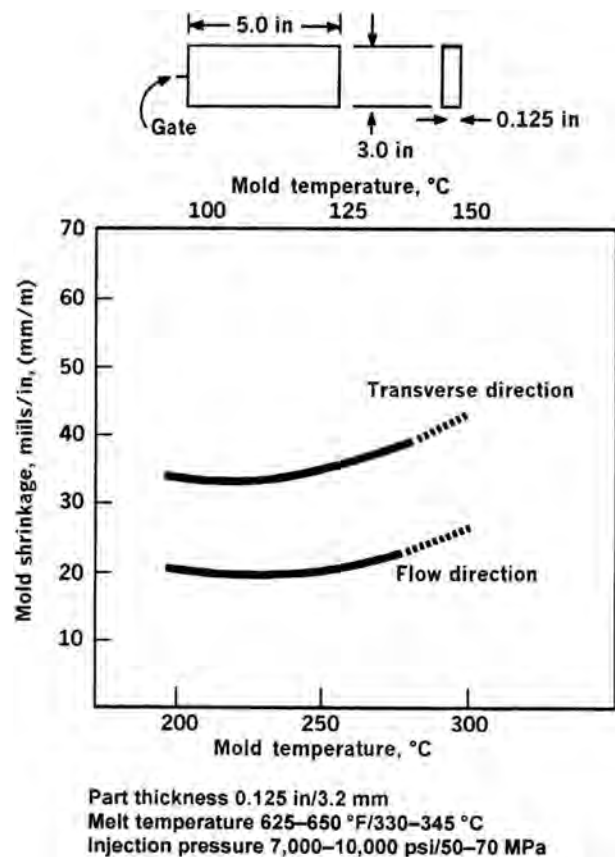


Figure 4.76 Example of shrinkage vs mold temperature in flow and cross directions.

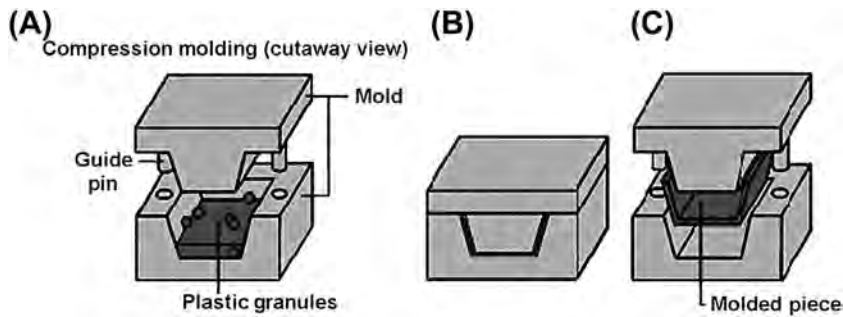


Figure 4.77 Schematic drawing of the stages of the compression molding process. (A) Filling the mold; (B) heating the closed mold; (C) opening the mold and removal of the molded part.

4.5 Compression Molding

Compression molding was among the first method to be used to form plastics (Fig. 4.77). It involves four steps:

- Preformed blanks, powders, or pellets are placed in the bottom section of a heated mold or die.
- The other half of the mold is lowered and pressure is applied.
- The material softens under heat and pressure, flowing to fill the mold. Excess material is squeezed from the mold. If it is a thermoset plastic, cross-linking occurs in the mold. In

thermoplastic molding, the part is hardened under pressure by cooling the mold.

- The mold is opened, and the part is removed.

As pointed out above, for thermoplastics, the mold is cooled before removal so the part will not lose its shape. Thermosets may be ejected while they are hot and after curing is complete. This process is slow, but the material moves only a short distance to the mold and does not flow through gates or runners like in injection molding. Only one part is made from each mold.

In the simplest form of compression molding, a molding powder (or pellets, which are also sometimes called molding powder) is heated and, at the same time, compressed into a specific shape. In the case of a thermoset material, the melting must be rapid since a network starts to form immediately and it is essential for the melt to fill the mold completely before solidification progresses to the point where flow stops. Commercial molding machines use high pressure and temperature to shorten the cycle time for each molding. The molded article is pushed out of the cavity by the action of ejector pins that operate automatically when the mold is opened. A schematic diagram of a complete compression molding press, the mold, and other process components can be seen in Fig. 4.78; a typical mold set is shown in Fig. 4.79.

In some cases, pushing the resin into the mold before it has liquefied may cause undue stresses on other parts. For example, metal inserts to be molded into a plastic electrical connector may be bent out of position. This problem is solved by transfer molding, in which the resin is liquefied in one chamber and then transferred to the mold cavity. When flat plates are used as the mold, sheets of various materials can be molded together to form a laminated sheet. In

Table 4.18 Effect of Various Parameters on Shrinkage

Increase Shrinkage	Decrease Shrinkage
	Increased injection pressure
Increased stock temperature	
	Filler addition
Increased mold temperature	
Increased part thickness	
	Increased polymer orientation
	Straight melt flow during molding

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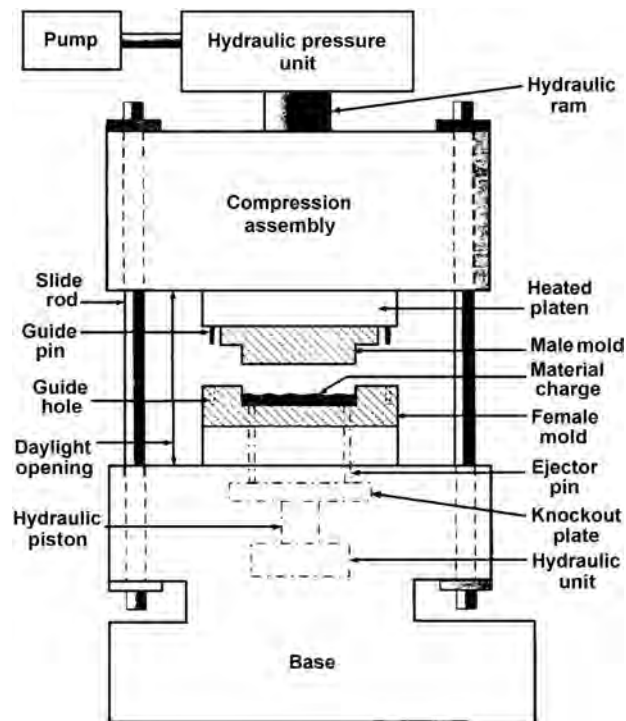


Figure 4.78 Schematic drawing of a compression molding press and its components.

plywood, layers of wood are both adhered to one another and impregnated by a thermoset such as urea-formaldehyde, which forms a network on heating.

4.5.1 Types of Compression Molds

Compression molds for thermoplastics are equipped with cooling and heating cores to allow melting and hardening the resin. Electricity or steam and cold

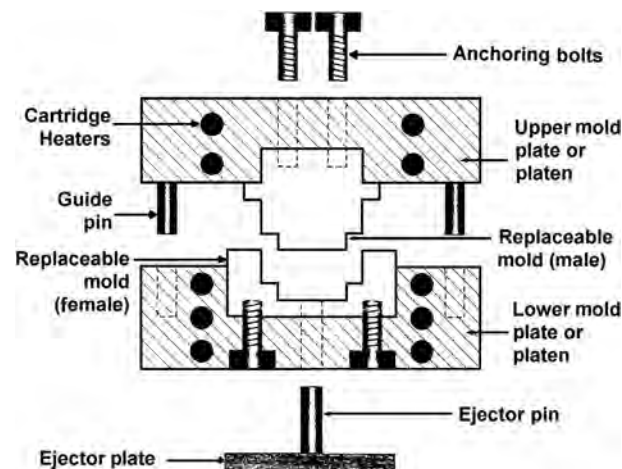


Figure 4.79 A typical compression mold set.

water are usually the heating and cooling medium of the mold.

There are three types of compression molds: hand molds, semiautomatic, and fully automatic. Hand molds are limited to prototypes, small size parts, and short runs. Semiautomatic molds are self-contained and securely installed in a conventional mold press. The operational sequence has to be carried out manually. Fully automatic compression molds are specially designed and constructed to fit a completely automatic compression press. Manual intervention in the operation is reduced to the loading of material hoppers and part removal from the press.

There are five standard designs for the cavities and the closure of compression molds as described following:

1. Flash Type. This is the oldest design of compression molds (Fig. 4.80) most suitable for manufacturing hollow parts. This type of mold may be used in the production of large parts, although part quality may be poor both from dimensional and aesthetics standpoints. This mold is overfilled slightly, forcing the excess plastic (flash) into the gap between the male and female mold halves. An insufficient charge of resin results in a part that is too small.
2. Fully Positive. Also called a direct positive mold (Fig. 4.81), this is solely used for large deep draw parts where maximum density must be obtained. These molds are limited to

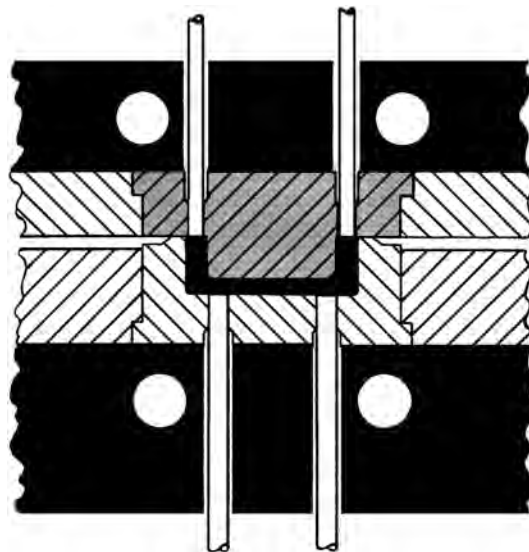


Figure 4.80 Flash mold design.

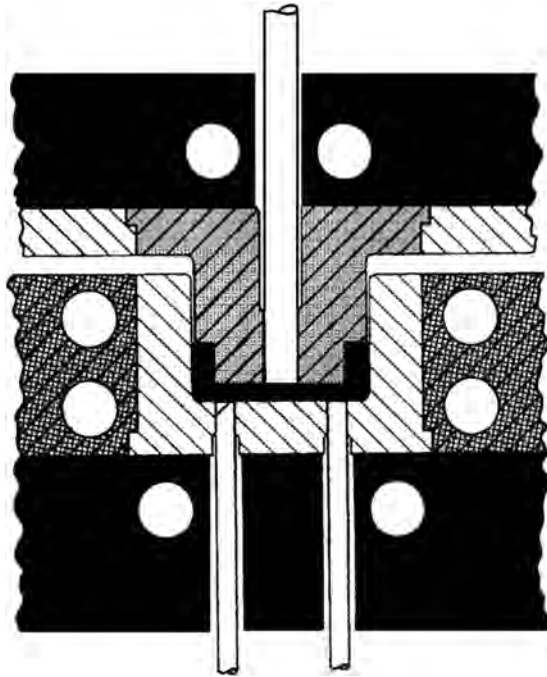


Figure 4.81 Direct positive mold design.

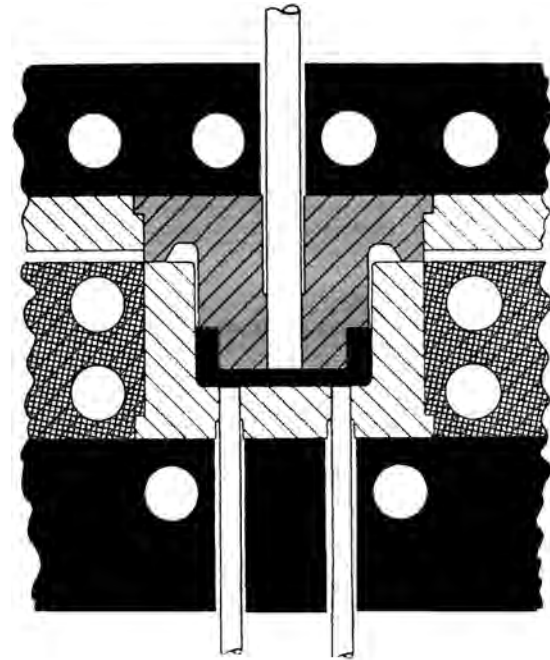


Figure 4.82 Landed positive mold design.

single-cavity production requiring the weighing of each material charge to assure the depth (or the height) and the density of the finished part.

3. Landed Positive. Multicavity molds may take advantage of this design (Fig. 4.82). Escape-ments are installed on the force to allow development of maximum density with cavity-to-cavity height uniformity.
4. Semipositive Horizontal Flash. This is the most suitable design for automatic molds and is most common in the industry (Fig. 4.83).
5. Semipositive Vertical Flash. This design (Fig. 4.84) is helpful in cases where a visual flash line scar may be present on the molded parts. The cost of this design is considerable because of the required proper fit between force and cavity.

The positive-type mold closure has a long shearing surface between the male and female segments of the mold. This surface is formed when the mold segments are in close proximity to each other. The gap between the male and female segments is maintained closely, thus no flash is formed. The amount of material charged into the mold is carefully controlled because excess material would prevent

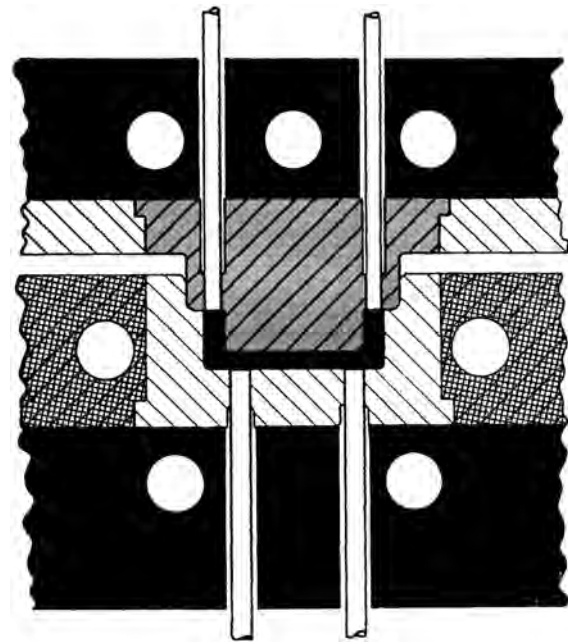


Figure 4.83 Semipositive horizontal flash mold design.

mold closure. Insufficient charge results in a short shot, that is, an incomplete part will form.

In semipositive-type closure, a horizontal land causes a gap to form between the plunger and the cavity. This gap is significantly larger than the gap in

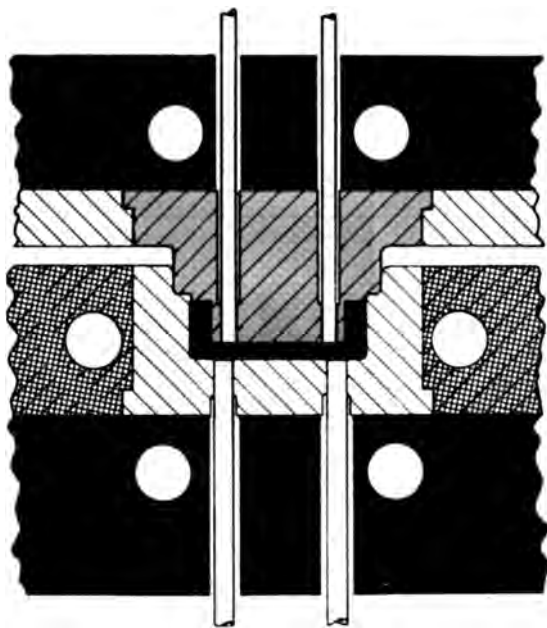


Figure 4.84 Semipositive vertical flash mold design.

positive closure. Any excess material moves along the horizontal land and further up the vertical land, facilitating flash removal.

The basic molding requirement calls for a mold that will compress the plastic into the desired shape and hold it under pressure and heat until the molding cycle has been completed. The operation must be done in the simplest manner and for the least cost, which requires that the mold be designed so that the resin and insert could be introduced easily and the part ejected. A good source to study the procedure for designing compression molds is *Plastics Mold Engineering Handbook* [65].

4.5.2 The Compression Molding Press

A compression molding press is usually a rugged piece of equipment that provides sufficient force to compress the material. The force necessary to mold a part must be smaller than the press capacity. The force required depends on the nature of the plastic and part geometry. Dependence on the nature of the material being compressed complicates the task of mathematical modeling of this process. There are complex approximate expressions that relate the force required to the geometry of the part and material properties.

Equation (4.4) [56] represents a practical approximation between the force and the part size. In this relationship, the required compression force (F)

equals the cavity pressure (P_A) multiplied by the projected area (A) of the mold up to a depth (part thickness) of d_e . An additional force is needed when the part thickness (d_p) exceeds this minimum depth. The value of d_e depends on the material and p is the additional pressure factor; both are determined experimentally.

$$F = (A)[P_A + p(d_p - d_e)] \quad (4.4)$$

Most parts of common plastics that are less than 3 cm thick require 10–55 MPa (1450–7980 psi) pressure for consolidation. Parts that are over 3 cm (1.2 in) (d_e) thick must be given 1–1.33 MPa/cm additional pressure (p).

A number of different types of presses are commonplace for compression molding. They include manual, semiautomatic, automatic, and automatic-rotary presses.

The conventional manual and semiautomatic press is vertical and closes upward, downward, or bidirectionally. The pressure medium is hydraulic fluid or air; clamp force is applied by hydraulic ramps or toggle clamps. The source of fluid can be separate or integrated in the press. Table 4.19 shows the force capacity (tonnage) of different press sizes.

Automatic presses are self-contained, and the cycles are computer controlled. Typically, these presses are vertical, and they are available from 22.7 to 273 tons. Other features such as the material loading mechanism and unloading trays are added to fully automate the operation of these presses. The tool cost is higher for automatic molds than manual or semiautomatic molds.

Automatic-rotary presses are suitable for producing small parts that have a shallow draw with a smaller diameter than 7.6 cm (3 in) [66]. This process should be considered whenever high production rates are required, so long as the part design would allow its use.

Table 4.19 Manual and Semiautomatic Press Sizes

Press Size	Press Force, metric tons
Small (hand or bench)	4.5–22.7
Production	45.5–455
Very large	Up to 2727

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4.5.3 Compression Molding of Thermoplastics

The general procedure for compression molding is applicable to the molding of thermoplastics except that cooling the mold under pressure hardens the article. The length of the heating and cooling cycles is determined experimentally. Thermoplastic compounds cannot be pressed into a preformed charge. In contrast, a thermosetting compound undergoes a chemical reaction (cross-linking) during the hardening of the part.

Thermoplastic elastomers generally have high melting points, thus they need to be heated to an elevated temperature during compression molding. Heating and cooling make for long cycles and great power consumption in conventionally heated compression molds. Small molds are preferable to larger ones. Separate platen presses are used where one is a hot press that is electrically heated and the other is a cold press that is water cooled. The article is shaped in the hot press under pressure. The mold is then transferred, as rapidly as possible, to the cold press to chill the article under pressure. The article is removed after it has been cooled down to a sufficiently low temperature. To ease the removal of the part from the mold, its surfaces can be covered with aluminum foil that has been sprayed with a mold release agent.

The length of cycle time depends on the mass of the part and the properties of the polymer. The hot press is usually preheated to decrease the overall cycle time. Pressure is gradually increased during the heating cycle. Thicker parts require significantly longer cycles (many hours) to melt and fuse the resin and eliminate bubbles and voids.

4.6 Transfer Molding

Transfer molding was originally developed for fabricating parts from thermosetting polymers. It is a combination of injection and compression molding processes in which the polymer is melted in a pot, transferred into a mold, and compressed into the designated shape. Transfer molding differs from compression molding in that the plastic is heated in a separate chamber but compression is carried out in a conventional compression press. Cooling hardens thermoplastics as opposed to thermosetting resins

that are hardened by cross-linking reaction. The mold design is modified to accommodate the melting pot or the heated mold.

4.6.1 Background

In general, transfer molding offers advantages for manufacturing certain parts:

1. Parts requiring side-draw core pins that must be removed prior to discharging the part from the mold.
2. Intricate parts that require inserts.
3. Complicated parts where tolerances are very close in three dimensions.
4. Small molded parts that assemble together.
5. Parts with low finishing cost (little flash is produced by this process).

For example, valves and fittings can be lined by the transfer molding process. The valve body or the fitting, along with mandrels and flange plates, direct and confine the flow of the molten resin and serve as the mold. The valve and fitting are preheated to above the melting point of the thermoplastic material before the melt is entered into the cavity. The source of the melt may be an extruder, an injection molding machine, or a melt pot. The molten resin is transferred into the cavity under pressure and held under compression for a length of time. At the end of the cycle, the resin is cooled under pressure before the mandrel assembly is removed. In the last step, the lined part undergoes minor finishing such as de-burring and trimming.

This method of molding requires the transfer of molten polymer from a well or a pot under pressure through runners and gates into the mold. Cavities are located inside a closed heated mold as shown in [Figs 4.85 and 4.86](#). The charge is often preheated before it enters the pot. Preheating reduces the pressure requirement for the transfer operation and shortens the mold cycle. The three variations of this technique include transfer in compression mold, plunger molding, and screw transfer molding.

Transfer molding is a versatile process capable of producing parts such as pump bodies, impellers, plug valve sleeves, and encapsulated butterfly valve discs. Generally, transfer molding can be divided into four

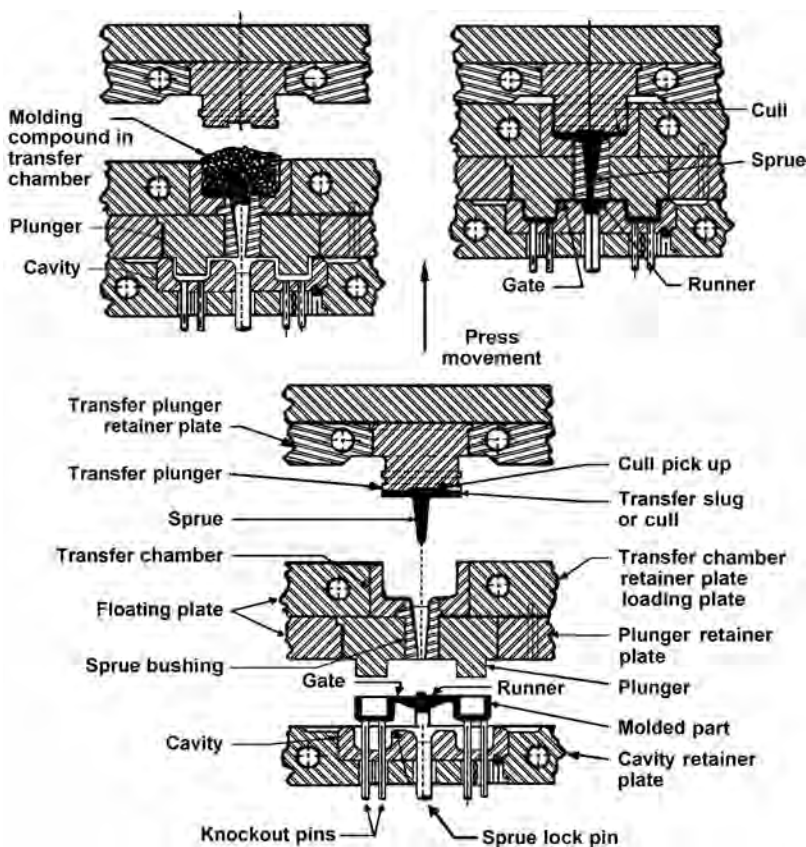


Figure 4.85 Schematic drawing of a pot-type transfer mold.

areas: mold, melt, melt transfer, and cooling and disassembly; each is discussed in this section.

4.6.2 Transfer-In Compression Molding

In this technique (Fig. 4.85), a hydraulic ram is used, and the plunger for the pot is fastened to the upper platen of the press. This arrangement allows pressure to be developed with the help of the hydraulic ram. The minimum differential between the area of the pot and the mold cavity should be $+10\%$ for successful melt transfer. This prevents the opening of the mold cavity and the formation of flash.

The productivity of this method exceeds that of compression molding even though the pot is usually manually operated. The pressure applied aids in filling the mold cavity rapidly, resulting in parts with good dimensional control and uniform density.

A three-plate mold is used with the plunger or ram positioned at the top plate (Fig. 4.87). The orientation of any elongated filler such as fibers is parallel to the flow because the molten plastic enters the mold at

a single point (gate). By the same token, shrinkage in the flow direction and perpendicular direction is likely to be different and difficult to predict, depending on the gate position and part design.

At the end of the cycle, when the mold is opened, the remaining polymer solidifies into a disk shape (cull). It is removed as a single piece along with the sprue. The part is removed by lifting the middle section of the mold followed by ejection pin action. In the transfer molding method, it is desirable to keep the sprue and the cull attached, contrary to injection molding.

4.6.3 Plunger Molding

In the plunger molding (also called auxiliary ram transfer) process, an auxiliary ram exerts pressure on the molten plastic for transfer to the mold cavity (Fig. 4.88). The pressure forces the preheated material through runners into the closed two-plate mold cavity. This process is mostly conducted in semi-automatic closed presses.

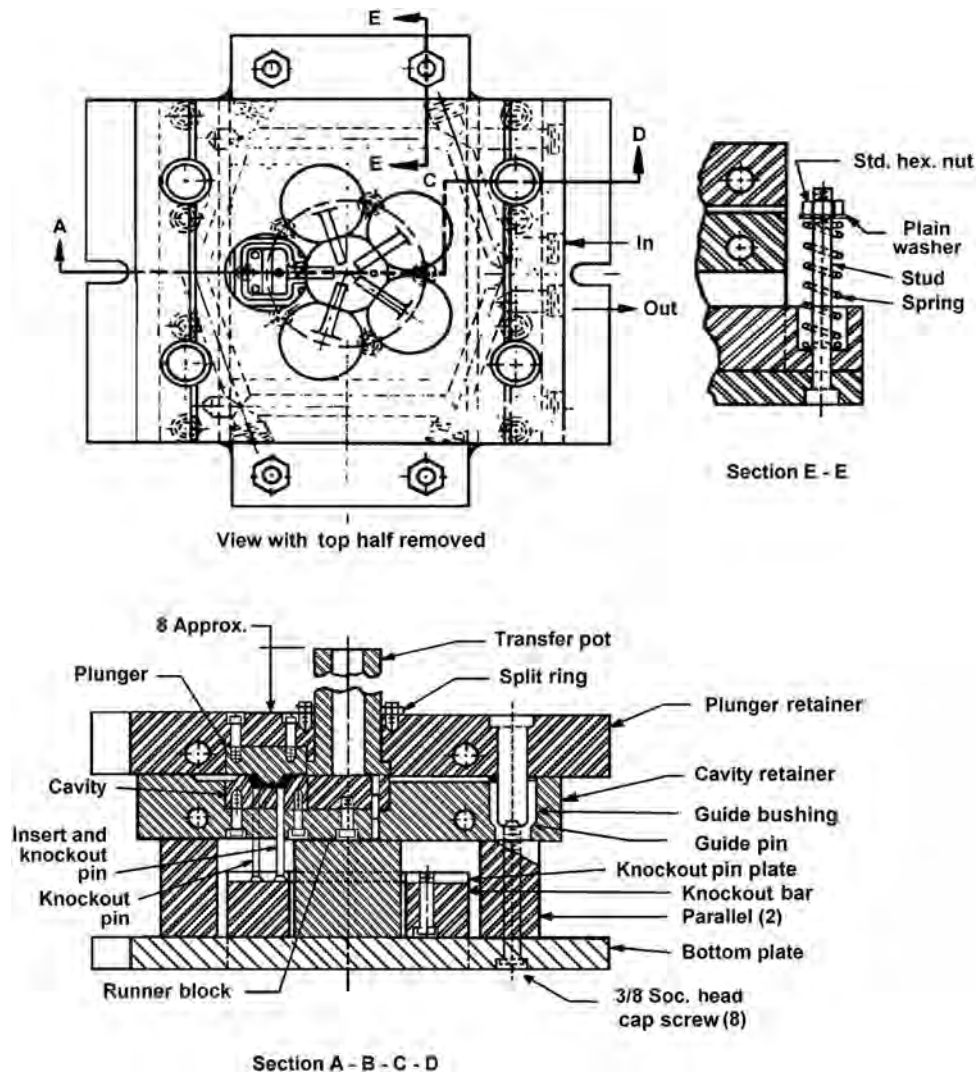


Figure 4.86 Design of a plunger-type transfer mold.

The basic steps of plunger molding are similar to those of pot molding. After the plunger has been withdrawn and the mold is opened, the molded part can be removed in one piece with the runners and the cull attached. The length of the total plunger molding is shorter than pot molding because the removal of the sprue, runners, and the cull do not require a separate operation. The mold temperature, pressure, and dwell must experimentally be determined for each part and resin type.

4.6.4 Screw Transfer Molding

In this process, the plastic is heated and melted in a screw and then dropped into a pot of an inverted plunger mold (Fig. 4.89). The molten polymer is transferred to the mold by the same procedure as shown in Fig. 4.86. The screw transfer method and

the sequence of the operational steps are depicted in Figs 4.89(A) and 4.89(B). Screw transfer molding is an excellent process for full automation.

Screw transfer presses are capable of preparing shots from 50 g to 2500 g. Certain requirements must be met to control the heating of the resin adequately. The compression ratio (ratio of the shallowest to the deepest depth of flight) of a thermoplastic screw is much larger than that of a thermosetting resin. The length-to-diameter ratio is also considerably larger for thermoplastics. The mechanism of operation of the screw is similar to that of injection molding (see Section 4.4).

4.6.5 Types of Transfer Molds

There are three popular designs of transfer molds: loose-plate, integral, and auxiliary molds. The loose-

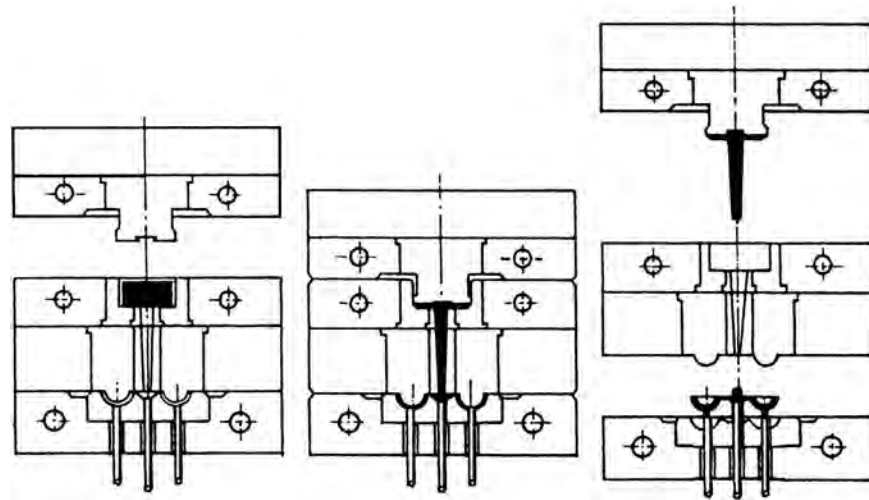


Figure 4.87 An illustration of the cycle transfer molding.

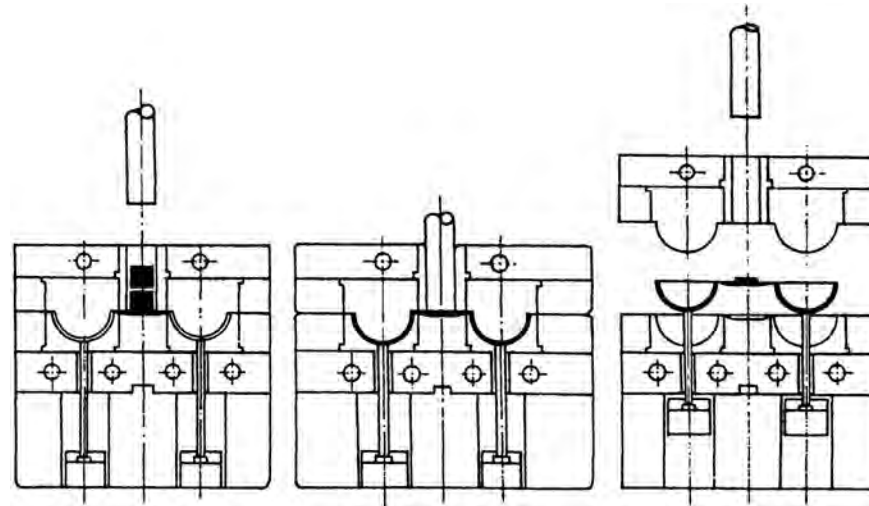


Figure 4.88 Schematic drawing of the plunger molding process.

type molds can be classified into manual and semi-automatic types based on the manner of mounting and mold operation.

Figure 4.90 illustrates one of the simpler manual transfer molds, which is particularly helpful when the molded piece contains a group of fragile inserts that traverse across the part. The mold is comprised of a plunger, a loose plate with bored-through holes in its perimeter, and the cavity. The chamber above the loose plate forms the pot.

Figure 4.91 illustrates a semiautomatic floating-plate (loose-plate) mold. The floating plate is a permanent component of the press. It has an opening at its center that will accommodate different sized pots and plungers that are needed to fabricate different parts. The floating plate moves either by

hydraulic or pneumatic force or by bolts/latches that are built into the mold. An important advantage of these molds is their low cost.

An integral mold comes equipped with its own pot and plunger (Fig. 4.92) and can be designed for manual or semiautomatic operation. The self-containment feature increases the efficiency of the mold because the design of the material transfer pot can be optimized with respect to specific cavity. The pot could be located above or below the mold. The molten plastic may flow through a sprue-runner gate to enter the mold, or the sprue can be placed inside the cavity, as is the case in the mold shown in Fig. 4.92.

Auxiliary-ram molds (Fig. 4.93) are “integral” in that the plunger action takes place using a separate

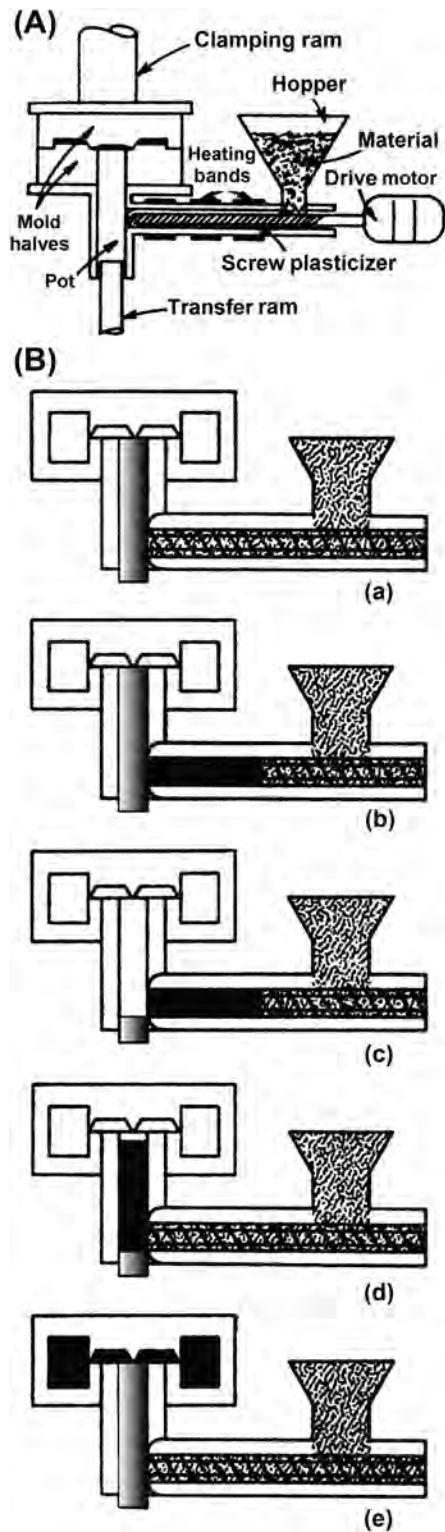


Figure 4.89 Schematic drawing of the screw transfer process. (A) Sequence of the screw transfer process. (B) Sequence of the screw transfer process. (a) Melting of resin in the screw; (b) material builds up at the end of the screw and drives the screw backward; (c) after the shot is prepared, the ram lowers

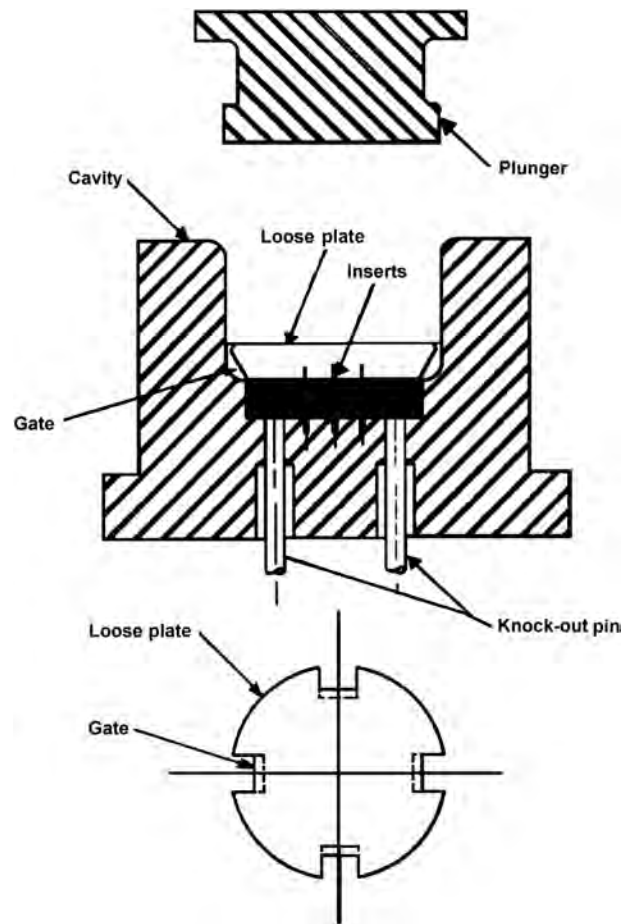


Figure 4.90 Design of manual loose-plate transfer mold.

double-acting cylinder that is installed on the press head. The cylinder/plunger system may be mounted on the bottom press platen within the ram, or on the tie rods or side column of the press. These methods of mounting and the corresponding molds are referred to as top-ram, bottom-ram, or side-ram. Auxiliary-ram molds provide the highest productivity and lowest mold cost. Material losses in the runners, sprue, and cull are minimized.

It is hard to compare the general benefits and shortcomings of the auxiliary-ram methods because of the strong impact of the design and the method of operation. The top-ram design is difficult to operate (load resin and eject part) due to space limitations.

to open the transfer pot; (d) the screw moves forward to press the melt into the pot; (e) transfer ram advances through a bottom-transfer molding to fill the mold.

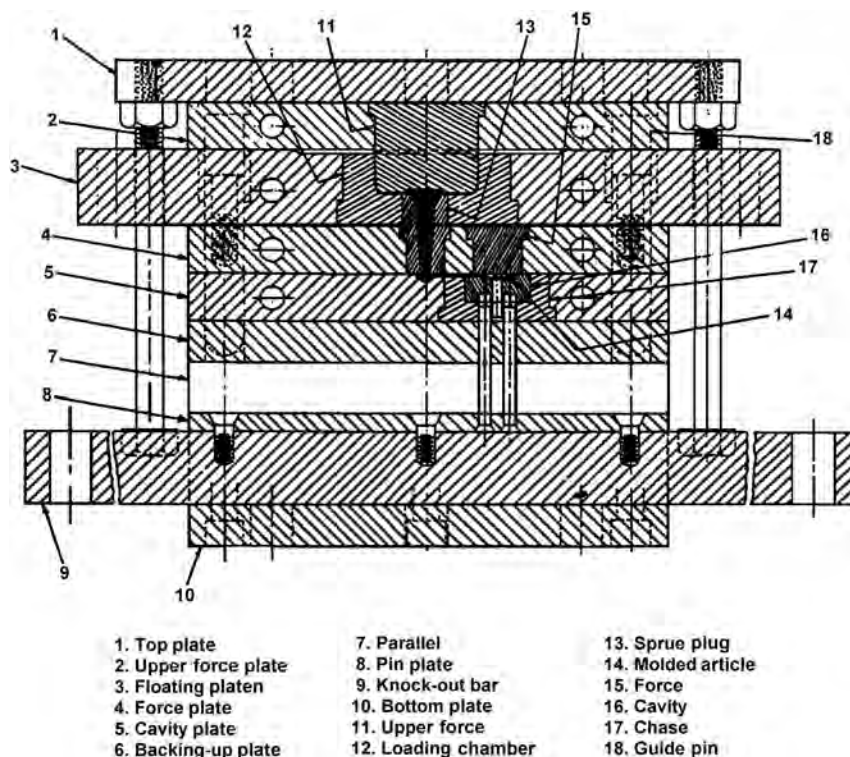


Figure 4.91 Design of semiautomatic floating-plate mold.

The bottom-ram type is easier to load because the transfer well is readily accessible when the mold is open. The molding cycle tends to be longer because the mold has to be completely closed prior to actuation of the plunger. The side-ram is less popular and is primarily used when the part design requires its ejection at the parting line.

4.6.6 Transfer Molding of Thermoplastic Elastomers

Generally, these polymers have relatively high melting points and high melt viscosity, and low critical shear rate, which renders them suitable for the slower processing rates of transfer molding techniques.

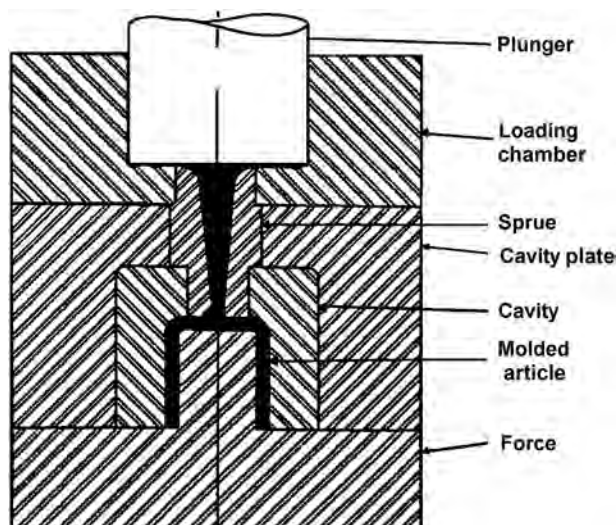


Figure 4.92 Design of integral transfer mold.

4.6.6.1 Mold Design

To minimize pressure and heat losses, the runners should be round and as short as possible. Another preferred choice is trapezoid runners that are easy to machine and provide the same amount of resistance to flow as round runners. They should blend smoothly into the gates, without abrupt cross-sectional changes. The runner's length should be reduced and its diameter increased when the thickness of the molded part increases. A runner diameter of at least 6 mm is required for a 10 mm thick part. Thicker parts require runners that are 50–100% larger in diameter than the thickness of the part. As in injection molding, pressure drop and material loss are determined by the length of the runners. In

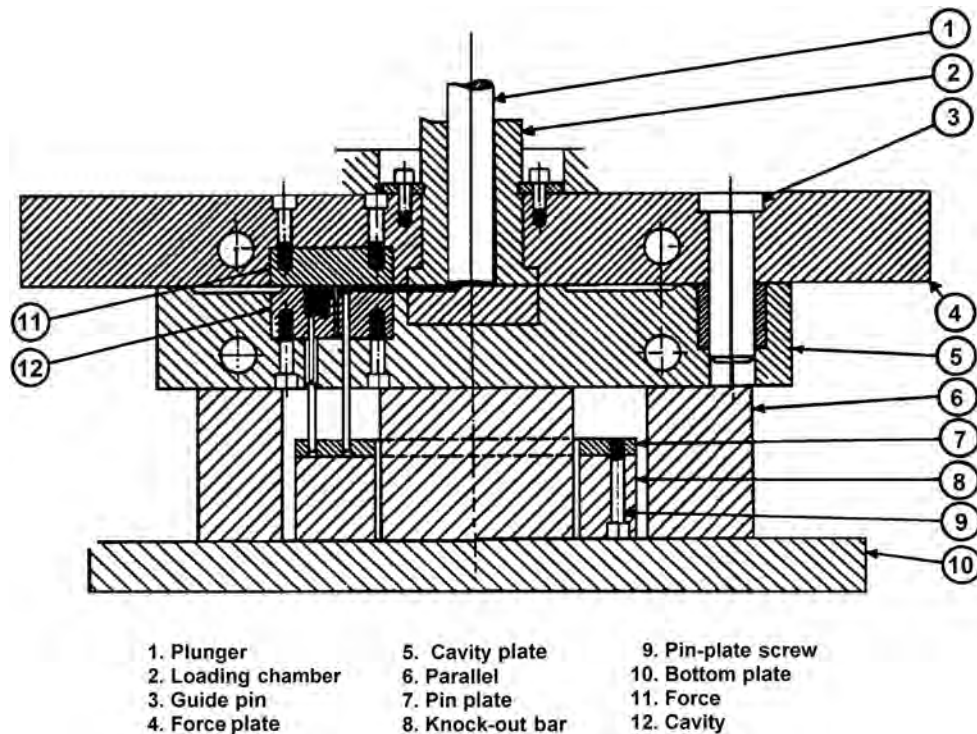


Figure 4.93 Design of auxiliary-ram mold.

multicavity molds, balanced or lateral runner layout can be selected (see [Section 4.5](#) for more explanation). A balanced runner provides an equal flow path between the sprue and all cavities. This means that the resin that reaches every cavity undergoes the same pressure drop and residence time.

All corners and edges must be generously rounded (minimum radius 2 mm or 0.08 in) to avoid stress concentration in the molded liner. Fitting liners that contain sharp corners may fail at these locations in chemical service after multiple temperature cycling. Unrounded liners may fail because of stress concentration that occurs by the hindrance of resin flow during the transfer operation and subsequent shrinkage during the cool down.

Shearing of the molten plastic should be minimized to keep the stress concentration low. This is accomplished by designing the gate thickness equal to the wall thickness of the liner at the gate. Demolding becomes difficult when the gates are very small. Molten polymer may degrade mechanically due to abrupt changes of flow direction or cross-sectional changes in the gate areas. Diaphragm gates are preferred whenever possible, otherwise rectangular tab or fan-type gates that are well flared in the mold cavity should be chosen.

In general, gates should be located at spots in the part that do not experience high impact or stress. Noncritical areas along the weld line are acceptable positions for the gates. The location of the gate should be such that minimal or no finishing is required and close to or at the thickest section of the part to reduce sink marks. Gate location should be at the center of a rotosymmetric part and, in all cases, consistent with the position of the vent.

Improper venting of the mold can damage the part. Venting the mold prevents corrosion damage to the mold, allows complete filling of the mold, and the production of parts with high-strength weld lines. Adiabatic compression of the molten resin in the mold can raise the temperature significantly to about 800 °C (1470 °F) [67], which would rapidly degrade any thermoplastic.

4.6.6.2 Operation of the Mold

The operations of mold and melt removal from the oven and melt transfer should be conducted as rapidly as possible to prevent premature cooling of the melt. TPEs have fairly high viscosity and require relatively long transfer time. To avoid premature cooling and freezing prior to the completion of

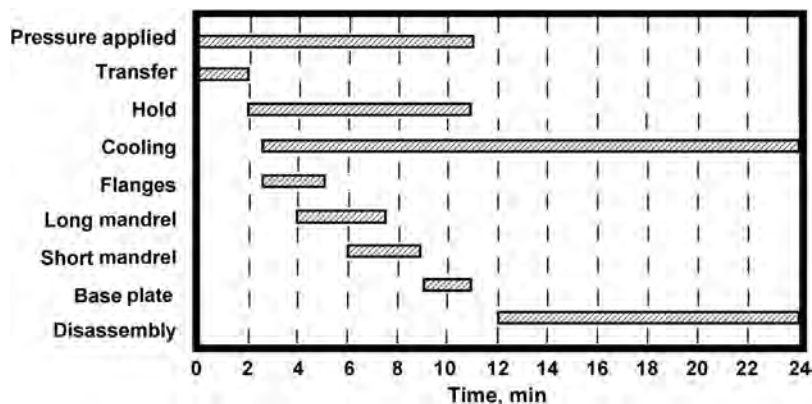


Figure 4.94 A typical transfer molding cycle.

transfer, mold temperature should be maintained at or above the melting temperature of the polymer.

After the melt transfer has taken place and the mold has been filled, a holdup time under pressure is required. This time allows shrinkage to take place while the resin is being cooled. The holdup time allows stress relief in areas where shearing may have taken place. Cooling proceeds under pressure until the gate has been frozen, beyond which point no further pressure need to be applied until demolding occurs. Figure 4.94 illustrates an example of a transfer molding cycle for a typical thermoplastic.

4.6.6.3 Transfer Molding Process Variables

The important variables of transfer molding are the polymer type, melt temperature, pot hold time, transfer pressure, transfer rate, holdup time in the filled mold, and the mold cooling. These variables are briefly reviewed in this section.

Viscosity of the molten polymer has a great influence on the transfer rate into the cavity. Temperature changes can alter polymer viscosity as long as it has sufficient thermal stability in the given temperature range. Cleanliness of the melt can affect the quality of the part and thermal stability of the molten resin.

The choice of temperature is significant because a small increase can have a substantial effect on reducing melt viscosity. Temperature uniformity of the molten resin is a common requirement regardless of the type of resin or part design. Screw plastification is more effective than the melt pot method due to the static nature of the latter and poor thermal

conductivity of TPEs. Melt pots require significantly longer heat-up time for the polymer to reach transfer temperature. There will always be a temperature gradient between the melt near the wall and the cooler material at the center of the pot.

After the molten polymer has been stored in the pot and reached the required temperature, it is transferred into the mold cavity under positive pressure. The pressure and rate of transfer are the significant variables of the process. Maximum flow rate (transfer rate) can be increased by enlarging the gate or increasing the temperature, which helps raise critical shear rate.

In transfer molding, pressure is used as the independent control variable because most presses are not equipped with speed controllers for the hydraulic piston. The general range of transfer pressures at which most thermoplastics approach critical shear rates is 15–25 MPa (2185–3625 psi). Filling the mold in the “super shear” mode results in adverse effects on the properties of the molded part.

Pressures above 15 MPa (2185 psi) help fill the mold before its components such as the mandrel and casings begin to cool down. Above 25 MPa (3625 psi) melt pressure, the mold part may crack at the gate. The equipment should allow control of transfer rate and transfer pressure. Once the filling is nearly complete (90–95%), the transfer pressure should be lowered to half to two-thirds of its initial value to avoid stress concentration in the gate area. The pressure profile has to maximize hold pressure for packing without crack formation at the gate [68].

Cooling of the filled mold is accomplished by ambient or by fluid such as compressed air and should take place slowly at a controlled rate. Low

thermal conductivity of thermoplastics does not permit rapid cooling. The mold cooling should be begin at positions farthest from the gate and proceed slowly. A frozen front forms that moves toward the gate during cooling [68]. This approach allows addition of molten resin to the mold to compensate for the volumetric shrinkage, thus eliminating sink marks and shrinkage voids. Premature gate freezing or pressure release leads to void formation.

4.7 Blow Molding

Although blow molding of plastics dates from about 1880, rapid developments in machinery and technology only began in the late 1930s, virtually contemporaneously with the introduction of polyethylene. Blow molding is a relatively low-pressure process, using only 1% or less of the pressure levels employed in injection molding. This requires a low melt viscosity, produced by high shear rates and temperatures.

4.7.1 Blow Molding Processes

Blow molding is a process for converting thermoplastics into hollow objects. Like injection molding, the process is discontinuous or batch-wise in nature, involving a sequence of operations that culminates in the production of a molding. This sequence or cycle is repeated automatically or semiautomatically to produce a stream of molded parts.

The blow-molded parts are formed in a mold that defines the external shape only. As the name implies,

the inner shape is defined by fluid pressure, normally compressed air. In this respect, blow molding differs radically from many molding processes where both inner and outer forms are determined by mold members. The major advantage is that the inner form is virtually free of constraints because there is no core to extract. The main drawback is that the inner form is only indirectly defined by the mold, so high precision and independent internal features are impossible. This has a bearing on wall thickness, which can never attain the consistency and accuracy of a full-mold process such as injection molding.

Blow molding is now a highly developed process with many variant forms (Fig. 4.95). At its most basic, the process involves melt processing a thermoplastic into a tube that is generally referred to as a *parison*. While still in a heated ductile plastic state, the parison is clamped between the halves of a cooled mold, so that the open top and bottom ends of the parison are trapped, compressed, and sealed by the mold faces. A blowing tube is also trapped in one of the parison ends, creating a channel through which air pressure is introduced within the sealed parison. Air pressure causes the parison to expand like a balloon, so that it takes the form of the mold cavities. Contact with the cooled mold chills the thermoplastic to its solid state, so the form is retained after the mold is opened and the part removed.

The many variations of the blow molding process are discussed later in this chapter, with an emphasis on those most important for processing thermoplastics. Two features, the extruder and parison head, are common to many blow molding processes and will be discussed separately.

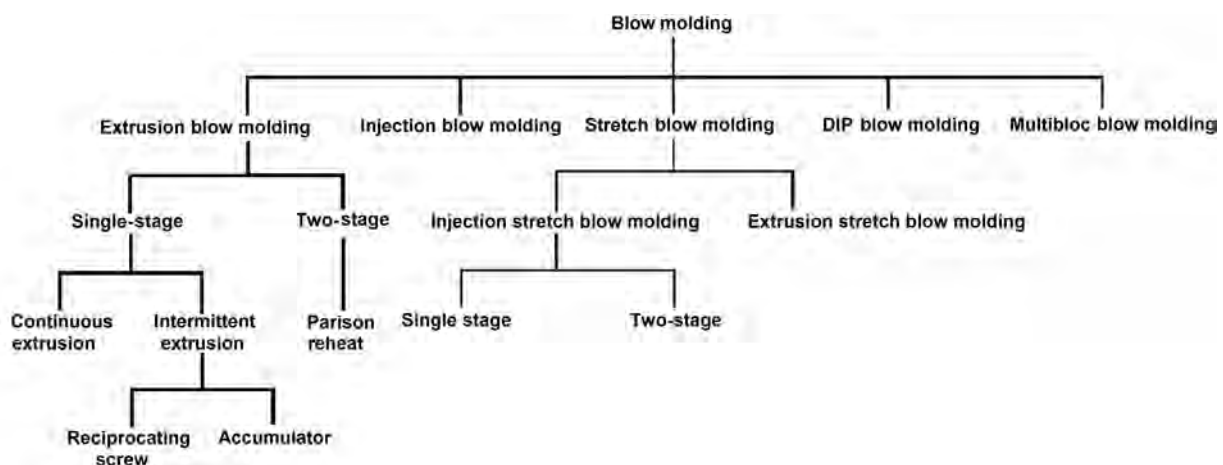


Figure 4.95 Blow molding processes.

4.7.1.1 The Extruder

Most blow molding processes begin with an extruded tube or parison. The extruder is of the single-screw type and follows the general principles described in Section 4.3.2 for an extruder for thermoplastics. The screw should have a length/diameter ratio of 24:1 to 30:1 or more. Screws at the high end of this range are preferable. The compression ratio should be about 3.5:1. A grooved barrel inlet improves extruder efficiency when working with thermoplastics. Melt temperatures depend on the type and grade of polypropylene and, in particular, on the melt flow index.

4.7.1.2 The Parison Head

The *parison head*, sometimes called the *die head* or simply the *die*, is a specialized form of tubular extrusion die. Its function is to deliver a straight parison in the correct diameter, length, wall thickness, and at the correct temperature for blow molding. Prior to being clamped in the mold, the parison is suspended unsupported in free air. To avoid undue deformation, it is necessary to extrude the parison vertically downward. The blow molder extruder is almost always arranged in a horizontal attitude, so the first task for the parison head is to turn the melt flow stream through a right angle. This is difficult to achieve in a way that meets the essential requirement for a constant flow rate at every point in the annular die gap. A second and related requirement is that the parison should carry as little evidence as possible of the weld line formed when the melt stream from the extruder flows around the torpedo. Many parison head designs have been evolved to deal with these problems. The example shown is known as the cardioid type (Fig. 4.96) [69]. Head design has benefited from computer analysis of the internal flow channels, which has removed much of the trial and error and given a greater assurance of success.

A further problem is one shared with pipe and tube extrusion dies. This is the difficulty of ensuring that the torpedo and mandrel remain coaxial with the die without dividing the melt stream with mechanical supports. The example shown in Fig. 4.96 uses no support in the melt stream, relying instead on an accurate seating between the torpedo and the housing. The parts need to be relatively massive for this design to be sufficiently rigid. Smaller torpedoes will need support in the melt stream, and here the

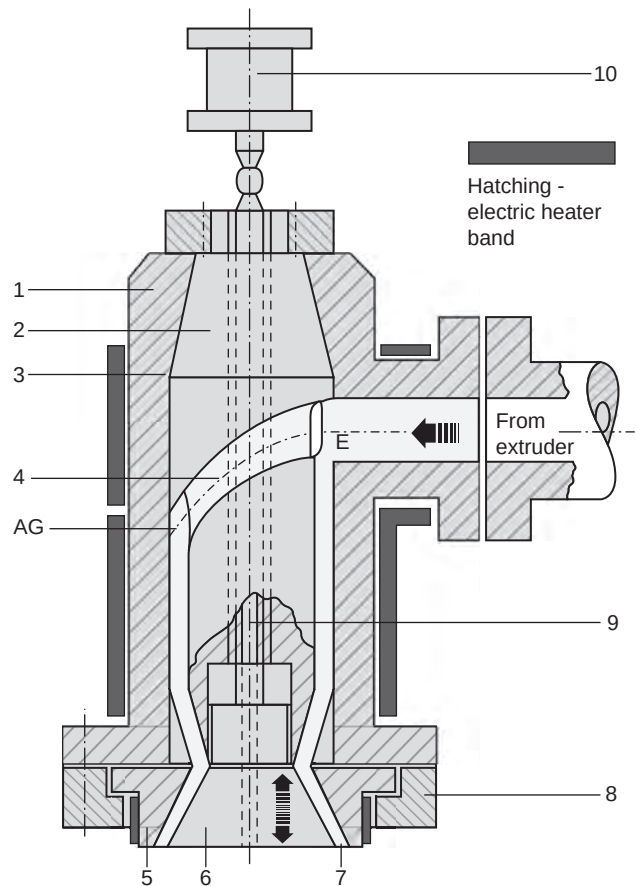


Figure 4.96 Typical parison head.

challenge is to minimize the formation of weld lines in the parison. Such supports include spider legs, staggered spider legs, breaker plates, screen tubes, and spiral mandrels. The problem is a difficult one and, in the worst case, the weld lines show up as local variations in the parison wall thickness.

The basic parison is a tube, which, in principle at least, has a constant wall thickness at all points around its circumference and along its length. In practice, circumferential thickness may vary as a result of weld lines, or if the mandrel is not truly coaxial with the die. Thickness along the parison length may vary due to tensile thinning caused by the weight of the dependent parison. However, the ideal parison with a constant wall thickness is not necessarily the optimum for blow molding. Even simple molded shapes encompass considerable variations in profile. For example, the body of a bottle is much greater in diameter than the neck. For some containers, there may be several significant variations along the axis, and the effect is usually pronounced in technical blow moldings. If such articles are blow

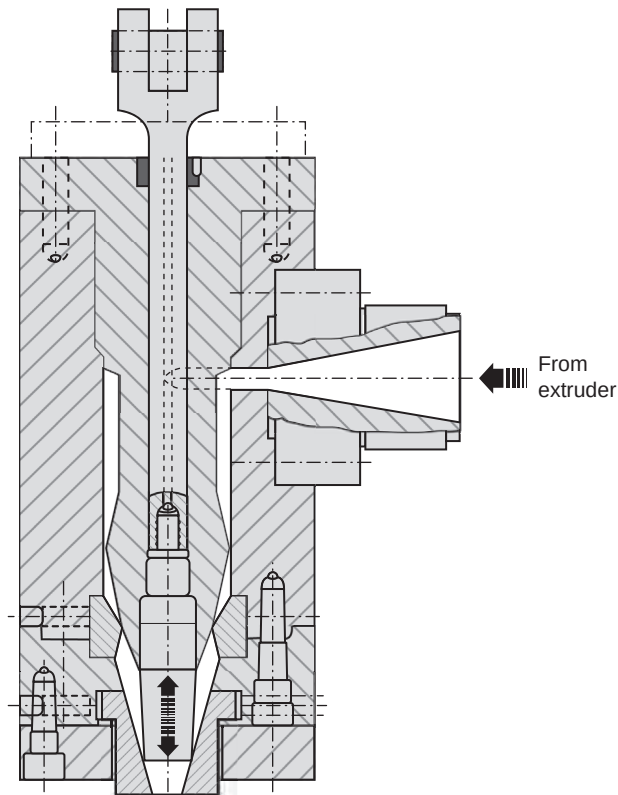


Figure 4.97 Principle of parison wall thickness control by axial movement of the mandrel.

molded from a parison of constant wall thickness, then the finished molding will be thinner where the parison has to expand the most and thicker where it has expanded the least. In most cases, the ideal is a finished product with a constant wall thickness at all points. To approach this ideal, a parison is needed in which the wall thickness varies along the length so that it is thickest where it must expand the most. This is achieved by parison programming or profiling.

The usual way to do this is by moving the mandrel in an axial direction relative to the die (Fig. 4.97) [69]. If both the die and the mandrel are provided with conical outlet features, this movement will increase or decrease the annular die gap between the two. The mandrel movements are controlled by a servo system acting on a preprogrammed thickness profile. The system may include a feedback loop to adjust parison profiling in response to screw speed variations in the extruder.

The concept is difficult to apply to the conical melt flow passage in variable die heads, but it can be taken to mean those zones in which melt passage thickness is substantially the same as the die outlet gap.

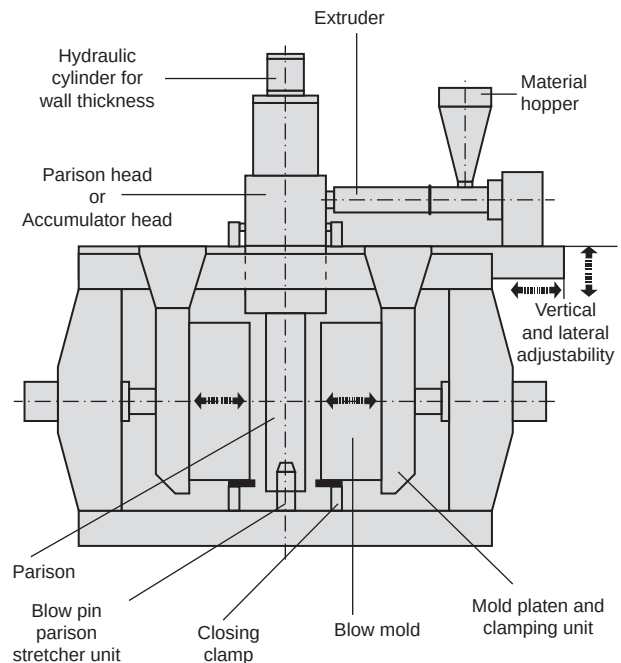


Figure 4.98 Typical extrusion blow molding machine.

4.7.2 Extrusion Blow Molding

In extrusion blow molding, an extruder feeding a parison head is used to produce a parison as a precursor or preform for the molding process. The configuration of individual machines may vary greatly, but some essential elements can be distinguished (Fig. 4.98) [69]. The extruder and parison head are arranged to extrude a parison vertically between the two halves of a blow mold. The mold halves are clamped to platens that are linked to a mold closing and clamping device. A blow pin is provided to inject air under pressure into the parison. Because blow molding is conducted at relatively low pressures, the construction of the machine and mold can be much lighter than is required for injection molding. Consequently, machines, and particularly molds, are much cheaper than those used in injection molding. Machine production rates can be increased by using multiple molds or multicavity molds with multiple parisons. These general principles apply to a number of distinct extrusion blow molding processes, which are described in the following sections of this chapter.

Single-stage extrusion blow molding produces a blown article in a single integrated process cycle. Blow molding immediately follows parison extrusion

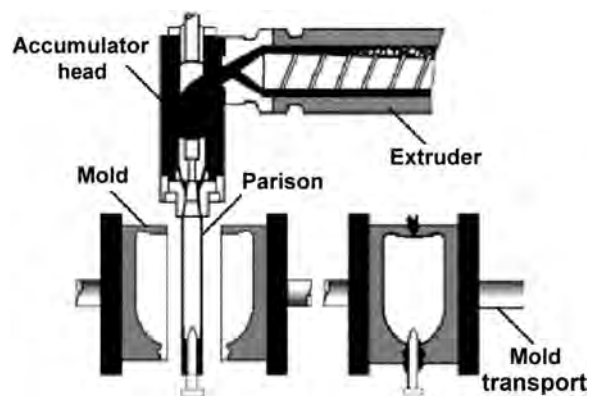


Figure 4.99 Basic extrusion blow molding process.

and relies on the melt condition of the parison for the deformation and flow necessary to take up the shape of the mold. There is no reheating of the parison before molding. The principal variants are the continuous extrusion and the intermittent extrusion processes. Extrusion in this distinguishing sense applies to extrusion of the parison rather than the operation of the extruder.

The *continuous extrusion* blow molding process is the most widely used for working with thermoplastics. In this process, the parison is extruded continuously from the parison head, between the open mold halves (Fig. 4.99) [70]. When the required length of parison has been produced, the mold is closed, trapping the parison, which is severed by a hot knife. Land or pinch-off areas on the mold compress and seal the upper and lower ends of the parison to make an elastic airtight object. Compressed air is introduced through the blow pin into the interior of the sealed parison, which expands to take up the shape of the mold cavities. The cooled mold chills the blown object, which can then be ejected when the mold opens.

The blowing air can be introduced in a variety of ways. In the simplest case, the parison is extruded downward so that the open end slips over a blow pin. Alternatively, the blow pin can be introduced from above the mold after the parison is severed, or blow needles can be built into the mold, where they pierce the parison as the mold closes.

Relative movement between the parison head and mold is necessary so that parison extrusion can proceed continuously while the mold is closed. This is achieved in many different ways. The mold may be lowered, moved aside laterally, or swung aside on an accurate path. Alternatively, the extruder may be moved while the mold remains stationary. Often, two

molds are used in a shuttle arrangement, so that one is open for parison extrusion while the other is performing the blowing cycle. One method of mold movement results in very high production rates. In such machines, generally known as *wheel machines*, a number of molds are mounted on a rotary table. Movement of the table carries the closed mold away and presents a new open mold to the die head, allowing extrusion to continue.

Except for special cases such as the shuttle and wheel machines, the extrusion rate of the parison must be synchronized with the blow cycle for a single mold. This may involve a relatively slow extrusion rate, running the risk of thinning the parison as it stretches under its own weight. For this reason, continuous extrusion blow molding is best suited to thermoplastics with a high melt viscosity or high melt strength or to short or thin-wall parisons.

In *intermittent extrusion* blow molding, the parison is extruded from the parison head discontinuously. When a parison of the required length has been produced, extrusion is interrupted until the next parison is required for the subsequent blowing cycle. This makes it unnecessary to have relative movement between the die and mold. The process is generally used to make larger blow moldings like drums or automotive fuel tanks. These articles require large and heavy parisons, which, when extruded normally, sag and thin down under their own weight. Intermittent rapid extrusion reduces this tendency, and it is achieved either by reciprocating screw or accumulator means.

Intermittent extrusion blow molding is best suited to long or heavy parisons and to thermoplastics with a low melt viscosity or low melt strength.

Reciprocating screw intermittent extrusion blow molding machines use an extruder unit in which the screw is capable of axial as well as rotational movement. The function is virtually identical to that of the injection unit on an injection molding machine, except that the blow molding unit functions at a lower melt pressure and flow rate. The parison is prepared in two steps:

- In the melt preparation phase, the screw rotates heating and melting the material, which is conveyed along the screw flights to the forward end of the screw. The extruder die block is closed by a valve, so the accumulating melt forces the still-rotating screw back against a controlled resistance until sufficient melt has

accumulated to make the next parison. At this point, screw rotation stops.

- In the parison extrusion phase, the extruder die block valve is opened and the screw performs the action of a ram by moving forward in the axial direction without rotating. This forces the accumulated melt at the forward end of the screw through the parison head, where it is extruded at a relatively high flow rate. In practice, the flow rate is limited by the onset of shear phenomena such as sharkskin or melt fracture.

Intermittent accumulator extrusion blow molding machines use a normal axially fixed continuously operating extruder to prepare the melt. The accumulator is a heated reservoir where the melt is temporarily stored in the intervals between parison extrusion. The parison is extruded by a ram acting on the stored melt. This means that the melt volume in the accumulator fluctuates in a cyclic manner. It is substantially empty immediately after the parison is extruded, then it gradually increases during the blowing phase, reaching a maximum immediately before extrusion. Accumulators introduce a number of problems. They increase the heat history of the melt, and they involve valves and complex flow paths that offer flow resistance and may also lead to difficulties with cleaning and even degradation. Accumulators should be designed on the FIFO principle: the first material in must be the first out.

Blow molding accumulators take one of two forms. The separate accumulator is a heated chamber, which is an integral part of the blow molding machine. The capacity of such a chamber can be very large and can, if necessary, be served by several extruders. The other type of accumulator is built into the parison head (Fig. 4.100). This takes the form of an annular ram that surrounds the mandrel and torpedo. The construction of the parison head becomes quite complicated, and there is the potential for melt leakage and degradation between the moving parts, so design and engineering must meet high standards. The shot volume available from an accumulator parison head is limited by practical considerations of head size and construction.

Two-stage extrusion blow molding treats the parison as a true preform by separating the functions of parison preparation and blow molding. Parisons are produced by conventional tube extrusion methods. The tube is cooled and cut into parison lengths that

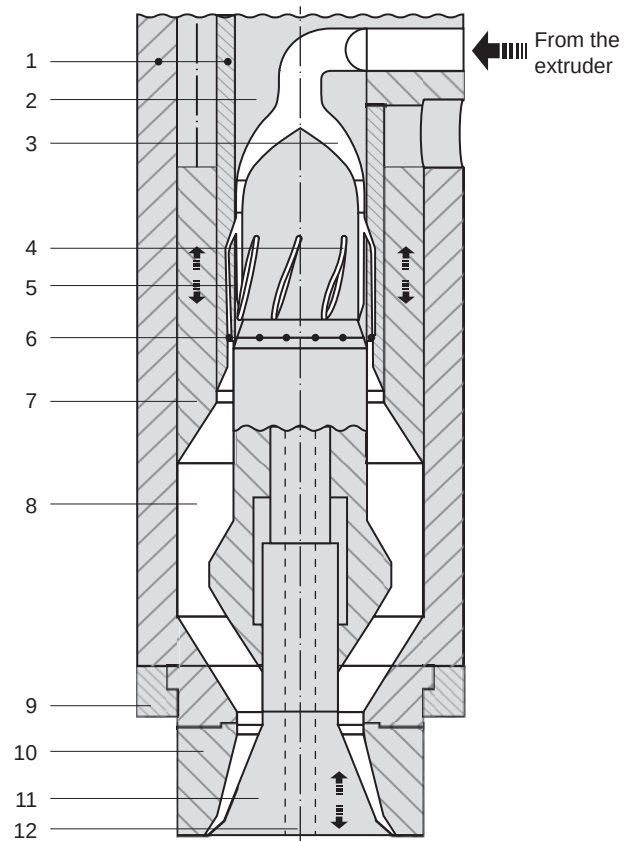


Figure 4.100 Example of accumulator parison head.

are stored before being reheated and blow-molded in the normal way. The reheating process can be selective, leading to a degree of control over the wall thickness in the blown article. The reheating process also tends to relax stress in the parison, resulting in a stronger product. However, the process has a number of disadvantages. The polymer heat history is increased by the use of two heating cycles, energy use is increased, and costs arise from the storage and handling of parisons. The process is not suited to high production speeds and is little used.

4.7.3 Injection Blow Molding

The injection blow molding process uses injection molding rather than extrusion to produce the precursor; it is generally known as a *preform* rather than a parison. The injection blow molding machine has an integral injection unit and a multi-impression mold assembly in which the mold cores are mounted on a rotary table. The cores double as blowing pins and index in 120° steps between injection, blowing, and ejection stations (Fig. 4.101) [71]. Station 1 is the preform injection mold where the preform is formed

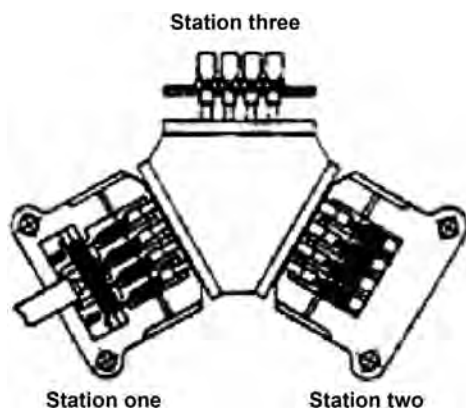


Figure 4.101 Injection blow molding stations.

over the core pin. The preform has a hemispherical closed end; the other end is an open bore, formed by the core pin. External details, such as the thread and neck flange for a screw-top container, are directly produced by injection molding. While the preform is still hot and plastic, the injection mold is opened and the preforms, still on the core pins, are rotated to station 2, the blowing station. Here the preforms are enclosed within the blow mold, and the molding is produced by introducing blowing air through the core pins. The blow mold is then opened, and the finished articles, still on the core pins, are rotated to an ejection station where they are stripped off. The machine has three sets of core pins, so that the three stages take place simultaneously.

The injection blow molding process has a number of advantages. The preform can be injection molded in a profiled shape that corresponds to the requirements of the blow mold form. The neck form is molded in its entirety at the injection stage, resulting in a quality and precision that is superior to a blow-molded neck. There is no pinch-off scrap to be removed and recycled and no bottom seam. There are some drawbacks too. The process is difficult to use with high melt viscosity materials. Integral handles, view stripes, and multiwall constructions are all impractical.

4.7.4 Stretch Blow Molding

Stretch blow molding processes are designed to produce biaxial orientation in the blown article. Conventional blow molding imparts a degree of circumferential orientation, caused by the expansion of the parison into the mold cavity, but there is little or no axial expansion and, correspondingly, no axial orientation. Stretch blow molding provides for axial

orientation by stretching the preform axially before or during blowing. This is normally accomplished by means of a stretch rod that is advanced axially inside the preform at a controlled rate. The disadvantages are that the process is more critical and complicated than conventional blow molding, and the capital cost of equipment is high. Stretch blow processes cannot produce containers with integral handles. Stretch blow molding may be performed by injection or extrusion means.

Injection stretch blow molding processes use hollow preforms produced by injection molding. The preform is short and thick walled relative to the finished blown article. The neck profile complete with screw thread is entirely formed by injection molding and is not modified by the blowing process. The other end of the preform is closed and typically dome shaped.

The design and precision of the preform has a critical influence on the degree of orientation and quality of the blown article. The actual wall thickness and any profiling will depend, of course, on the shape and size of the blown container. Like other preform processes, the finished blown article is free of seams, flash, and pinch-off scrap, and is characterized by precise neck dimensions. The injection-molded preform may be converted to a blow molding either by the single-stage or the two-stage process.

In the *single-stage* injection stretch blow molding process, the preform injection molding step is integrated with the stretch blow machinery. The machines are generally arranged for rotary operation, so that the preforms pass directly from the injection molding station to a thermal conditioning station and thence to a stretch blow molding station (Fig. 4.102) [72].

The thermally conditioned preform is transferred to a blow mold and stretched and oriented axially by an internal stretch rod, either immediately prior to, or simultaneously with, the blowing operation that provides radial stretch and orientation.

The *two-stage* or *reheat injection stretch blow molding* process completely separates the preform injection molding operation from the blow molding operation. Indeed, the two operations may be carried out in different locations by different manufacturers, with a substantial time interval between them. On the other hand, the process involves two heating operations, resulting in a greater energy use and increased heat history in the polymer. Another disadvantage is the need to store and handle preforms.

Before being blown, the preforms must be reheated from room temperature, then thermally

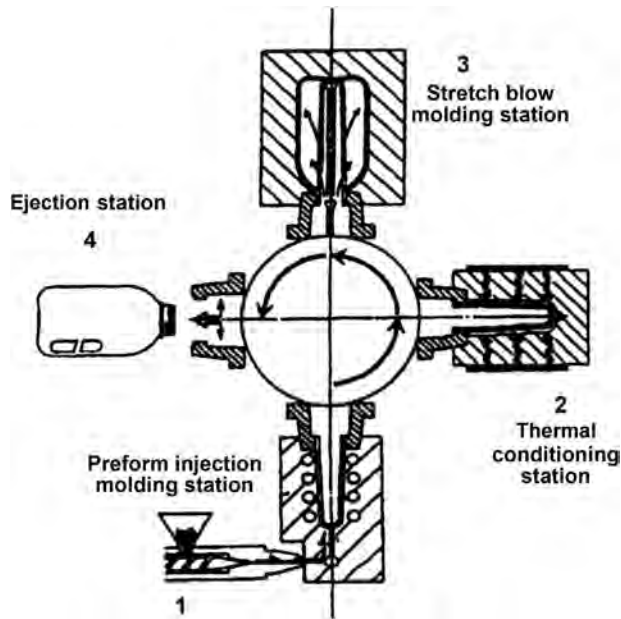


Figure 4.102 Single-stage injection stretch blow process.

conditioned and stretch blown in a similar manner to the single-stage process. The two-stage or rehear stretch blow machine is usually arranged for rotary high-speed continuous operation.

Extrusion stretch blow molding is a two-stage process using two mold/mandrel sets—one for pre-blow and the other for final blow. An extruded parison is first pinched off and blown conventionally in a relatively small pre-blow mold to produce a closed-end preform. The preform is then transferred to the final blow mold where an extending stretch rod

within the blowing mandrel bears on the closed preform end to stretch it axially. The stretched preform is then blown to impart circumferential stretch. Standard blow molding machines can be converted for extrusion stretch blow molding.

4.7.5 Dip Blow Molding

The dip blow molding process bears some resemblance to injection blow molding in that it is a single-stage process performed with a preform on a core/blow pin (Fig. 4.103) [69]. The difference is in the way the preform is made. The process uses an accumulator cylinder, which is fed by an extruder. The cylinder has an injection ram at one end, while the other is a free fit over the blow pin. The blow pin is plunged into the melt so that a neck mold on the pin seals the end of the accumulator cylinder. The injection ram is advanced to fill the neck mold; then the blow pin is withdrawn at a controlled rate so that it is coated with a melt layer extruded through the annular gap between the pin and the accumulator cylinder. The thickness of the coating can be varied or profiled to an extent by varying the speed of the blow pin and the pressure on the injection ram. After trimming, the preform is blow molded in the same manner used for injection blow molding.

4.7.6 Multiblock Blow Molding

The multiblock process is used for high volume blow molding of very small containers such as

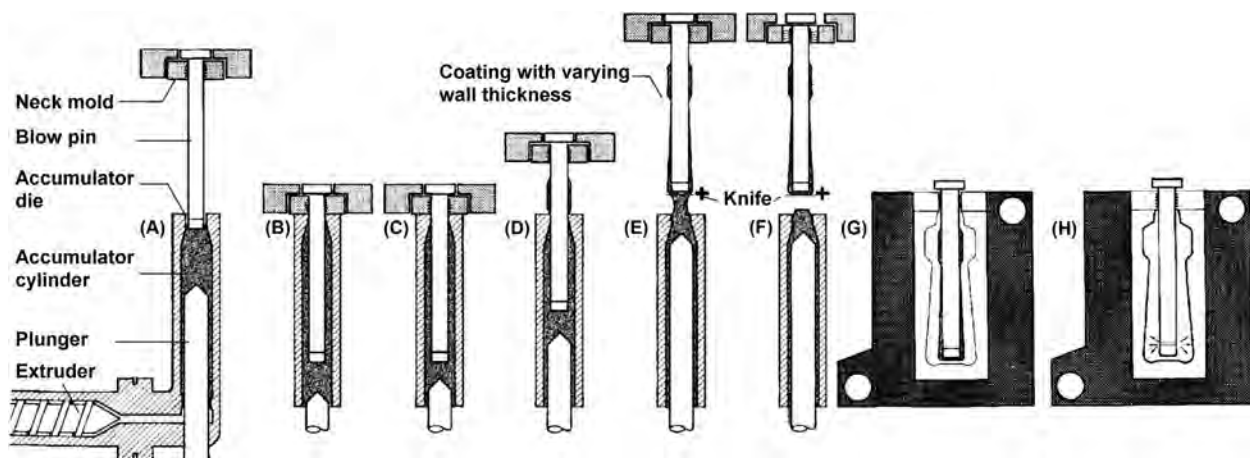


Figure 4.103 Stages in the dip blow molding process. (A) Accumulator filled; (B) Blow pin inserted; (C) Neck mold filled; (D) Blow pin partially withdrawn; (E) Blow pin fully withdrawn at variable speed; (F) Preform trimmed; (G) Preform clamped in mold; (H) Preform blow molded.

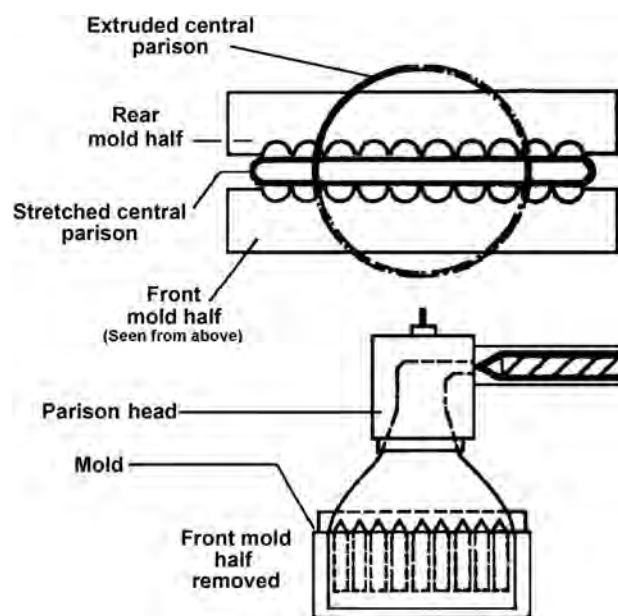


Figure 4.104 Multiblock blow molding process.

pharmaceutical vials. A multicavity mold is used with an extruded parison whose circumference approaches twice the total width of the closely spaced cavities. Before the mold closes, the parison is stretched and semiflattened laterally so that it extends across the full width of the cavities (Fig. 4.104) [69]. The process is usually combined with blow/fill/seal techniques.

4.7.7 Coextrusion Blow Molding Techniques

Just as in the production of film, coextrusion is now an essential technique in the production of high-performance blow-molded containers. The parison is coextruded with a number of different layers, each of which contributes an important property to the finished package.

Coextruded blow moldings commonly include from two to six layers, although more can be accommodated if necessary. The construction usually includes one or more barrier layers. These are polymers with a particular resistance to the transmission of water vapor or gases such as oxygen or carbon dioxide. Examples are polyamides, polyvinylidene chloride (PVDC), and ethylene vinyl alcohol (EVOH). Their presence greatly enhances the performance of the blow molding as a package for foodstuffs and other critical products.

4.7.8 Sequential Extrusion

Sequential extrusion blow molding is a special multimaterial technique (Fig. 4.105) [69] used for the production of technical articles. The different materials are chosen typically to contribute complementary mechanical properties and are present in distinct sequential zones in the finished part. Normally two materials are used, but three or more are possible. The die head is served by separate external ram accumulators for each material. These are operated sequentially, typically in A-B-A sequence, to produce a parison with three distinct material zones in axial succession. The parison is subsequently blow molded by normal techniques.

Because blow molding is performed on a cylindrical parison, the process is not well suited to the production of technical articles with complex forms that deviate substantially from the parison axis. Such forms can be produced by conventional blow molding, but only by using a large parison that, in its flattened form, blankets the complex mold cavity. The penalty for this is the formation of an excessive amount of pinch-off scrap.

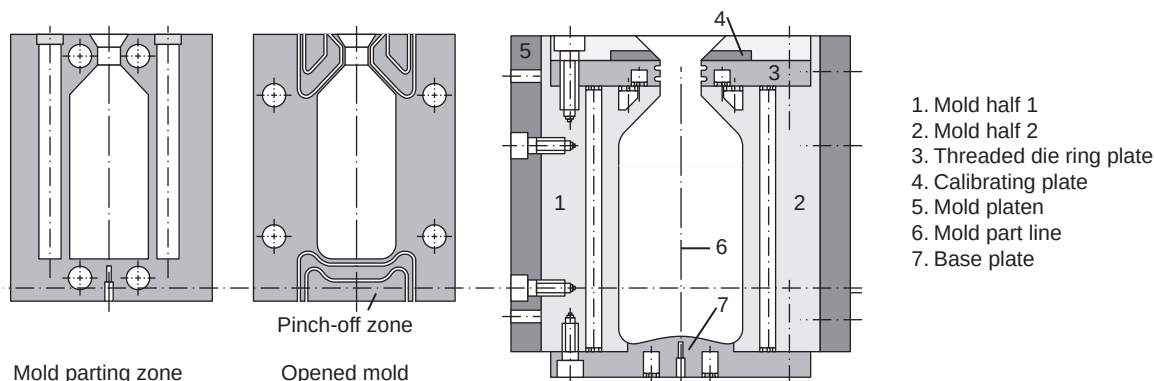


Figure 4.105 Principal features of an extrusion blow molding mold [1].

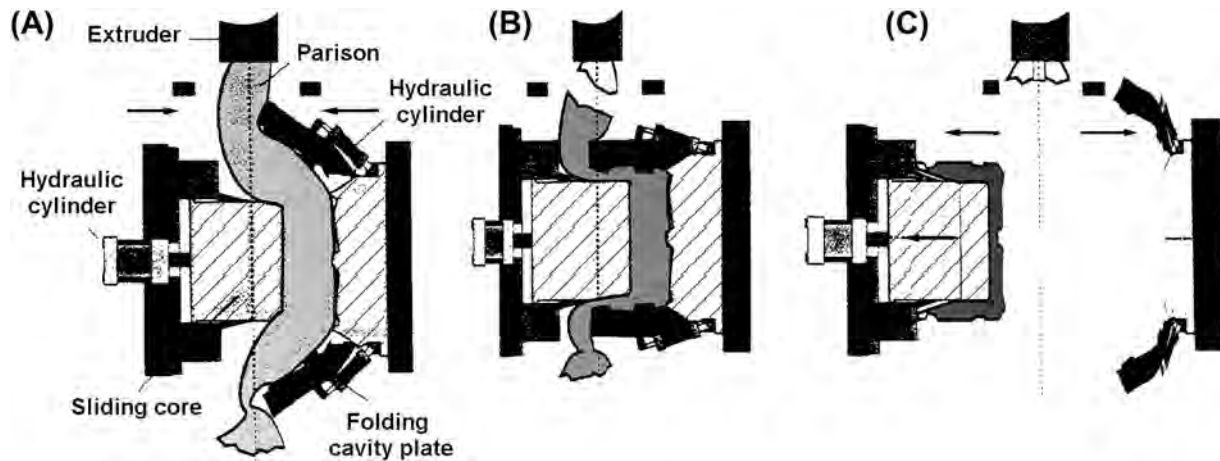


Figure 4.106 Placo Process for 3D blow molding. (A) The mold begins to close on pre-pinched parison; (B) Mold fully closed with core forward and sidewalls hinged in; (C) Mold open and core retracted.

Recent developments in parison handling equipment and in blow mold design now make it possible to manipulate a relatively small parison into the complex mold cavity. The result is a blow molding largely free of flash and scrap and offering considerable process savings. There are many such techniques, some of them proprietary property, and they are collectively known as *3D blow molding* (Fig. 4.106) [73].

4.7.9 Molds for Blow Molding

Essentially, the blow mold consists of two halves, each containing cavities that, when the mold is closed, define the exterior shape of the blow molding. Because the process produces a hollow article, there are no cores to define the inner shape. The blow molding process is carried out at relatively low pressures, so blow molds can be more lightly engineered than injection molds and are correspondingly cheaper and quicker to manufacture. Single-cavity molds are used when working with a single parison. When multiple parisons are in use, a number of single-cavity molds may be mounted on the machine platen, or the requirement may be met by a multiple-cavity mold. Mold details will vary considerably according to the geometry of the product and the blow molding process in use.

4.7.9.1 Basic Features

The mold consists of two halves that meet on a plane known as the *parting line*. The plane is chosen so that neither cavity half presents an undercut in the

direction of mold opening. For articles of asymmetrical cross-section, the parting line is placed in the direction of the greater dimension. The two mold halves are aligned by guide pillars and bushings to ensure that there is no mismatch between the cavities. The parison passes across the mold in the axis of the cavity and is pinched and compressed between the faces of the closing mold at the neck and base regions of the cavity. These are known as the *pinch-off zones*. The base and neck regions of the mold are typically formed by separately inserted mold blocks. The mold includes channels for the circulation of cooling water.

4.7.9.2 Pinch-off Zone

The pinch-off zone performs two functions. It must weld the parison to make a closed vessel that will contain blowing air, and it must leave pinched-off waste material in a condition to be removed easily from the blown article. To accomplish this, the pinch-off zone has a three-stage profile, consisting of pinch-off edge, pressing area, and flash chamber (Fig. 4.107) [69]. The pinch-off edge is flush with the mold parting line and forms part of the cavity periphery. The edge should be as narrow as possible depending on the material of construction. Steel (corrosion resistant metals for corrosive melts) edges can be from 0.3 to 1.5 mm (0.012–0.06 in) wide; for softer materials the dimensions should be 0.8–2.5 mm (0.032–0.10 in). The pressing area is recessed into the mold parting face by an amount depending on the parison thickness. Its function is to displace melt into the weld area to ensure a strong weld that is substantially equal in

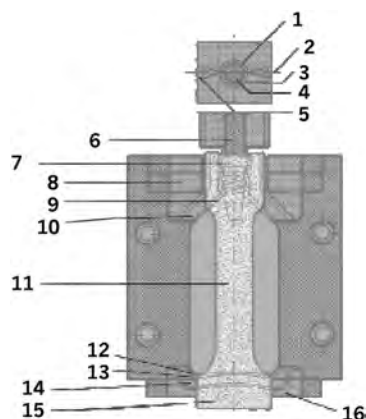


Figure 4.107 Pinch-off zones.

thickness to the blown wall thickness at the same point on the parison axis. The pressing area depth is typically determined by trial and error and is often given a ribbed surface to improve cooling of the waste material by increasing the area available for heat transfer. The flash chamber is recessed to a greater depth than the pressing area, typically to about the thickness of the parison. If it is made too deep, heat transfer will suffer and the parison scrap will cool too slowly. Its function is to limit the extent of the pressing area and so limit the force opposing mold closing. The steps between the different levels should be strengthened by angling the riser face by 30–45° to the parting face.

4.7.9.3 Blowing and Calibrating Devices

The *blow pin* is the means by which blowing air is inserted into the parison through what will become a hole in the finished blow molding. In the case of a bottle (Fig. 4.108) [69], the blow pin is inserted through the neck before or after mold closing. The blow pin body has the secondary function of calibrating the bore of the bottle neck. If the blow pin is plunged into the neck after mold closing, it is possible to produce a flash-free bottle mouth. After the mold opens, the finished bottle is stripped off by retracting the blow pin through a stripper plate. The blowing pin contains channels for the circulation of blowing air and cooling water.

Many blow-molded articles do not have an integral aperture that can accept a blow pin. In such cases, blowing air can be supplied through a blow needle that punctures the parison wall after the mold closes (Fig. 4.109) [69]. The needle can be advanced and

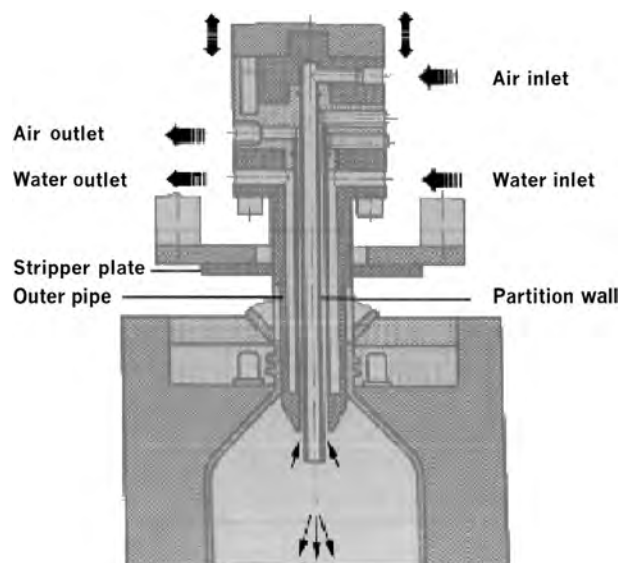


Figure 4.108 Example of calibrating blow pin.

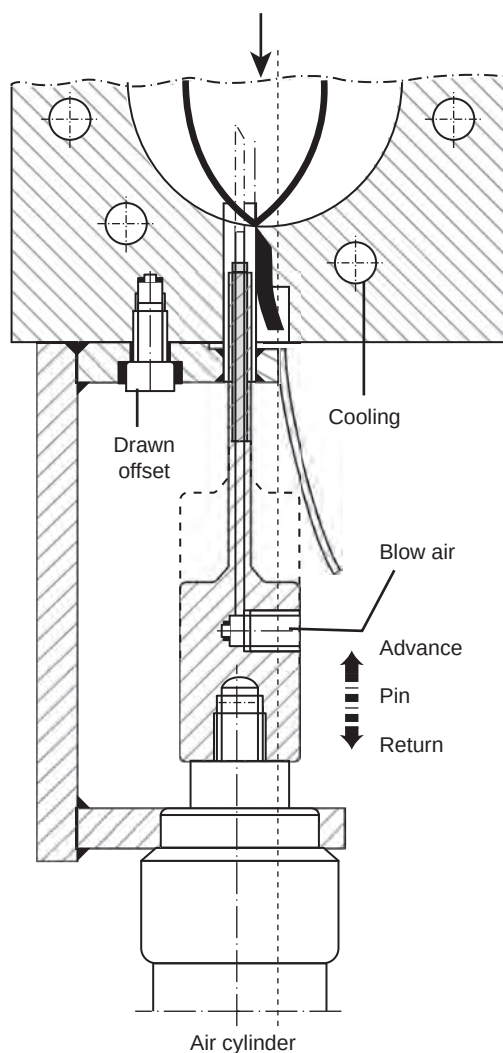


Figure 4.109 Example of blow needle.

retracted by means of an air or hydraulic cylinder and is located at a point close to a pinch-off edge. The parison is gripped by the mold at this point and so is unable to deflect away from the advancing needle point. The blow needle leaves a small witness hole, which can be sealed by a secondary operation.

4.7.9.4 Venting and Surface Finish

When a parison is blown, a large volume of air must be displaced from the mold cavity in a short time. Because blowing is carried out at relatively low pressure, it is essential to provide venting to allow this air to escape without resistance. Unless a gloss finish is required on the molding, it is common practice to sandblast the cavity to a fine matte finish. This helps air to escape as the expanding parison touches the cavity face, but it is not sufficient in itself. Vent slots may be cut at appropriate points into the mold parting face to a depth of 0.05–0.15 mm (0.002–0.006 in), and venting can also be provided within the mold cavity by means of inserts provided with vent slots, porous sintered plugs, or by holes with a diameter not greater than 0.2 mm (0.08 in). Such holes are machined only to a shallow depth and are relieved by a much larger bore machined from the back of the mold.

4.7.9.5 Cooling

Efficient mold cooling is essential for economical blow molding. Typically, up to 80% of a blow molding cycle is devoted to cooling. Molds are constructed as far as possible from high thermal conductivity alloys, and water cooling channels are placed as close as possible to the surface of cavities and pinch-off zones. Because blow molding is a relatively low-pressure process, the channels can be quite close to the surface and quite closely spaced before mold strength is compromised. The actual dimensions will depend on the material of construction, but as a guide, channels may approach within 10 mm of the cavity and center spacing should not be less than twice the channel diameter. If the mold body is cast, the cooling channels can be fabricated in copper pipe to closely follow the cavity contours before being cast in place. If the mold is machined, channels will be produced by drilling and milling, and it is not usually possible to follow the cavity contours so closely. An alternative in cast molds is

a large flood chamber. However, efficient water cooling requires turbulent flow, and this may not be attained in a flood chamber or in large coolant channels. Many small channels are better than a few large ones. The cooling circuits will normally be zoned so that different areas of the mold can be independently controlled.

4.7.10 Examples of Blow-Molded Parts

A majority of blow-molded parts have a multilayer construction to combine the properties of other plastics in a composite structure. The most common technique for producing multilayer sheet/film is coextrusion.

Coextrusion blow molding technology was employed [74] to produce corrugated tubing, pipe, and hose for applications that require flexibility and close tolerances such as in the automotive industry. Composites of two or more layers form the walls of these articles to take advantage of different materials. Tubing made by this technique has a high degree of flexibility, resistance to hydrolysis and bursting, and stability with respect to linear extension. For instance, in gasoline filler necks, it is important that the corrugated tubing has areas of great stretching stability and areas with reduced stretching stability, such as provided by this technology.

Monolayer hoses or pipes of two or more layers of polymers, which were compatible with each other or required an interim tie layer, have been fabricated in many sizes, designs, and from many thermoplastics.

4.8 Rotational Molding

Rotational molding (also called *rotomolding* or *rotational casting*) is a process for manufacturing seamless hollow plastic parts for a variety of applications ranging from liquid storage tanks to containers of various shapes. Consumer products such as furniture, playground equipment, and toys are made by this technique. Rotational molding produces dolls, doll parts, sit-in and sit-on toys, and various sizes of heavy-wall balls.

The past decade has seen a large growth in the applications of rotational molding and lining technology. Along with this growth, interest has increased in understanding the complex technical aspects of this technique. Rotational lining is employed when the

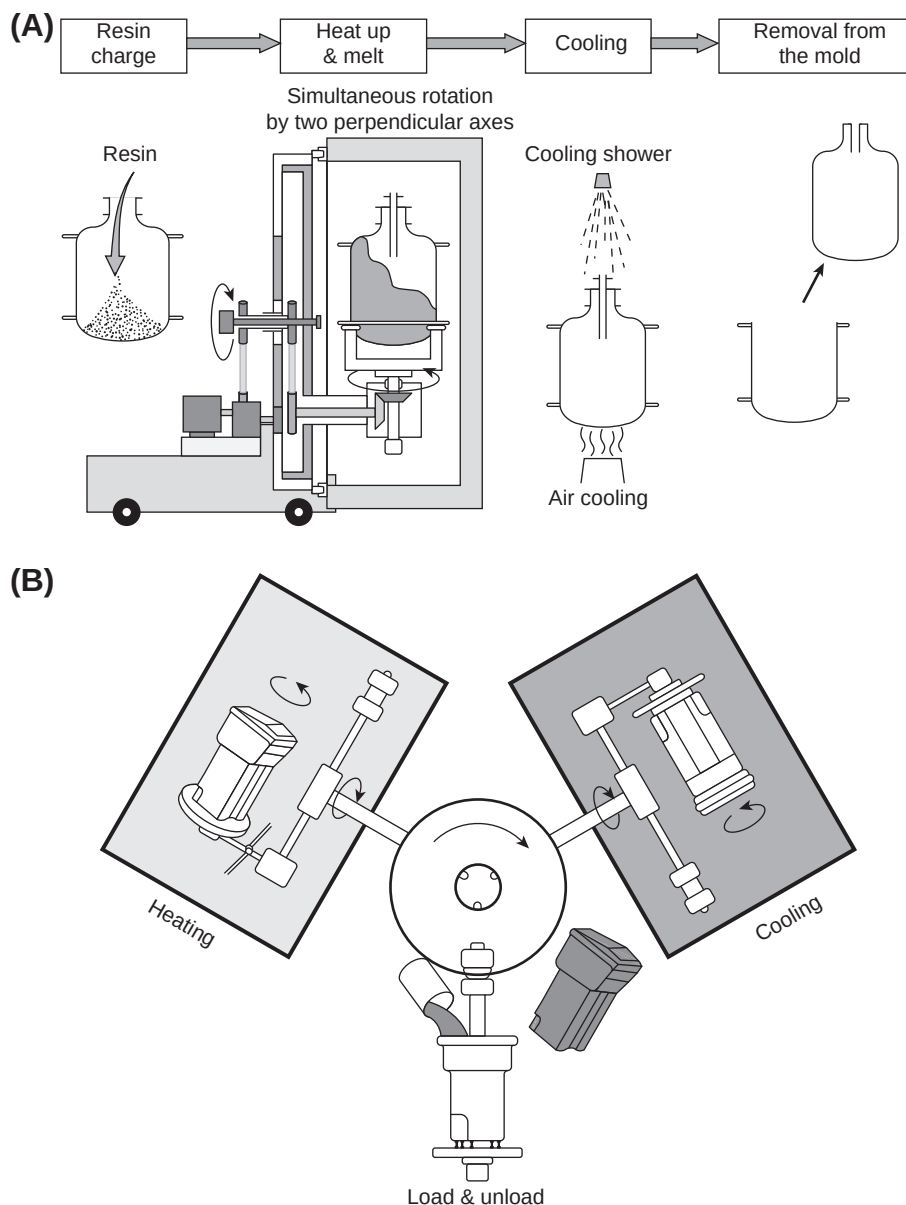


Figure 4.110 Schematic diagram of rotational molding process.

objective is to coat the interior of a metallic part, instead of manufacturing a plastic part.

Rotational molding (Fig. 4.110) involves the external heating of a thin-walled hollow metal mold containing a polymer powder. Heating occurs while the mold is rotated multiaxially. The powder melts and coats, or sinters, onto the interior wall of the cavity. The mold is then cooled, which allows the part to solidify and crystallize in the case of thermoplastics. Finally, the part is removed and the mold is charged to repeat the cycle.

The rule of thumb for selecting rotational molding technology is part quantities of less than 25,000 per year and sizes larger than 200 l (530 gal). In the case of thermoplastic elastomers, smaller parts are also produced by this technology. It allows the production of parts with intricate geometry without imparting significant residual stresses or orientation to the part. These are the advantages of this process over blow molding in addition to its ability to fabricate larger parts. Rotomolding requires significantly smaller capital investment than injection and blow molding

processes, thanks to its low-pressure requirement. Parts made by rotational molding often cost more than those manufactured by more conventional processes because of its relatively long cycle time.

Certain thermoplastic elastomers can be fabricated into hollow objects by rotomolding. They are, however, hard to mold due to their relatively high melting point and melt viscosity, and usually only specific grades can be used for that. The TPEs reported to be processed by rotomolding include COPE, TPO, TPU, SBS, and SEBS.

4.8.1 Background

The modern-day concept of rotational molding originated in the early 1900s. Today's technology resembles the *slush* molding process for fabricating hollow articles from polyvinyl chloride plastisols in the late 1940s. Due to the absence of other suitable plastics, applications for rotational molding technology did not expand. Then polyethylene became available, which allowed the application of this technique in making parts for end uses where polyvinyl chloride was not economical. Large tank molding became a reality with the advent of modified and cross-linkable polyethylene in the 1970s.

Starting in the mid-1970s, more polymers became available, including linear low-density polyethylene, polyamides, polypropylene, and polycarbonate. Almost 90% of the solid polymer consumed by rotational molding worldwide is comprised of polyethylene [75]. The most suitable form of a plastic for rotational molding is powder or liquid form. This technique permits uniform wall thickness and higher thickness than blow molding. Undercuts, inserts, and ribs can be easily achieved in rotomolding. Thick corners are obtainable by this technique compared to other hollow molding methods.

4.8.2 Basic Process Technology

Rotational molding is used to produce a broad array of seamless hollow plastic products. Except for permanent adhesion to the cavity wall, processing considerations in rotolining are otherwise identical to those in rotomolding. In this process, a premeasured amount of a plastic powder, granules, or liquid is charged inside a mold cavity. The mold is closed and heated in an oven while being rotated multiaxially (usually two axes). Fig. 4.111 depicts a biaxial rotomolding machine. The major axis is the

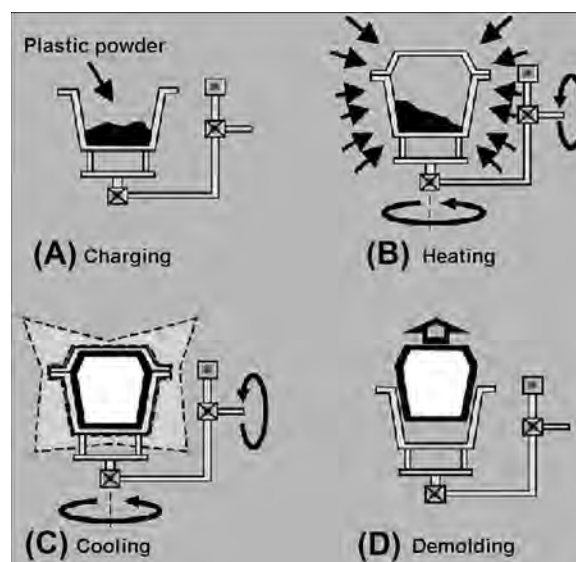


Figure 4.111 Biaxial rotomolding machine. (A) Charging; (B) Heating; (C) Cooling; (D) Demolding.

centerline of the arm of the mold. The minor axis rotates the mold perpendicular to the major axis. Typically, the minor axis revolves four times to every one time of the major axis. The basic steps of mold charging, heating, cooling, and part removal are shown in Fig. 4.111. In an alternative design, the molds undergo a “rock-and-roll” motion, rotating 360° around one axis and rocking about a perpendicular axis. In a majority of cases, the mold is heated by forced hot air. Open flame burners, as well as infrared, conductive, inductive, and dielectric heating techniques, have also been reported. The wall of the mold is usually heated to a temperature above the melting point of the polymer.

Heat transfer, from the hot air in the cavity and from the wall of the mold to the powder, melts the polymer, which sticks to the hot cavity (Fig. 4.112). It results in the formation of an even coating on the interior wall of the cavity. The mold is cooled while it is rotated to retain the uniform wall thickness. Finally, after the polymer has solidified, the rigid part is removed from the mold. Volatile material formed during the heating period is removed from a vent port. The rotation rate, temperature, heating rate, and cooling rate are controlled throughout the process.

General advantages and limitations of the rotational molding process are listed in Tables 4.20 and 4.21, respectively.

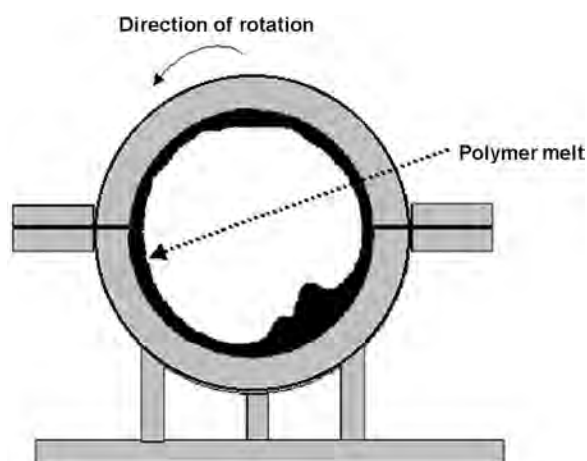


Figure 4.112 Schematic of adhesion of polymer melt to the mold wall and part formation.

The rotomolding process is differentiated from *spin casting* or *centrifugal casting* by its relatively low rotation speed that is usually in the range of 1–20 rpm. Rotation speeds range up to 40 rpm on the minor axis and 12 rpm on the major axis. These speeds are slow enough to prevent development of significant centrifugal forces.

The essential feature of centrifugal casting is the introduction of molten metal or plastic into a mold that is rotated during solidification of the casting. The centrifugal force shapes and feeds the molten material with great detail as the force of gravity drives the molten matter into the designed crevices and details of the shape. Centrifugal casting improves the homogeneity and accuracy in special circumstances. The process imposes limitations on the shape of

Table 4.20 Benefits of Rotomolding Process

Benefits	
1	A hollow part can be made in one piece with no weld lines or joints.
2	Simultaneous molding of different-shaped parts.
3	The molded part is essentially stress-free.
4	The molds are relatively inexpensive.
5	The lead time for the manufacture of mold is relatively short.
6	Wall thickness can be quite uniform compared to blow molding or twin sheet forming.
7	Wall thickness distribution can be altered without modifying the mold.
8	Inserts are relatively easy to mold in.
9	Short production runs can be economically viable.
10	It is possible to make multilayer, including foamed, parts.
11	Low scrap rate.
12	Low initial capital investment.

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Table 4.21 Limitations of Rotomolding Process

Limitations	
1	The manufacturing cycles are long.
2	The choice of molding materials is relatively limited.
3	Material costs are fairly high due to the need of special additive packages; moreover the material has to be ground to a fine powder.
4	Some geometrical features, such as solid ribs, are difficult to mold.
5	Sharp thickness variations cannot be easily accommodated; gradual transitions work best.
6	Tight tolerances are hard to maintain.
7	Wall thickness variation averages about $\pm 10\%$.
8	Molds must be designed using the proper shrinkage rate of the resin.

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castings and is normally restricted to the production of cylindrical shapes.

The rotational molding process takes place in two stages. During the first stage, the polymer melts, sinters, and densifies; while in the second stage, the melt flows on the walls of the mold and fills all channels, undercuts, and other cavities in the geometry of the mold under shear stresses developed during the rotation. The main force acting on the polymer is gravity because, due to the low rotation speed, the centrifugal forces are negligible. The absence of significant shear requires high molding temperatures to reduce the viscosity of the polymer and expedite its mold filling action.

This method is ideally suited to the casting of spherical shapes, but the outer shape may be modified with the use of special techniques. Normally, metal molds are used and plastic is poured into the rotating mold that may spin about a horizontal, inclined, or vertical axis. The centrifugal force improves both homogeneity and accuracy.

Rotational molding of plastic foams (e.g., polyethylene) has become increasingly important due to its ability to obtain thicker walls with less weight increase, sound dampening, thermal insulation, and high stiffness. So far, rotomolding of TPE foams has been less commonplace than the foams of other thermoplastics. Foaming technology is discussed in [Section 4.9](#).

4.8.3 Rotational Molding Equipment

The equipment for rotomolding is typically characterized by: (1) the weight of the maximum load that can be supported by the arms, including the weight of the mold and the resin charge; and (2) by the diameter of the sphere of rotation by the mold. Rotomolding machines are capable of producing small objects like ping pong balls and large objects with a capacity of 4.5 metric ton weight and over 5.5 m (216 in) mold swing that can fabricate large tanks (85,000 l or 22,500 gal).

Mold heating is usually done by hot air. The air can be heated by any means such as natural gas, oil, or electric sources. Some systems are heated by open flame, which is attractive for its lower tooling cost. Cooling is initially achieved by ambient or forced air, usually followed by water spray to achieve uniform cooling. An enclosed cooling chamber can be used optionally.

4.8.3.1 Batch Systems

This is the simplest and least costly form of the equipment, but it requires the most labor. The mold is rolled into the oven for rotation and heating. Then it is moved out at the end of the cycle, and another mold takes its place. The completed mold is transferred into the cooling station, and, finally, the part is removed.

4.8.3.2 Carousel Machines

The most commonplace type of rotomolder is the *carousel* machine ([Fig. 4.113](#)) that has three stations or positions. It has a loading/unloading station, heating station (usually an oven), and cooling station. Cooling usually takes place in an enclosed compartment. The mechanism, as the name indicates, resembles that of a carousel. One or more spindles are connected at one end to a turret or central hub, and to one or more molds at the other end.

A typical carousel can rotate a full circle freely. The spindles, or arms, are motorized and their motions are controlled independently of the central hub or the oven temperature and dwell time. Individual arms are simultaneously undergoing different phases. One arm is in the loading/unloading station, the second arm is rotating in the oven, and the third arm is in the cooling station. At the end of each cycle, the turret rotates 120° to move each mold to the next cycle. This means that no arm is idle at any time.

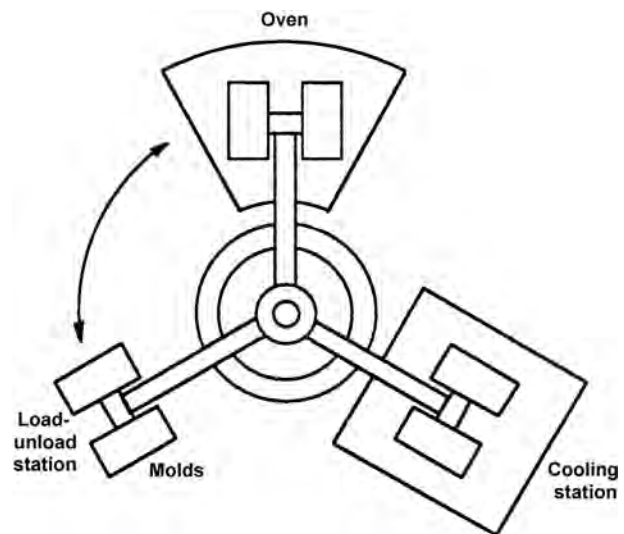


Figure 4.113 Schematic diagram of a carousel rotomolder.

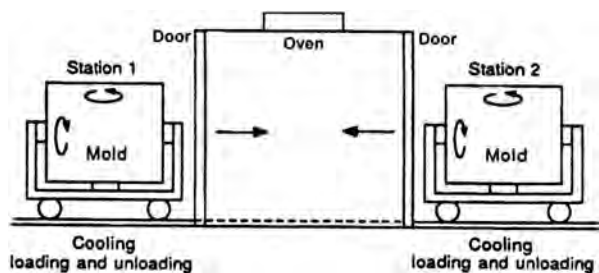


Figure 4.114 Schematic diagram of a shuttle rotomolder.

Some units have more than three arms to increase productivity. With a multiple arm machine, more than one arm/mold can be in the oven.

4.8.3.3 Shuttle Machines

Larger products, such as big containers, are fabricated in the *shuttle* rotomolder (Fig. 4.114) that generally operates in a straight line with the oven and the cooling stations at opposite ends. A movable mold cartridge holds the mold and the motors that drive its biaxial motions. The cartridge is mounted on a rail track that allows it to be rolled in and out of the oven. At the conclusion of the heating cycle, the mold is transferred into the cooling chamber. Another mold can be rolled into the oven to start the next heating cycle. By positioning the loading/unloading station between the cooling and heating stations on parallel tracks, transfer of molds occurs smoothly.

4.8.3.4 Clamshell Machines

The *clamshell* rotomolder is the third type of machine (Fig. 4.115). In this design, there is one arm,

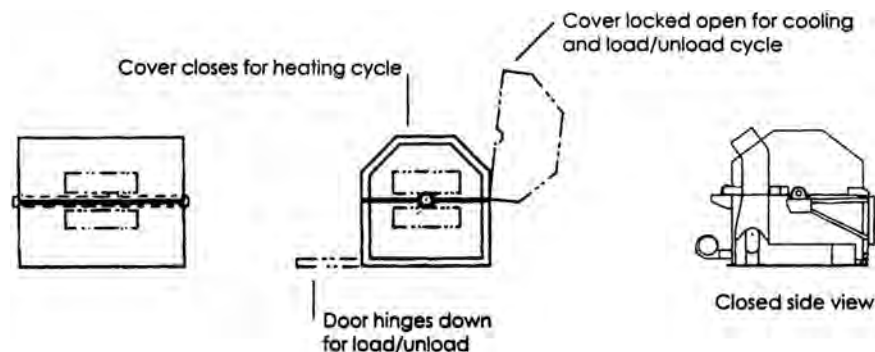


Figure 4.115 Schematic diagram of a clamshell rotomolder.

Table 4.22 Design Considerations for Rotomolding

Design Considerations	
1	Heat transfer of the mold and plastic materials.
2	Parting line locations.
3	Part size.
4	Molding machine size.
5	Mold weight and material on the arm.
6	Shot size.
7	Vent location.
8	Fill ports.
9	Mold clamping mechanism.
10	Mold mounting mechanism.
11	Construction material of the mold.
12	The number of parts that the mold can make.
13	Tooling construction.
14	Color matching.

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and the three stations are combined. Heating and cooling both occur in the same enclosure.

4.8.4 Equipment and Process Design

A number of factors should be taken into account in the design of a rotomolding process, regardless of the type of the rotational molding equipment. A list of the items to be considered is provided in Table 4.22.

Table 4.23 Guidelines for Rotomolding Process and Equipment Design

Guidelines	
1	Place the high stress away from parting lines.
2	Design for very high coefficients of thermal expansion.
3	Avoid designing flat surfaces and straight lines.
4	Alter the deep pocket areas for better heat flow and thicker walls.
5	Design in very high tolerances, larger than ARM recommendation.
6	Put in a drop box to contain excess powder that may not fit in the cavity.
7	Keep the component mount loads below 0.7 MPa (102 psi).
8	Keep inserts away from the sidewalls to allow proper material fill.
9	For parts requiring good aesthetics, keep parting lines above the normal level of eyesight.

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Additional design information about the process can be found in a publication by the Association of Rotational Molders (ARM) titled, “Introductory Guide to Designing Rotationally Molded Plastic Parts”. A number of often-overlooked considerations in designing a rotomolding process are listed in [Table 4.23](#).

4.8.4.1 Molds

Molds for convection heating are relatively inexpensive; however, the cost is dependent on the type of plastics to be fabricated, processing temperatures, and the size, shape, and desired quality of the molded part. Multiple cavities are designed in the mold except for very large parts. The molds in this process are shell-like and are made from two, three, or more pieces for complex parts. The mold halves are retained together at the parting line by means of bolts or clamps. The mold is always equipped with a vent tube to equalize the internal pressure of the mold with the external environment. The location of the vent tube depends on the part design, although the fill port of the tank is often a good place to locate the vent.

Molds undergo a great deal of thermal stress because of cycling from room temperature to in excess of 400 °C (752 °F) for thermoplastic elastomers. The selection of the metal should take into account not only temperature but also the corrosive nature of the degradation products of certain TPEs. The most common molds in the processing of the majority of thermoplastics, e.g., PE, are cast aluminum. Rapid heat transfer and low cost are their

major advantages. Cast aluminum is sometimes porous, and molds made from it can be easily damaged. This material is not suitable for most TPEs, due to the high temperature requirements of these polymeric materials.

Machined metal molds, especially aluminum, are used for applications that require extreme precision. Machined molds yield parts that are free of voids and surface porosity. Their use is limited to special cases due to the high cost of material and fabrication of these molds.

Sheet metals can be used to produce prototype and production molds. They are often used when a single cavity mold is required to produce large cavities. Sheet metal molds are frequently fabricated in-house by custom molders. The various pieces of the mold are welded together. Their advantages include light-weight and uniform thin walls.

Electroformed or vapor-formed nickel is suitable for molding corrosive resins. These molds are unique in their capability to replicate fine surface details. Special construction material requirements related to the corrosive nature of degradation products of certain TPEs have been discussed in [Section 4.4.8](#).

It is very important to consider the polymer that is going to be molded in rotomolding.

Some materials are sufficiently flexible to allow some undercuts in the mold and still be easily removed. Other polymers shrink, and still others require a light draft angle (1° or 2°) to allow release of the part. The shrinkage rate of the polymer must be known in order to design tooling that is capable of producing parts that meet the specifications. Large

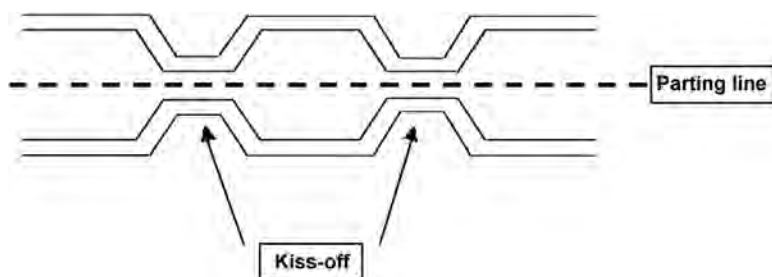


Figure 4.116 Cross-section showing two kiss-off areas.

flat surfaces are the most difficult to mold rotationally. Proper mold release techniques and internal air pressurization during cooling can minimize deformation of the flat surfaces. It would be best to design some type of stiffening into the flat sections. Contoured ribs or embossing are two examples of such designs. It is advantageous to design a convex mold to counter the tendency of flat plastic surfaces to cave inward. If aesthetics of the part permit, it would be helpful to put in “kiss-offs” which require a hollow insert on each half of the cavity (see Fig. 4.116) to form a support from one wall to another. The net effect is an increase in the modulus of the section containing the kiss-off areas, resulting in substantial stiffening. The recommended depth of the corrugations is four times the thickness of the part.

Mounting one mold on the arm is fairly straightforward. Multiple molds require careful design for mounting on a single spider. Improper mounting can result in an abnormally high rate of wear and tear on the mold and excessive flash formation on the part.

One of the most difficult maintenance issues in rotational molding is the parting line deterioration and flashing. There are steps to reduce this problem. Parting lines on sharp corners, along knife-edges or vertical lines should be avoided. Whenever possible, multiple pieces of the mold should be designed to use a slide or a hinge system to guide the opening and closing of the mold pieces. This design reduces the damage to the parting line and eases the operation of the mold.

A variety of clamps and quick-release devices are available for holding the mold together, but the best parting line is the pin-and-bushing type. It produces the cleanest parting line, but quick-release clamps are appropriate when a clean parting line is not required. Some examples of parting lines are given in Fig. 4.117. Stepped and fabricated parting lines are less common than tongue-and-groove and pin-and-bushing types.

Rotational molding creates some unusual effects that are not encountered in other molding techniques. For example, outside corners of the part are thicker (Fig. 4.118) than the general thickness of the part because the resin powder accumulates in the corners of the mold. On the other hand, inside corners are thinner because the powder tends to fall away from the mold in these areas. The recommended corner radii (Fig. 4.118) help the uniformity of the part thickness. Altering the rotation speeds around the major and minor axis (discussed later in this chapter) can control wall thickness variations.

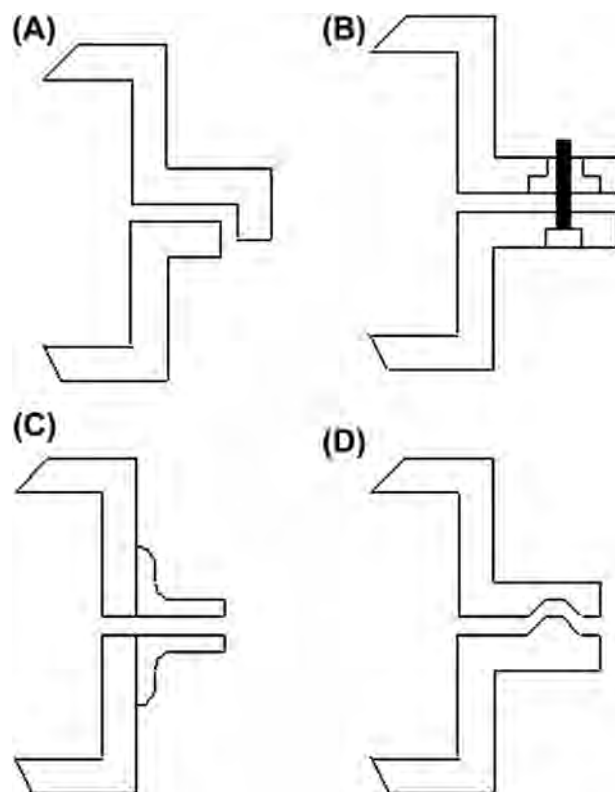


Figure 4.117 Examples of parting lines. (A) Stepped; (B) Pin and bushing; (C) Fabricated; (D) Tongue and groove.

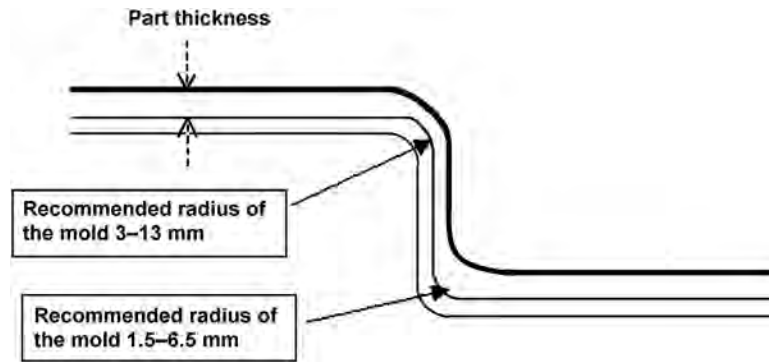


Figure 4.118 Part thickness and recommended radii in the corners of the mold.

4.8.4.2 Mold Surface Preparation

The mold surface must be clean and free of chemicals and debris for a successful rotational molding and lining. A complete procedure includes multiple steps described here, but the exact method depends on the type of resin, machine type, and the part. After a cycle or a production campaign has been completed, the inside surface of the mold must be degreased, followed by shot (grit) blasting. Afterwards, the mold is baked in a vacuum oven or under an inert gas such as nitrogen. This sequence removes the leftover resin, degradation products, and moisture from the mold.

4.8.5 Operation of Rotomolding Processes

In a typical rotomolding operation, the mold is charged with a determined amount of polymer powder, the mold pieces (halves) are assembled together, and the mold is put in an oven and rotated biaxially. The resin melts during the heating cycle, fuses, adheres to the wall of the mold, and forms the part. The mold is transferred into a cooling chamber where it is cooled down with air and/or water. At the conclusion of the cooling cycle, the mold is taken out, and the finished part is removed.

The particle size of the resin is very important in the rotomolding process. Although an average particle size of 0.5 mm (0.02 in) is an industry standard, smaller or larger particle sizes can also be processed.

Wall thickness can be decreased or increased by adjusting the amount of charge and the cycle time. Reducing the heat that is supplied to certain areas of the mold reduces the thickness of the part at those points. Areas that should be thinner can be shielded

by insulation to reduce the buildup of molten resin. Conversely, extra heat is directed at the areas where more thickness is required. The distance between adjacent walls should be at least four times the wall thickness of the part to prevent bridging of the resin [76].

Surface texture can be controlled on the outside surface of the part because the molds are female. Rotationally molded parts generally have a good appearance on the outer surface without sink marks. Matte finish and grains can be readily obtained on the exterior part surface. A glossy finish is difficult to obtain and significantly increases the cost of the mold. Comparable parts with much smoother finish (gloss) can be obtained by injection molding.

The inside surface of the part is in contact with air. Cycle time and mold temperatures both affect the finish of the inside surface. Insufficient heat and cycle time leave some of the resin particles unmelted and result in a rough finish on both surfaces of the part. Excessive heat and cycle time causes discoloration of the part.

In practice, most molds are designed with little or no draft angle. They must be treated with a release agent. After each molding, the mold should be cleaned with a solvent and an abrasive.

4.8.5.1 Oven Dwell Time

The oven dwell time is the length of time that the mold containing the resin spends in the oven, known as the *oven residence cycle*. The time elapsed in the oven can be divided into two parts: *buildup time* and *fusion time*. The mold heats up and reaches the melt temperature of the resin during the buildup time. The part is formed on the wall of the mold during the fusion time.

4.8.5.1.1 Buildup Time

A number of variables influence the length of the buildup time. They are listed in Table 4.24 in descending order of significance. The most significant factor is the nature of the heat transfer medium. It has a significant effect on the efficiency of heat transfer to the plastic material, thus on the length of the molding cycle.

Air is the dominant heat transfer medium for rotomolding. It is also the simplest choice from a safety and handling standpoint. Hot liquids, such as oils, could be sprayed on the mold while it is being rotated, but hazards and operational problems have precluded their use. Liquid heat transfer medium can be used in jacketed molds, which results in improved heat transfer. The increase in the cost of fabricating jacketed molds makes it difficult to justify their

inclusion in commercial operations unless they are required. For example, parts from PA66 are rotomolded in jacketed molds to avoid oxidation of the polymer.

4.8.5.1.2 Fusion Time

Fusion time is dependent on a number of parameters that are similar to those influencing the buildup time, but not all the same variables are in the same order. They have been listed in Table 4.25 in the order of importance. The first two variables have a drastic influence on the fusion time. It is directly proportional to the wall thickness of the part, which is specified by its intended application. This means that, at a given temperature, to double the wall thickness of the part, the fusion time must also be doubled. Oven temperature has a large impact on the cycle time. Increasing

Table 4.24 Variables Influencing the Buildup Time

Variable	Importance
Heat transfer medium: convection or conduction	Most ↓ Least
Oven temperature	
Melt temperature of the resin	
Velocity of the heating medium over the mold surface	
Wall thickness of the mold	
Surface-to-volume ratio of the mold	
Heat transfer coefficient of the mold material	
Oven recovery time	

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Table 4.25 Variables Influencing the Fusion Time

Variable	Importance
Wall thickness of the part	Most ↓ Least
Oven temperature	
Velocity of the heating medium over the mold surface	
Surface-to-volume ratio of the mold	
Particle size of the resin	
Heat capacity of the unit area of the mold	
Melt temperature of the resin	
Heat of fusion of the resin	

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the mold temperature by 100 °C (180 °F) can increase the fusion rate by as much as 25%.

The fusion time is the key factor in the determination of the total dwell time in the oven. A number of measures can be taken to reduce/minimize the length of time. They include thermal stabilization of the polymer to allow higher mold temperatures, reduction of the wall thickness of the mold, and improvements in the heat transfer to the mold by design improvement such as multiple zone temperature control. Another strategy is to vary the air temperature during the cycle, which can be designed to obtain a high-quality molding. Cycle time may also be somewhat reduced.

Thermal degradation, manifested by discoloration, bubbles, or surface roughness, should be taken into account when deciding to increase the mold temperature to shorten the molding cycle. A loss in physical properties of the part accompanies these visible changes and would occur even if there is no perceptible color or appearance change.

Another consideration in raising the mold temperature is the longevity of the mold itself. It has been demonstrated [77] that operating the mold at extreme temperatures, even in the absence of thermal degradation of the plastic, detrimentally affects the mold life and maintenance costs. The balance of cycle time reduction and cost increase is unfavorable, especially for resins that require high temperatures.

One trick to lengthen the fusion time is to delay cooling after the mold has been taken out of the oven. The large thermal capacity of the mold stores a great deal of heat that will continue heating the resin for some time. The advantage of this approach is to shorten the oven cycle and increase throughput.

As the particle size of the molding powder is increased, a longer fusion time is required to obtain a surface smoothness equivalent to that of a smaller particle size powder. The likely cause of less efficient heating is the reduced contact surface area between the wall of the mold and the powder.

Melt temperature of the resin and the ratio of the mold surface to its volume are usually fixed by the part geometry and the requirements of the application. They cannot be changed during the cycle to influence the molding performance or the length of the cycle.

Air (heat transfer fluid) velocity is set at a value recommended by the oven manufacturer. This value is based on experimentation to maximize the heat transfer (flow is fairly turbulent) to the mold.

4.8.5.2 Cooling Cycle

Molds can be cooled externally by air or water and sometimes internally by pumping a cold fluid into the mold to directly cool the molded part. An effective way is to spray water on the mold to cool it down. The rate of water spray can be controlled so that it would be compatible with the use of oven inertia to complete the fusion of the resin. The cooling rate determines the extent of recrystallization of the molten polymer. Slow cooling of semicrystalline polymers increases the crystallinity of the molded part and reduces its tendency to warp. Rapid cooling (quenching) of the part increases its amorphous content, resulting in an enhancement of the impact strength and flex fatigue of the part. Table 4.26 shows the impact of the cooling rate on a number of physical and mechanical properties of a part. A drawback to quenching is the thermal shock of the mold increasing required maintenance and shortening its life.

Internal cooling with air or water is also effective but more complicated than the external method. Water requires a special system that vents out the steam produced during the cooling. Water drops can leave marks on the molten resin, called “pock marks”: they are considered quality defects. The most common technique is air cooling, in which air is forced into and out of the mold. In addition to cooling, air pressure counteracts the shrinkage effect. The part tends to separate from the mold after it shrinks. Air holds the part against the mold, which can be an advantage to heat transfer when the mold is being cooled both externally and internally. The normal

Table 4.26 Effect of Mold Cooling Rate on the Part Properties

Properties	Cooling Rate
	Fast → Slow
Crystal size	Increases
Elongation	Decreases
Tensile strength	Increases
Flexural modulus	Increases
Flexural strength	Increases
Flex fatigue life	Decreases

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range of air pressure is 10–20 kPa (1.45–2.90 psi). Care must be exercised, as internal pressurization can damage molds, which are not designed to withstand internal pressures.

4.8.5.3 Venting

A vacuum forms during the cooling cycle of the rotomolding process. Cooling of the trapped air can create a fairly high vacuum causing quality problems in the part. Distortion of the part, particularly the flat section, is the most frequently encountered problem. The second problem is at the parting line, which, if not maintained carefully, can result in small bubble formations in the part. Moisture and air are drawn into the parting line and end up forming bubbles or holes through the wall of the part.

The simplest cure for the vacuum formation is to design a vent line that connects the inside space of the cavity with the atmosphere. A simple vent line is a tube made of inert material such as polytetrafluoroethylene that is inserted in a hole in the mold. Care must be taken to place the tube sufficiently deep into the mold to prevent its obstruction by the resin. Loose fiberglass batting should be stuffed in the line to prevent outside moisture from entering the mold. The batting also prevents the powdered plastic from spilling through the vent tube. Other stuffing materials can be used as long as they are not combustible. The size and location of the vent line is also important to the prevention of moisture backflow.

4.8.5.4 Part Stripping

Parts are often removed while they are still warm. Cooling rates are uneven at different locations of the mold, leaving residual stresses in the part. There are also stresses that result from the weight of the part. These forces cause the part to distort after removal. The part is placed in a device that holds its geometry until the part has cooled and becomes stiff. The alternative approach is to increase the cooling rate and/or the length of the cooling cycle. The choice depends on the economics of the specific molding process.

Release agents are sometimes applied to the surface of the mold to facilitate demolding. These agents could have an adverse effect on the quality of the part surface [78]. Voids and bubbles are eliminated from the bulk of the polymer melt under the driving force of surface tension to minimize the available free

surface. Bubbles are more stable at the interface of the part and the mold because of a reduced surface area where the mold release agents are present. The difficulty of eliminating the bubbles could result in the survival of some of them. Consequently, these surface agents can impart poor surface formation in the part.

4.8.5.5 Rotation Rate and Ratio

The axes in rotational molding have different lengths. The speed of rotation of the mold and the ratio of the two axes are very important variables of the rotational molding process. *Rotation ratio* is the ratio of the speed of the mold around the two axes according to Eq. (4.5). Speed is a function of the flow properties of the polymer, and the ratio is related to the shape of the part. Shorter cycles and thinner part walls amplify the sensitivity of these two variables [77].

$$\text{Rotation Ratio} = R_1/R_2 - R_1, \quad (4.5)$$

where

R_1 = Rotation speed of major axis, rpm

R_2 = Rotation speed of minor axis, rpm

Rotational molding does not occur due to centrifugal forces, and, indeed, development of these forces is detrimental to the proper formation of the part. A large variation in the wall thickness is an indication of the development of centrifugal force development. The forces that develop because of high rotation speeds cause the molten resin to flow into the areas where the forces are concentrated contrary to even distribution on the wall of the cavity. Care must be exercised if high speeds are required in rotomolding. Large molds may damage the machinery at high speeds.

Melt flow and the rheological properties of the resin are the determining factors in setting the rotation speed. A high viscosity resin forms a uniform coating on the wall of the cavity at low rotation speeds. The slow rotation speed lengthens the molding cycle, thus requiring a lower temperature to avoid degrading the polymer. The longer cycle allows sufficient passes of the powder over the molten coating on the cavity surface to result in complete consumption of the polymer powder.

The rotation ratio of the two axes depends on the shape of the molding. Symmetric parts can be

Table 4.27 Typical Rotation Ratios for Various Shapes

Shapes	Rotation Ratio	Rotation Speed of Major Axis, rpm ^a
Horizontally mounted oblong articles and straight tubes	8:1	8
Cubes, balls, odd shapes, and rectangular boxes	4:1	8
Rectangular shapes with more than two or thin sides when run at a ratio 4:1	2:1	8
Flat rectangles such as gas tanks	1.3	4
		6
		9.5
Pipe angles and curved air ducts	1:4	5
Vertically mounted cylinders	1:5	4

^aSpeed around the minor axis can be calculated from Eq. (4.5) by substituting for the rotation speed and ratio.

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molded at a ratio of 4:1; examples include spheres, cubes, and regularly shaped articles. Table 4.27 shows rotation ratios for a few different shapes. Irregular objects require ratios ranging from 2:1 to 8:1. It is impractical to calculate the rotation ratio of a new part. A starting value can be estimated based on the shape of the part. The optimal ratio is then determined by trial and error and evaluation of the part made at a given value of the ratio.

4.8.6 Rotolining Process

So far, the discussion has focused on rotational molding to produce hollow parts. Rotation lining or rotolining (also rotocasting) allows the application of a seamless plastic lining to the interior surfaces of a metal part. Rotolining is ideally suited to lining the internal surfaces of complex-design parts such as pumps, valves, pipes, fittings, and vessels. Rotolining differs from rotomolding in that the metal component forms the internal cavity, and, after the completion of the process, the lining is an integrated component of it. On the other hand, the products of rotomolding are free standing or are later inserted in another structure.

Rotolining has a number of advantages over the other methods of coating and lining. It allows a much thicker lining than electrostatic- or dispersion-coating techniques. Rotolining yields a more uniform thickness coating than the spray-on method. It is automated, compared to spray and electrostatic procedures, which are both manually applied.

Rotolining is limited to the interior surfaces, while other methods, such as sheet lining, can also coat the

exterior surface of a part. In the sheet lining process, the sheet is bonded to glass cloth fabric, which is then attached to the vessel (in general, any part) wall by an adhesive. Afterwards, the seams are welded and sealed using strips of the same, or another compatible, polymer. Sheet lining is suitable for large tanks that are beyond the size limitation of rotolining. It is not easy to line complex-geometry parts, while in rotolining any geometry can be coated without difficulty. Sheet lining is also very operator sensitive and requires full access to all surfaces.

An important issue is the adhesion of the liner to the cavity wall. Shrinkage of the resin during the cooling period pulls the liner away from the wall, which is undesirable in rotolining but a positive phenomenon for rotomolding. Different strategies have been reported to obtain good adhesion. Both formulation and design approaches have been implemented to achieve this objective.

4.8.7 Melting of Polymer and Part Formation

In rotational molding, the particles of resin soften, stick to the mold surface, and then adhere to other resin particles, during which voids must be eliminated as a continuous layer of molten polymer is formed. It is widely accepted that sintering is the mechanism of void elimination as opposed to melt flow, which occurs in extrusion or injection molding. Sintering of polymer particles is defined as densification of polymer particles by coalescence. During coalescence

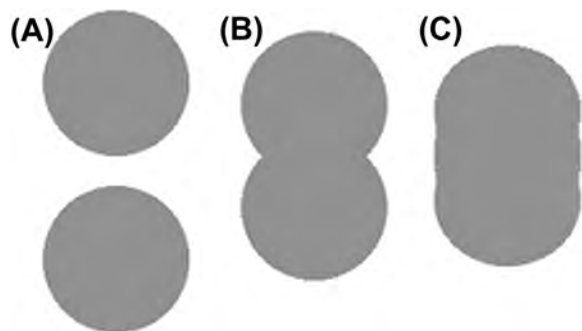


Figure 4.119 Schematic diagram of coalescence sequence of two adjacent polymer particles. (A) Two adjacent particles; (B) Particles form a neck; (C) Coalescence has been completed.

(Fig. 4.119), adjacent polymer particles combine under the driving force of surface tension. The first model for viscous sintering of two particles was developed by Frenkel [79] and improved upon by Kuczynski [80]. More recent studies have argued the inadequacy of Frenkel's and Kuczynski's models because of the exclusion of the role of melt viscosity and viscoelasticity in sintering [81]. The validity of Frenkel's model has been assessed for a number of polymers. Based on experiments with ultrahigh-molecular-weight polymers, it has been suggested that other factors, in addition to surface tension and melt viscosity, should be included [82].

Experimental studies have demonstrated that, in addition to viscous flow's [83,84,85,86] dominant role in sintering, viscoelasticity of the polymer [86,87,88] should be considered in polymer sintering and in rotational molding [89]. Bellehumeur and Vlachopoulos [90] have derived one such model where Frenkel's approach has been modified [91] to include viscoelastic effects. The proposed model predicts that the sintering rate decreases as the relaxation time of a polymer increases, and it becomes independent of relaxation time when particle size or viscosity becomes very large.

Fundamental research in rotomolding has been aimed at estimating and reducing the length of the molding cycle, optimizing the mechanical properties of the part, and assessing the moldability of different polymers. Heat transfer in rotational molding has been studied to develop models for process and part property optimization. Rao and Throne [92] were first to model the rotomolding heat transfer. A number of other researchers have attempted to improve this model. Crawford and Nugent [93] have developed

a numerical simulation of the process. Gogos et al. [94] proposed a solution for the heat transfer that used a lumped parameter for the heating cycle. This model is fairly simple, and its predictions agree with the experimental data. A commercial numerical simulation of the rotomolding heat transfer [95] is available, but it is restricted to simple geometries and does not allow the prediction of part porosity.

Heat transfer takes place through the outside surface of the mold in rotomolding during both heating and cooling cycles. Researchers have analyzed the effects of internal heating and cooling [96] to improve the heat transfer and shorten the molding cycle. The model predicted significant shortening of the cycle, which was corroborated by experimental data. Introduction of internal cooling increased the uniformity of the part structure and reduced warping.

4.8.8 Troubleshooting

Rotomolding is affected by a number of variables that are difficult to control and hard to scale when the size and design of the part change. It is important to follow a set of troubleshooting guidelines to take corrective action when the part is defective. Table 4.28 provides a list of typical problems and suggested corrective actions.

4.8.9 Conclusion

Rotational molding is a complex process and involves numerous related variables and details that must be set correctly to produce quality parts repeatedly. The details concern the design of the part, the choice of the plastic, the design and fabrication of the mold, and, finally, the actual rotational molding process. The end use requirements usually provide guidance for specifying the construction material and the design and dimensions of the part. On the other hand, any design must be practical and economical. The costs of mold construction and the operating process are strongly influenced by the design of the part. TPEs pose additional restraints on the process and part design due to their high melting temperature and viscosity.

A reader who would like to engage in rotomolding must consult other references that have addressed the subject in a thorough and in-depth manner. Complete coverage of this technology can easily occupy a separate volume that is beyond the scope of this book. This task has been most ably

Table 4.28 Rotational Molding Troubleshooting Guideline for Most Thermoplastics

Part Problem	Possible Causes
Poor part release from the mold	Insufficient draft angle.
	Roughness on the mold surface.
	Resin decomposition.
	Insufficient application of release agent.
	Undercuts are trapped.
Rough part surface	Resin degradation.
	Presence of foreign particles on the mold surface.
Warping	Vacuum developed inside the part due to poor venting.
	Part has pulled away from the mold surface because of cooling quickly.
Nonuniform wall thickness	Incorrect mold rotation because of equipment problem or wrong rotation ratio.
	Variation in the thickness of the mold wall resulting in uneven heat transfer, thus melting and fusion rate of resin.
	Variation in the heat transfer to the mold.
Poor mechanical properties	Cooling too slowly leads to excessive crystallinity.
	Resin fusion is incomplete.
	Poor filler dispersion in the polymer.
Incomplete resin sintering	Short heating cycle.
	Low mold temperature.
	Slow heat transfer due to excessive wall thickness of the mold.
Bridging of the resin in the mold	Poor resin powder flow.
	Slow rotation rate.
	Radii of the undercuts, ribs, and other recesses are too small.
	Air trapped in the recesses, consider venting in these locations.

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accomplished by a number of authors and experts. Some particularly helpful resources can be found in Refs [75], [97–100].

4.9 Foaming of Thermoplastics

4.9.1 Introduction

Polymeric foams or *cellular* or *expanded* polymers have played an important role in everyday life. Because of their special characteristics, they became attractive for many industrial and household applications.

The most important attributes of polymeric foams are light weight and good thermal insulation

property. Other advantages are relatively high strength per unit weight and lower dielectric constant when compared to solid polymers. General attributes and drawbacks of polymeric foams are in Table 4.29.

The first commercial foam was rubber sponge, a polymeric material with open cells (see below) introduced in 1910 [101], but the oldest foam is wood that is a naturally occurring foam of cellulose.

4.9.2 Background

Foam cells are bubbles that have been frozen in size and shape after solidification of molten polymer. Such a material can contain two types of cells: *closed cells* and *open cells*. In the *closed cell* foam, each cell

Table 4.29 Advantages and Disadvantages of Polymeric Foams in Comparison to Solid Polymers

Advantages	Disadvantages
Light weight	Variable density
Good thermal insulation property	Loss of certain mechanical properties
High strength per unit weight	
Ease of molding	
Impact strength	
Lower dielectric constant	

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is an independent closed entity. The cells resemble small glass bubbles that have been dispersed in the polymer. The walls of a closed cell have no holes in them. The cells will contain gas if the polymer is impermeable to the gas used for the formation of the cellular structure. The cells in the *open* cell foam are interconnected, thus unable to hold gas. Liquids and gases can move through the open cell structures, like through common sponges.

Polymeric foams are also classified according to their mechanical properties. If the walls of the cell are stiff under stress and relatively inflexible, the foam is called *rigid*. If, on the other hand, the cells collapse under stress, the foam is called *flexible*. Both open cell and closed cell structures can form rigid and flexible foams.

Densities of polymeric foams range from about 1.6 to 960 kg/m³ (0.1–60 lb/ft³). Their mechanical properties are usually proportional to their densities. Low density polymeric foams (~30 kg/m³) are used in applications such as furniture or automotive seating; high density foams are required for structural, load-bearing applications. Mechanical properties of conventional polymeric foams are lower than in solid parts due to a lower material content; however, microcellular foams with a pore or cell size 1–10 μm provide good mechanical properties in addition to weight reduction.

Polyethylene, polypropylene, and polystyrene are most common thermoplastic foams, although other base polymers, such as EVA, melt-processable fluoropolymers, and thermoplastic elastomers can be converted into cellular materials.

4.9.3 Foaming Technology

Many resins can be foamed by a variety of processes. Each method of foam manufacturing involves the following steps:

- Cell initiation
- Cell growth
- Cell stabilization

There are three general methods of producing foams from thermoplastics: mechanical, chemical, and physical.

Initiation or *nucleation* is the formation of cells in the thermoplastic, which are small discontinuities in the melt continuum. The expansion condition of the foam allows the growth of the nuclei. The governing drive force for the growth of each cell is the difference between the pressure inside and the pressure outside that cell as shown by Eq. (4.6) [102]. The surface tension of the melt (γ) and the cell radius (r) are the two factors determining the pressure difference (ΔP):

$$\Delta P = 2\gamma/r \quad (4.6)$$

The surface tension of the melt is a function of many factors including the type of the polymer, temperature, pressure, and the additives present. The pressure outside the cell is the pressure that the melt is under, and the pressure inside the cell is the pressure that is exerted by the blowing/foaming agent. A gas or a solid can be used to initiate foaming.

Cell growth is a very complex process because the properties of the melt change during the cell growth phase. Several quantitative models have been established that completely describe the cell growth [103]. The viscosity change affects the cell growth rate and polymer flow. The pressure drop in the blowing agent is inversely proportional to the radius (see Eq. (4.6)) in contrast to volume. It is important to note that the pressure is higher in small cells than in larger cells, leading to intercell gas diffusion or to breaking of the cell walls.

Thermodynamically speaking, generation and growth of cells in a polymeric melt is destabilizing. A fluid tends to minimize its free energy by reducing its surface area. The cell formation significantly increases the surface area of the polymer melt. The unstable foam at the end of growth phase requires *stabilization* to retain the cells in the foamed state.

Table 4.30 Examples of Organic Chemical Blowing Agents (CBAs)

Commercial Name	Chemical Name	Decomposition Temperature, °C (°F)	Gas Yield, ml/g
OBSH	4,4'-oxybis(benzene sulfonyl hydrazide)	157–160 (315–320)	125
ABFA	Azodicarbonamide	204–213 (400–415)	220
TSSC	p-toluenesulfonyl semicarbazide	228–236 (442–456)	140
5-phenyltetrazole	5-phenyl-1H-tetrazole	240–250 (460–480)	190
THT	Trihydrazinotriazine	250–275 (480–527)	225

These stabilization methods have traditionally been used to classify the foaming technique as either *physical* or *chemical*. Also, a limited use of *mechanical* foaming is made in the industrial practice.

4.9.3.1 Mechanical Foaming

This technique is similar to whipping cream, during which air is mixed in with the bulk of the melt. Mixing simply entrains air into the molten plastic where air becomes the foaming gas. An example of an application of this method is foaming of vinyl plastisols for producing thick vinyl flooring. Otherwise, the application of mechanical foaming for thermoplastics is limited [104].

4.9.3.2 Chemical Foaming

In this method, chemistry controls the foam formation process [105]. This may be the rate of formation of polymer, that is, the conversion of viscous fluid to a cross-linked (three-dimensional structure) or expanding a partially cross-linked polymeric melt (e.g., polyolefin foams) or expanding a thermoplastic melt with subsequent cooling. Chemistry also controls the rate of activation of the blowing agent, which is either by a drop in solubility in the monomer solution as the reaction proceeds or by thermal decomposition. Blowing agents are used to decrease the density of the polymer, typically by 40–60% with loading levels of 0.5–20.5% by weight on the amount of polymer. The characteristics of the blowing agent determine the amount of gas generated, the rate of gas generation, the foaming pressure, and the net amount of gas retained in the cells. Chemical

blowing agents can be classified as organic and inorganic, and their decomposition may be endothermic or exothermic. They often require activators, such as alcohols, glycols, antioxidants, and metal salts, which lower their decomposition temperature.

Inorganic blowing agents include sodium bicarbonate, sodium borohydrate, polycarbonic acid, and citric acid. These evolve primarily carbon dioxide upon thermal decomposition. Sodium bicarbonate is the most widely used blowing agent from this group. It decomposes over a broad range of temperatures, namely from 100 to 140 °C (212–240 °F) and yields 267 ml/g of gas. Polycarbonic acid decomposes at about 160 °C (287 °F) and yields about 100 ml/g of gas.

Organic blowing agents evolve gas over a specific narrow temperature range. They produce a gas mixture composed mainly of nitrogen. Examples of organic blowing agents are in Table 4.30.

Chemical blowing agents are available as dry powders, liquid dispersions, and pellet concentrates.

4.9.3.3 Physical Foaming

In the physical foaming technique, a blowing (foaming) agent is added to the thermoplastic and volatilizes and/or expands during the melting. This agent can be either a liquid or a gas. A *nucleating agent* may have to be used to promote the cell nucleation and/or control the cell size and the number of cells formed. The chemical structure and composition of the polymer define the conditions of the foaming process. The key variables are temperature, type of foaming agent, and the cooling rate of the expanded structure in order to stabilize it dimensionally. The nature of the foaming agent and its concentration in the polymer

Table 4.31 Examples of Physical Blowing Agents (PBAs)

Name	Chemical Formula	Boiling Point, °C	Flammable
n-Pentane	C ₅ H ₁₂	36.1	Yes
Methyl chloride	CH ₃ Cl	−24.2	Yes
CFC-11	CFCl ₃	23.8	No
CFC-12	CF ₂ Cl ₂	−29.8	No
CFC-113	CFCl ₂ CF ₂ Cl	47.6	No
CFC-114	CF ₂ ClCF ₂ Cl	3.6	No
HCFC-22	CHF ₂ Cl	−40.8	No
HCFC-142b	CF ₂ ClCH ₃	−9.2	Yes
HCFC-152a	CHF ₂ CH ₃	−24.7	Yes
HCFC-123	CHCl ₂ CF ₃	27.1	No
HCFC-123a	CHFCICF ₂ Cl	28.2	No
HFC-124	CHFCICF ₃	−12	No
HFC-134a	CH ₂ FCF ₃	−26.5	No
HFC-143a	CH ₂ FCF ₃	−46.7	Yes
Carbon dioxide	CO ₂	−78.5	No

determine the rate of gas evolution, gas pressure, gas retention in the cells, and heat absorption/release due to the degradation/activation of the blowing agent [105]. Physical blowing agents are compressed gases or volatile liquids. Compressed gases, usually nitrogen, are injected under high pressure into the polymer melt; as the pressure is relieved, the gas becomes less soluble in the polymer melt and expands to form the cells. Nitrogen is inert, nonflammable, and can be used at any processing temperature. It produces coarser foams than nitrogen produced from organic chemical blowing agents. The use of nucleating agents can be added for a finer cell structure. Other gases besides nitrogen used as physical blowing agents include hydrogen, helium, air, mixture of helium and air, and CO₂.

Liquid physical blowing agents are volatile and change from liquids to gaseous state when heated to polymer processing temperatures. Some of them are aliphatic hydrocarbons that can present a safety hazard due to their flammability. Others, short-chain chlorinated and fluorinated hydrocarbons (CFCs) have been phased out from most formulations due to their role in reduction of stratospheric ozone and replaced by hydrogen-containing CFCs (HCFCs).

Examples of physical blowing agents are in [Table 4.31](#), and the ozone depletion potential (ODP) for selected PBAs is in [Table 4.32](#).

Table 4.32 Ozone Depletion Potential^a of Selected PBAs

Blowing Agent	Boiling Point, °C	Ozone Depletion Potential
CFC-11	23.8	1.0
CFC-12	−29.8	0.9
HCFC-142b	−9.6	0.066
HCFC-22	−40.8	0.05
HFC-134a	−26.4	0
HFC-152a	−24.7	0
Carbon dioxide	−78.5	0

^aOzone depletion potential (ODP) is defined as a number that refers to the amount of ozone depletion caused by substance. It is the ratio of the impact on ozone compared to the impact of a similar mass of CFC-11.

Environmental Protection Agency (www.epa.gov).

4.9.4 Foam Manufacturing Processes

A variety of processes are used to produce foamed parts. The process used has to accommodate the three key stages of initiation, growth, and stabilization (see Section 4.9.3). These processes are classified by the manner of achieving the manner of pressure differences between the outside and inside of the foam cell. If the external pressure is lowered, the process is called *decompression* foaming. The process in which the internal cell pressure grows is called *expandable* foaming. Other methods of creating a cellular structure are sintering the resin particles in the presence of a gas or a solid (e.g., glass hollow beads) in the molten polymer. Decompression and expandable foaming can be stabilized by both chemical and physical methods.

Common melt processing methods, such as extrusion, injection molding, compression molding, blow molding [106,107,108], and rotomolding [109] are used to produce foamed articles.

Foam extrusion is a widely used process, consisting of the following steps:

1. Extrusion
2. Mixing
3. Cooling

4. Expansion
5. Aging

The process is illustrated by a block diagram (Fig. 4.120).

Commercially, these process steps can be executed on single-screw extruders having a long screw, twin-screw extruders, and on tandem-extruder lines. Such lines consist of a *primary extruder* that melts the polymer and mixes the melt with solid additives and liquid blowing agent. The second, *cooling extruder*, cools the mixture to the optimum temperature (Fig. 4.121) and can also be designed to act both as a mixer for the blowing agent and as a cooler (Fig. 4.122) [110]. A foam extrusion line is shown in Fig. 4.123.

Other foam extrusion processes include *accumulating extrusion* and *flash extrusion* and are described in Ref. [110].

4.10 Thermoforming

4.10.1 Process Basics

Thermoforming is a process for converting thermoplastics into shell forms, using sheet material as a preform. At its most basic, thermoforming is performed by clamping a heated thermoplastic sheet over a mold cavity and drawing a vacuum in the

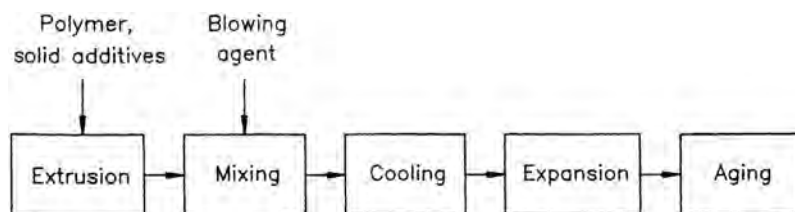


Figure 4.120 Flow diagram of foam extrusion process.
With permission

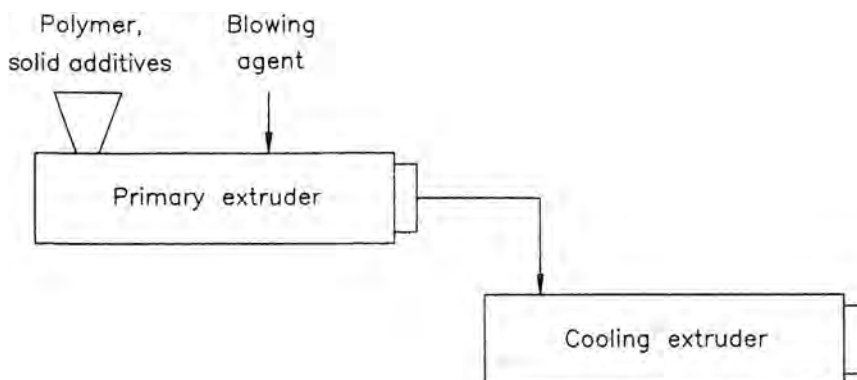


Figure 4.121 Schematic diagram of a tandem extruder for foam.
With permission

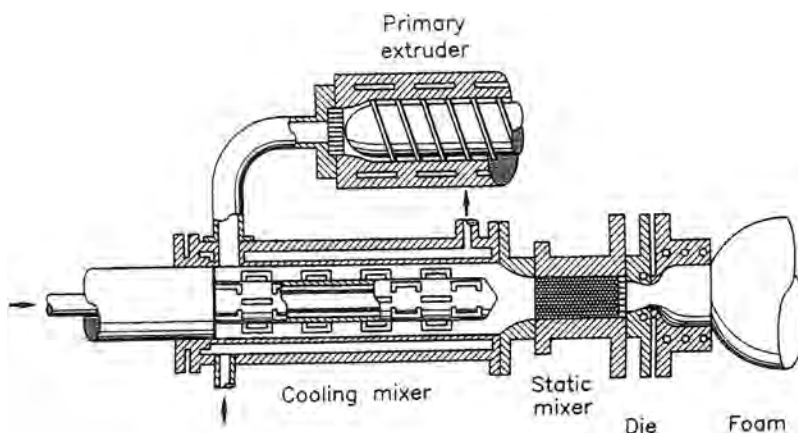


Figure 4.122 Tandem with the second extruder as mixer and cooler.

With permission



Figure 4.123 Foam extrusion line.

Courtesy: Battenfeld Gloucester Engineering Company

cavity. This causes atmospheric air pressure to press and plastically deform the sheet into the mold cavity, where it is cooled to retain the formed shape. This is known as vacuum forming, a term that is less comprehensive than thermoforming, although the two are often erroneously treated as interchangeable and synonymous. In practice, the key factors in thermoforming all have two to three optional forms (see Table 4.33). For example, the forming force can be supplied by vacuum, by positive air pressure, or by power press. These options can be assembled in many different permutations to create a very wide

variety of thermoforming processes. In this chapter, the principal processes (Table 4.34) and the main factors are discussed.

4.10.2 Process Factors

The principal factors in thermoforming are the forming force, mold type, method of prestretching the sheet, the material input form, and the process phase condition. These factors have a critical influence on the appearance, quality, and performance of the thermoformed part.

4.10.2.1 Forming Force

Thermoforming is essentially a low pressure process, in which the forming force is generated by vacuum or positive air pressure or by a combination of both. However, in a matched mold (or matched die) thermoforming, the force is supplied by a power press and may be much greater.

In *vacuum forming* (Fig. 4.124), the heated sheet forms part of the closed cell together with the mold. When the air in this cell is evacuated, the atmospheric pressure forces the sheet into contact with the mold. The force so generated clearly cannot exceed atmospheric pressure and in practice is rather less because of the difficulty of creating perfect vacuum in the mold/sheet cell. A vacuum of 85–90% of theoretical maximum is more likely, and this will generate a forming force no greater than 90 kPa (13 psi).

Pressure forming (Fig. 4.125) overcomes the force limitations of vacuum forming by applying air under pressure on the non-mold side of the sheet instead of

Table 4.33 Principal Options Available in the Thermoforming Process

Process Factor	Options
Forming force	Vacuum
	Positive air pressure
	Power press
Mold type	Female
	Male
	Matched male/female
Sheet pre-stretch	Vacuum
	Positive air pressure (billow)
	Mechanical plug
Material input	Extruder (in-line, hot forming)
	Reel (reheat, cold forming)
	Cut sheet (reheat, cold forming)
Process phase	Solid phase
	Melt phase
Heating mode	One side of sheet
	Both sides of sheet (sandwich)
Heating means	Radiation: rod, ceramic, quartz, or infrared heaters
	Convection: hot roller, contact panel, or hot oil bath

Maier C, Calafut T. *Polypropylene: the definitive user's guide and databook*. Norwich (NY): *Plastics Design Library*; 1998.

Table 4.34 Principal Thermoforming Processes

Process	Forming Force	Mold Type	Sheet Pre-stretch
Basic vacuum	Vacuum	Female	None
Basic pressure	Positive air pressure	Female	None
Drape	Vacuum	Male	None
Snap back	Vacuum	Male	Vacuum
Billow	Vacuum	Male	Positive air pressure
Plug assist	Vacuum	Female	Mechanical plug
Billow plug assist	Vacuum	Female	Positive air pressure and mechanical plug
Air slip	Vacuum	Male	Positive air pressure
Air slip plug assist	Vacuum	Male	Positive air pressure and mechanical plug
Matched mold	Power press	Matched male/female	None
Twin sheet	Positive air pressure	Matched male/female	None

Maier C, Calafut T. *Polypropylene: the definitive user's guide and databook*. Norwich (NY): *Plastics Design Library*; 1998.

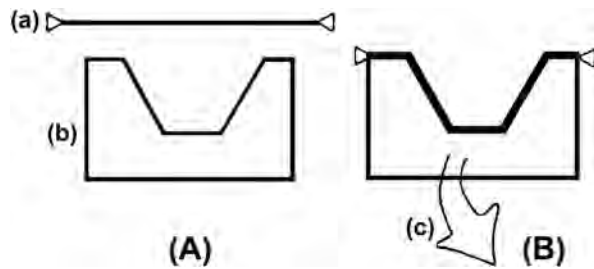


Figure 4.124 Vacuum forming. (A): Preheated sheet prior to forming. (B): Formed sheet into female mold: (a) Preheated, clamped sheet, (b) Female mold with vacuum holes, (c) Vacuum.

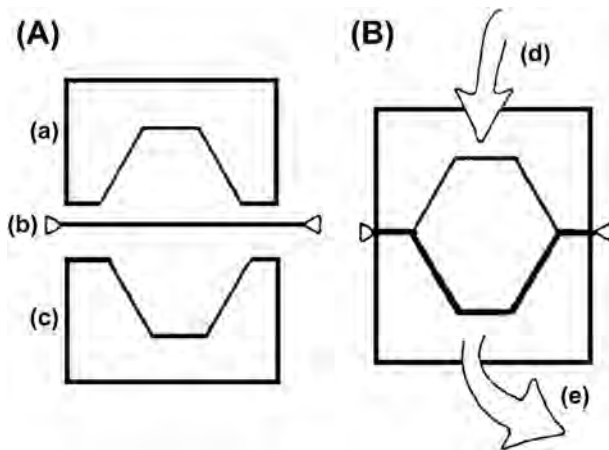


Figure 4.125 Pressure forming. (A): Preheated sheet prior to forming. (B): Formed sheet into female mold: (a) Pressure box, (b) Preheated, clamped sheet, (c) Female mold with vacuum/vent holes, (d) Applied air pressure, (e) Venting of vacuum.

vacuum on the mold side. Typical air pressures used in this method are in the range 550–710 kPa (80–100 psi), and this pressure may be sufficient for many applications.

The pressure in *matched mold (die) forming* (Fig. 4.126) is supplied by a power press, as mentioned earlier, and the force used in this method is usually in the range from 1.5 to 4 MPa (218–580 psi).

Examples of typical production thermoforming equipment are in Figs 4.127 and 4.128.

4.10.2.2 Mold Type

Thermoforming is a shell process in an open mold that defines only one surface of the product.

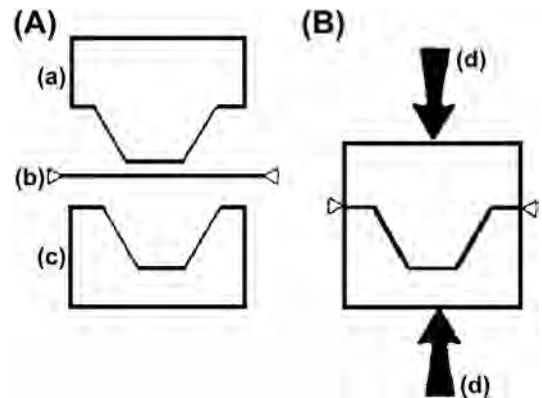


Figure 4.126 Matched mold (die) forming. (A): Preheated sheet for forming. (B): Sheet formed by simultaneous motion of two mold halves: (a) Male mold half, (b) Preheated, clamped sheet, (c) Female mold half, (d) Applied force.

Definition of the second surface is indirect and imprecise. Thermoforming molds are classified as male and female and matched.

The *female mold* consists of a recessed cavity or cavities formed in a mold block. This is the most common mold form because it is easy to clamp the heated sheet across the unobstructed mold face.

The *male mold* consists of a form or punch projecting from a mold block. The punch interferes with the plane of the sheet preform, so sheet clamping must take place outside the mold.

The third mold type used in thermoforming is the *matched mold*. This is a closed mold consisting of two halves, each defining one surface of the finished article. The matched mold is similar in concept to a compression mold, but the cavity geometries remain limited to shapes attainable by the sheet preform.

4.10.2.3 Sheet Prestretch

It is often advantageous to prestretch the heated sheet immediately prior to forming it in the mold. There are two principal reasons for that. First, particularly when simple vacuum forming is combined with solid phase forming, the available force might be insufficient to stretch and form the sheet efficiently. A second reason is that some shapes, for example, cup or box forms of relatively high aspect ratio, give rise to excessive variations in wall thickness when formed without prestretch.



Figure 4.127 Direct extrusion thermoforming line.

Courtesy: Brown Machine

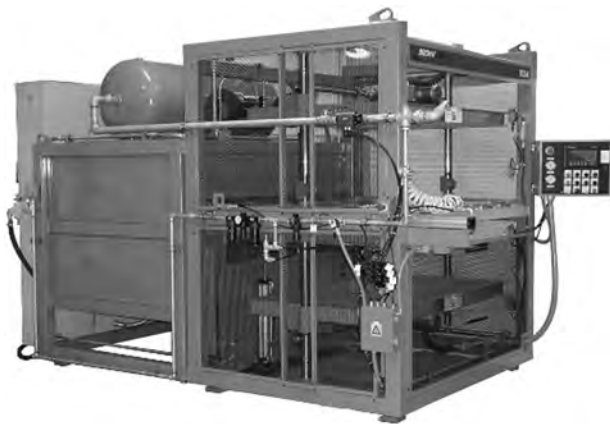


Figure 4.128 Cut sheet equipment for heavy gauge industrial products.

Courtesy: Brown Machine

Selective prestretching, necessary for more complex shapes, is achieved by means of specially shaped plugs, which are mechanically advanced into the heated sheet to produce local stretching in a way calculated to counteract the thinning tendency imposed by the mold geometry. This method is generally referred to as *plug assist*.

4.10.2.4 Material Input

The raw material for thermoforming is a thermoplastic material in sheet form. The sheet is mainly produced by extrusion and can either pass directly into the extruder to the thermoformer or can pass through an intermediate storage. After being stored,

the material must be completely reheated before forming.

4.10.2.5 Process Phase

If a semicrystalline material is thermoformed, it can be processed either below or above its crystalline melting point. When forming is done below the crystalline melting point, it is known as *solid phase forming*; *melt phase forming* is done at temperatures above the crystalline melting point.

The two techniques result in products with rather different characteristics (see [Table 4.35](#)). Melt phase

Table 4.35 Comparison of Product Characteristics between Solid Phase and Melt Phase Forming

Property	Solid Phase Forming	Melt Phase Forming
Wall thickness distribution		More even
Residual stress		Lower
Optical properties	Clearer	
Mechanical properties	Stronger	
Heat resistance		Greater

Maier C, Calafut T. Polypropylene: the definitive user's guide and databook. Norwich (NY): Plastics Design Library; 1998.

forming requires less force and so generates lower residual stress in the finished part. Another advantage of this technique is that the part has a reduced tendency to distort or to revert to the original sheet form. Modern solid phase thermoforming can produce high quality products, particularly when carried out with multilayer coextruded film and sheet [111].

4.10.2.6 Heating

The heating process is of critical importance in thermoforming, both economically and technically. Heating accounts for some 80% of the total energy demand for thermoforming. Heating of the sheet can be performed by radiation, convection, or conduction. When radiation or conduction is used, there is the option to apply heat to either one or both surfaces. In the case of convection, both sides of the sheet will be heated. Given the difficulty of heating the sheet core uniformly, it is preferable to heat both surfaces of the sheet. The upper limit of sheet thickness for effective single-sided heating is about 1 mm (0.040 in) [112].

Infrared radiant heating is now the most widely used means of sheet heating for *reel-fed* or *in-line* thermoforming machines. The heaters are normally arranged in a heating tunnel in a series of independently controlled zones that gradually increase the sheet temperature first to stress relaxation temperature (typically about 120 °C or 248 °F) and then to the forming temperature.

The arrangement for *cut-sheet* machines is different. It is usual to preheat the sheets by convection in static ovens, followed by final heating of both surfaces in a radiant sandwich heater operating near the mold. Other methods, used less frequently, are heated rolls or heated flat contact plates or immersion baths filled with heat transfer liquid.

4.11 Calendering

Calendering is a process originally developed for shaping rubber compounds into sheets and films and for applying rubber compounds onto different types of fabric. The equipment, called *calender*, is a heavy duty machine equipped with three or more chrome-plated steel rolls, which revolve in opposite directions. The rolls for conventional rubber processing are heated by steam or circulated water, and have gears

that allow them to operate at variable speeds. Over the years, calenders have developed into a useful machinery for some thermoplastic materials, most notably PVC to produce films and sheets. Calenders for thermoplastics have typically four rolls that are heated with circulating oil or other heating liquids or electrically, since higher processing temperatures are required than for conventional rubber compounds. During operation, the melt is mostly fed between the rolls by means of an extruder or directly from a continuous mixer. Several TPEs, namely TPV [113], MPR [114], TPU [115], and TPO [116,117], are reported as being processed by calendering.

The advantages of a calender over an extruder are:

- Higher output than extruder
- Easier access and possibility for rapid material changes
- Possibility to produce embossed films and sheets
- Possibility to produce laminates

Drawbacks are the high initial cost, the large size of the calender, additional equipment, and high operating cost (mainly energy consumption).

Different roll arrangements of four-roll calenders are in Fig. 4.129.

4.12 Secondary Manufacturing Processes

4.12.1 Film and Sheet Orientation

Polymer sheets and films made by the usual techniques, such as extrusion, casting, and calendering, can be oriented by drawing. Certain amount of orientation occurs already during the processing; particularly in extrusion and calendering since the processed melt is stretched in the direction of flow and in blown film process, the stretching is along the circumference of the bubble. In these cases, the amount of orientation is relatively small because of competing molecular processes. While melt drawing tends to straighten out the polymer molecules and align them in the direction of the force applied, there is always a countering force within the molecule to return it to its natural coiled state. How fast this relaxation occurs depends on the viscosity of the melt, but it is generally fast enough so that very little permanent molecular alignment can be achieved by drawing a polymer melt.

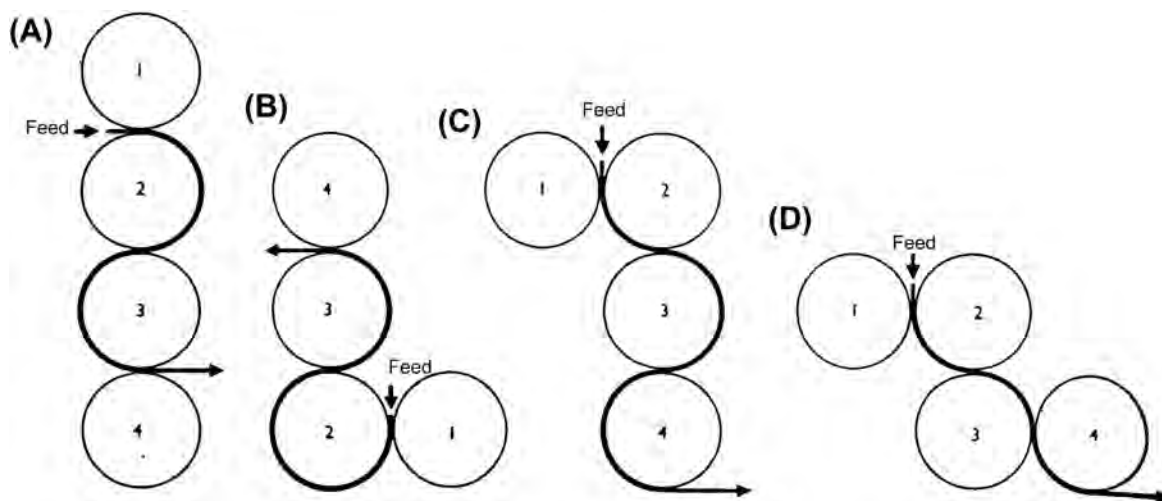


Figure 4.129 Different roll arrangement in four-roll calendars. (A) I (Four in line); (B) L; (C) Inverted L; (D) Z.

Orientation of amorphous polymers or polymers with low degree of crystallinity is a relatively simple process. Such material is heated up above its glass transition temperature to bring it into the viscoelastic region. Then it is cooled to the proper temperature and stretched at the appropriate rate. If desired, it is then annealed at carefully controlled conditions to reduce thermal shrinkage. The annealing process is omitted if thermal shrinkage is desired (see below).

A crystalline polymer has to be first heated up above its crystalline melting temperature (T_m) to destroy crystallinity and then quenched rapidly to a temperature below its crystalline melting temperature to minimize crystallinity and preserve the amorphous condition. In the next step, it is reheated and oriented by stretching at a temperature somewhat above T_g but below T_m . Then it is annealed (if desired) or quenched rapidly to freeze in the shrink energy. For this step, it is constrained from shrinkage during the heating [118].

When a film is drawn in only one direction, the molecular chains and/or crystallites align themselves in that direction. The film then exhibits great strength and stiffness in that direction, but the strength in the other direction is low. Although there are some applications where orientation in one direction is sufficient, in most cases orientation in two perpendicular directions, *biaxial orientation*, is required.

4.12.1.1 Machine Direction Orientation

Machine direction orientation (MDO) is accomplished by drawing the film or sheet between rolls

rotating at different speeds, with the second set of rolls running faster than the first set (see Fig. 4.130). The first set of rolls stabilizes the sheet surface temperature and allows time for inner sheet temperature balance. The nip controls simultaneous rolling and stretching at optimum orientation temperature. The final two rolls are used for heat setting and/or cooling the uniaxially stretched polymeric sheet. The stretching of the web is typically 3 to 16 times that of the original length. Very often machine direction orientation is the first step in biaxial orientation and is followed by *transverse direction orientation*.

4.12.1.2 Transverse Direction Orientation

Transverse direction orientation (TDO) is stretched on a *tenter frame*—a machine consisting of two continuous chains like two racetracks mounted side by side [119]. Clamps (see Fig. 4.131) are mounted on top of each link, and these grip each edge of the film. Then the film is carried along as the chain is driven forward. The two chains move gradually apart, and as they do, they draw the film in the transverse direction between them. The chain rides on well-lubricated sliding surfaces or ball bearings at speeds up to 1000 feet per minute [119]. At the end of the stretching section, the clamps release the film, and the chain turns around a wheel and is returned to the beginning of the stretching section where it reverses direction again. The clamps that ride on the chain must be able to grip the film securely as the film enters the stretching section, hold it against the

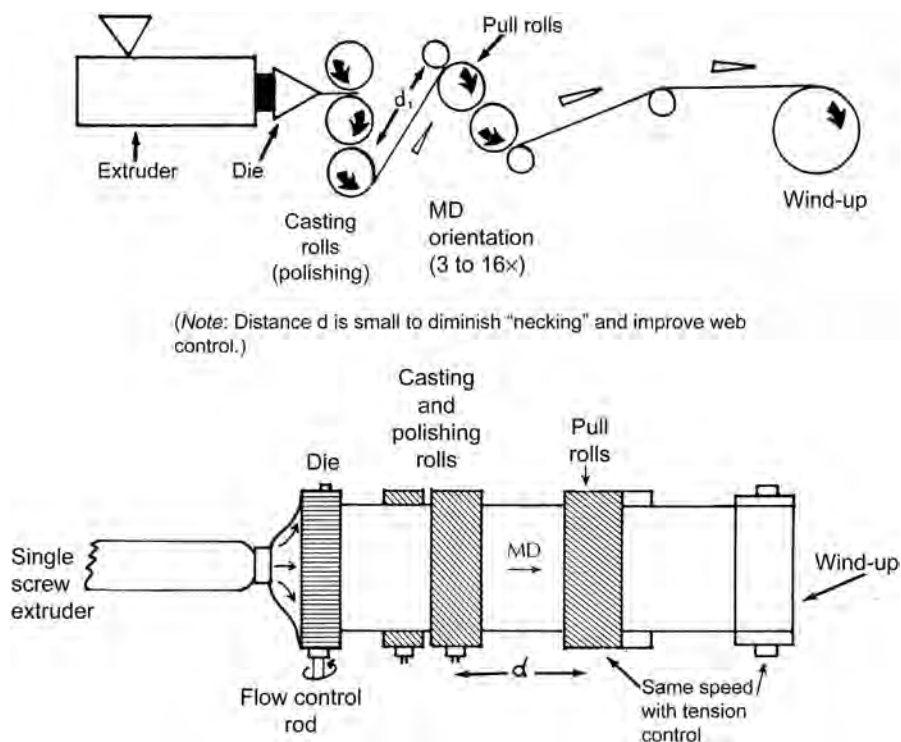


Figure 4.130 Schematic diagram of machine direction orientation.
With permission

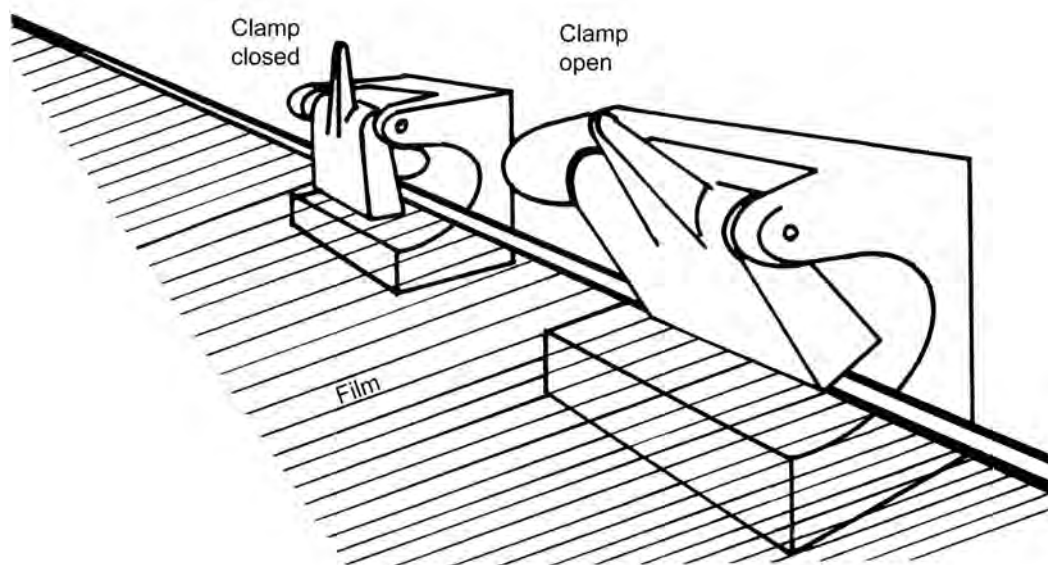


Figure 4.131 Tenter clips (schematic diagram).

stretching force applied to the film, and then release the film as it leaves the stretching section.

The tenter frame is enclosed in an oven that is usually heated with hot air. The temperature for TDO

is generally higher than that for MDO, since during the MDO some crystallization has been induced that increases the resistance to stretching. Typically, the oven is often separated into two zones, each of them

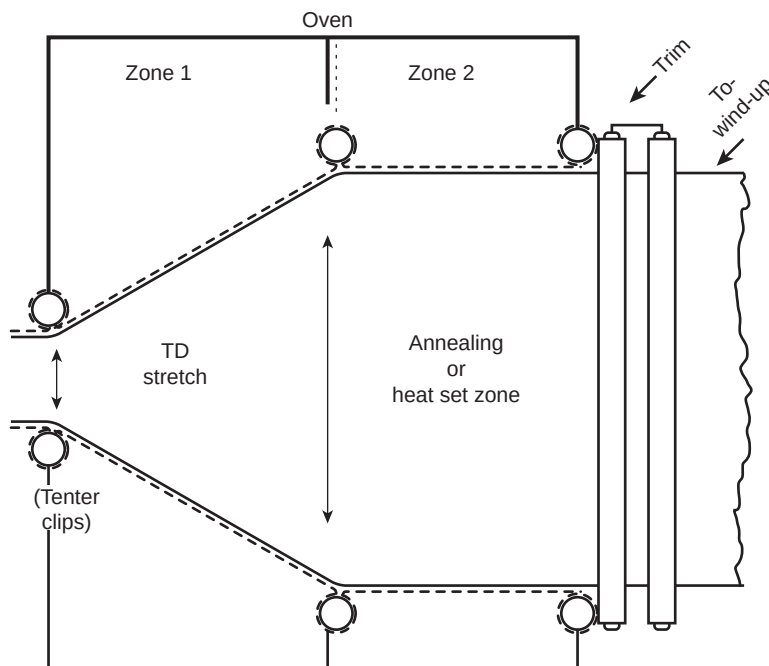


Figure 4.132 Schematic diagram of a tenter frame.
With permission

being heated to a different temperature (Fig. 4.132). The usual stretch ratio in a tenter frame is 3:1 to 8:1.

4.12.1.3 Biaxial Orientation

Biaxial orientation is a process whereby a plastic film or sheet is stretched in such a way that the polymeric chains are oriented parallel to the plane of the film. Biaxially oriented films exhibit exceptional clarity, very high tensile properties, improved flexibility and toughness, improved barrier properties, and can be relatively easily made shrinkable.

The widely used *two-step biaxial orientation* process is the combination of the MDO and TDO as mentioned in Section 4.12.1.1. The system consists of an extruder, MDO equipment (two or more sets of rolls running at different speeds), and a tenter frame for the MDO. An example (biaxial orientation of polystyrene) is shown in Fig. 4.133. *One-step biaxial orientation* eliminates the MDO stretching part and uses a tenter frame with accelerating clips. The process is mechanically rather complicated, and it is difficult to adjust the balance between the two stretch directions, so it is used less frequently [120].

Bubble process, also called *blown process* or *tubular process*, uses a tubular die to extrude a relatively thick-walled tube in a vertical direction, either

upwards or downwards. Downwards extrusion (Fig. 4.134) allows the tube to be quenched rapidly in a water bath, after which it is collapsed as a layflat for passage over nip and idler rollers. The film passes through a reheating tunnel where it is raised to a temperature above the softening point but below the melting point. The heated tube is then inflated by internal air pressure that forms a bubble in which the film is stretched in all directions. Some machine-direction stretch may take place in the ovens upstream of the bubble; the haul-off rate can be adjusted if necessary to secure an orientation balance. An air ring similar to that used in other blown film processes provides bubble cooling. Subsequent calibration and bubble collapsing operations are also similar. The stretch ratio in the bubble process can vary from 3:1 up to 12:1 [121].

At this point, the film retains shape memory. If it is reheated, it will shrink and revert to dimensions approaching its prestretch shape. If a shrink film is required, the layflat is edge-trimmed, separated, and reeled as two webs at this stage. Nonshrink film is produced by subjecting the layflat to a further heat treatment in which it is annealed or heat set under tension in an oven. The annealing temperature is set slightly higher than the stretching temperature.

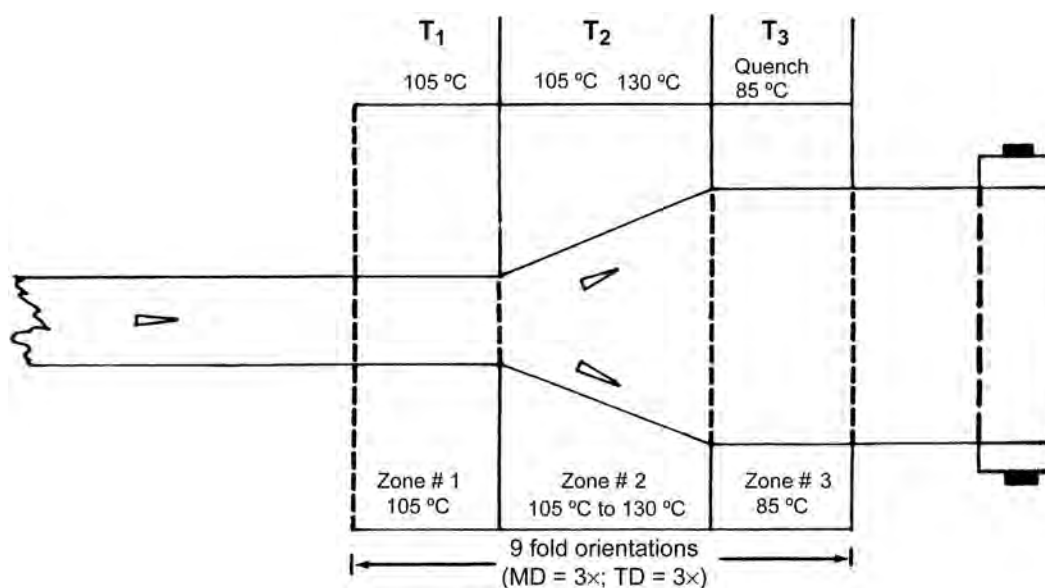


Figure 4.133 Schematic diagram of two-step biaxial orientation of polystyrene.

With permission

In general, films oriented by the bubble process have more balanced properties in the machine and transverse directions than tenterd films, as shown on the example of oriented polypropylene films (Table 4.36).

4.12.1.4 Heat Shrinkable Films and Tubing

This class of oriented films exhibits high shrinkage (25% or more) at relatively low temperatures (less than 100 °C, or 212 °F, in most cases). Generally, polymeric systems with reduced crystallinity are employed. Since it is rather difficult to produce a film with balanced shrinking properties by the two-step flat orientation (MDO plus TDO), the tubular process is the one most often used in shrinkable films and tubing [122].

For good shrinking properties, some polymer systems must be modified either by copolymerization or cross-linking (frequently by electron beam irradiation). The properties of shrinkable films depend largely on the polymer system used. Tensile strength, for example, ranges from 9500 psi (62 MPa) for LDPE to 26,000 psi (179 MPa) for polypropylene. Also, the temperature range over which significant shrinkage occurs varies from 65 °C to 120 °C (150–248 °F) for polyethylene to 120–165 °C (248–329 °F) for polypropylene [123,124].

4.12.2 Welding

Welding is a method of joining parts without sacrificing the load-bearing capacity of the part. There is a variety of welding techniques for thermoplastic polymers that allow formation of strong joints, even approaching the strength of the parent material itself. All welding methods are not applicable to all thermoplastics, including TPEs. In general, applicability of a specific welding method is related to the rheology of the polymer. High melt viscosity makes welding difficult and reduces the number of applicable methods. Some of the most common methods include heated tool (hot plate), hot gas, ultrasonic, vibration, spin, and infrared welding techniques.

4.12.2.1 Heated Tool Welding

In heated tool (hot plate) welding, a heated platen is used to melt the joining surfaces of two thermoplastic surfaces. After the interfaces of the plastic parts have melted, the heated platen is removed, and the plastic parts are held together under low pressure to form a permanent and hermetic seal (see Fig. 4.135). A hot plate is used for flat joining surfaces; for curved or irregular joining surfaces, complex tools that allow the hot surfaces to match the contours of the joint interface are required. The platens can be coated by a polytetrafluoroethylene

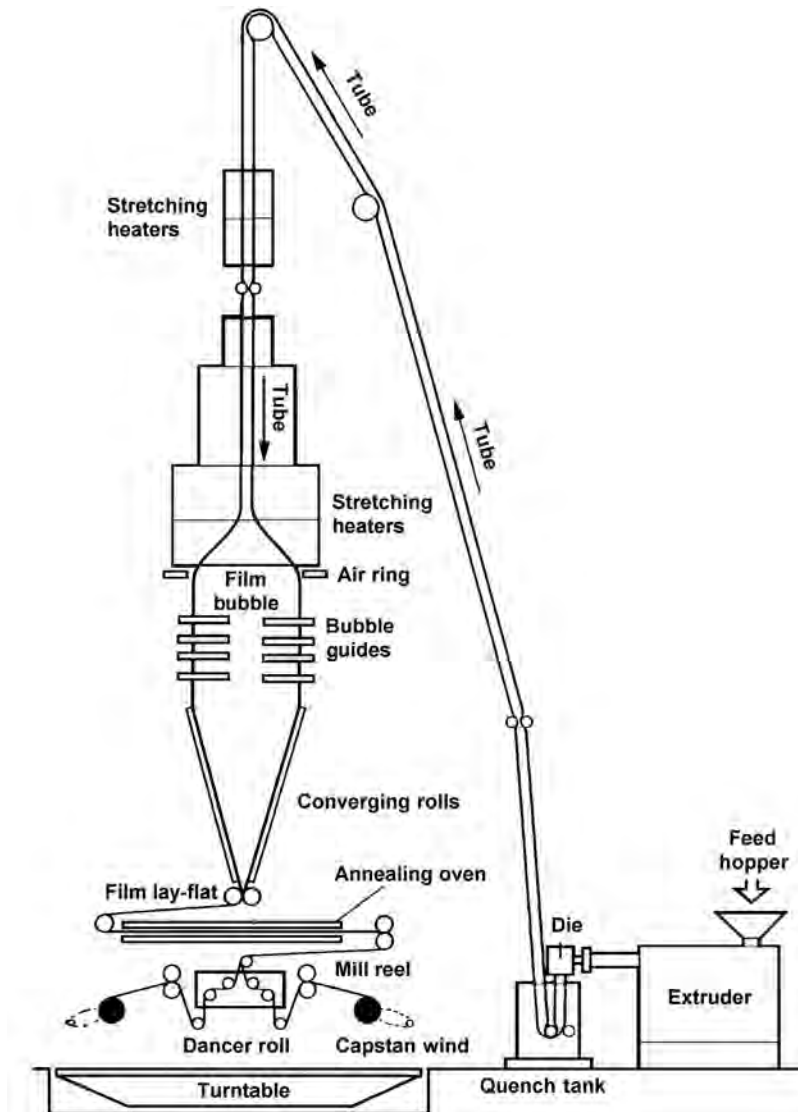


Figure 4.134 Bubble process for biaxially oriented film.

(PTFE) coating, tape, or film to inhibit melt sticking [125,126,127].

4.12.2.2 Hot Gas Welding

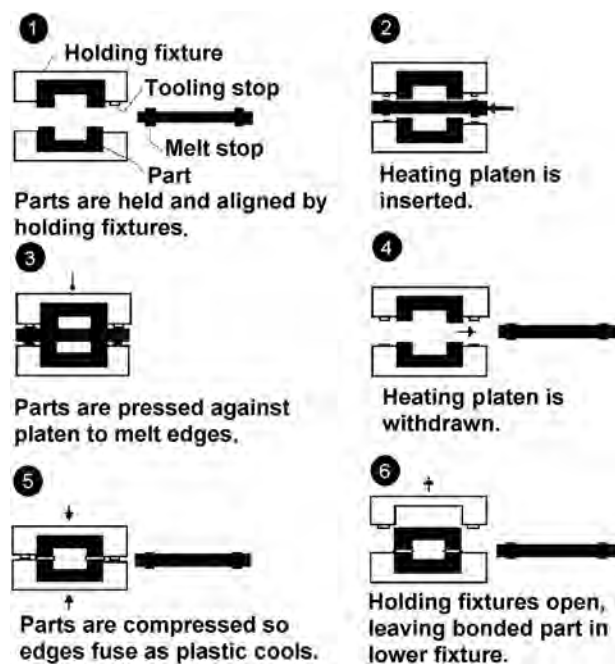
In *hot gas (hot air) welding* [126,127,128,129,130] a heated gas is used to heat thermoplastic parts and a filler rod. The rod and the parts then soften and fuse, forming a high-strength bond upon cooling. Hot gas welding is commonly used for fabrication and repair of thermoplastic components and for lap welding of thin sheets or membranes. The bond strengths achieved by this method can be as high as 90% of the bulk material. Gases that can be used are air,

nitrogen, carbon dioxide, and oxygen, with air being the most common. The gas is heated to the melting temperature of the thermoplastic and is applied to the part and the thermoplastic rod through a nozzle or a tip (see Fig. 4.136). The filler rod is almost always composed of the same material as the part and is positioned at the joint. Hot gas welding methods may be manual or automatic, the manual method being used mostly for short seams. Gas temperatures usually range from 200 °C to 600 °C (390–1110 °F) depending on the melting temperature of the plastic material. Joint surfaces must be cleaned to assure a good bond. The cleaning can be done by mild soap, detergent, or a solvent (e.g., methyl ethyl ketone).

Table 4.36 Properties of Oriented Polypropylene

Property	Bubble Process	Tenter Process
Thickness, mil	0.60	0.75
Tensile strength, psi		
MD	26,000	17,000
TD	26,000	42,000
Elongation, %		
MD	40–50	120
TD	40–55	20
Shrinkage, %, 1 h at 124 °C		
MD	8	3.5
TD	15	3.5

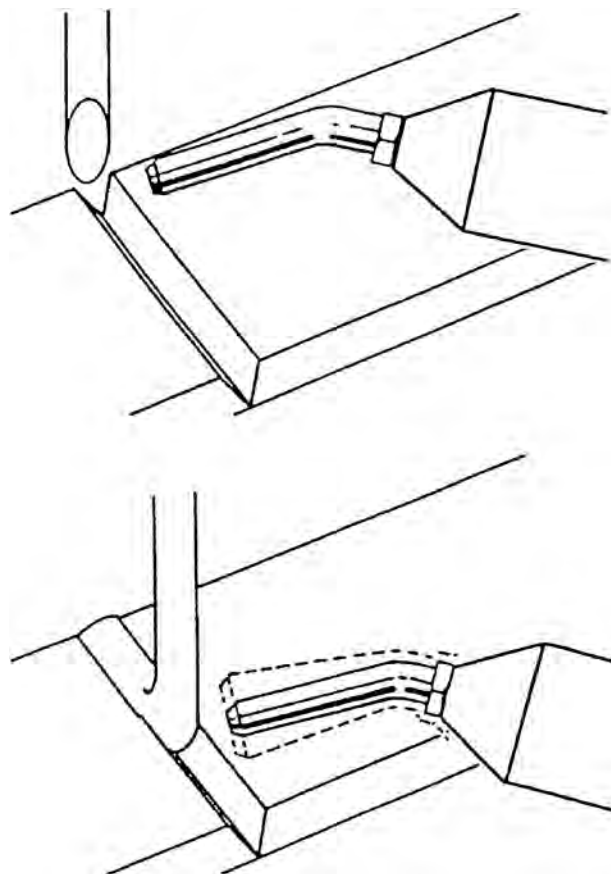
Benning C.J. *Plastics films for packaging*. Lancaster (PA): Technomic Publishing Co., Inc.; 1983.

**Figure 4.135** The hot tool welding process.

A good bond has a fine bead on both sides (see Fig. 4.137).

4.12.2.3 Ultrasonic Welding

Ultrasonic welding [131,132,133], the most widely used welding method for thermoplastics, uses ultrasonic energy at high frequencies (20–40 kHz) to produce low amplitude (1–25 μm) mechanical

**Figure 4.136** Manual hot gas welding.

vibrations. The vibrations generate heat at the joint interface of the parts being welded, resulting in melting the thermoplastic materials and weld formation after cooling. Ultrasonic welding is the fastest known welding technique, with weld times of less than 1 s. Ultrasonic welding is used for both soft and rigid thermoplastics and for thermoplastic composites.

Components necessary for ultrasonic welding are a generator or power supply, a converter or transducer, booster, and a horn or sonotrode (see Fig. 4.138). The generator converts low voltage electricity at 50–60 Hz and 120–240 V to high frequency (20–40 kHz) and high voltage (13 kV) electrical energy. The electric current enters the converter, which contains piezoelectric ceramic crystals that expand and contract when excited by electrical energy. The electrical energy is converted into mechanical energy, and the converter expands and contracts at the frequency of the crystals [131,132,133]. The booster increases or decreases the amplitude of the mechanical vibrations of the

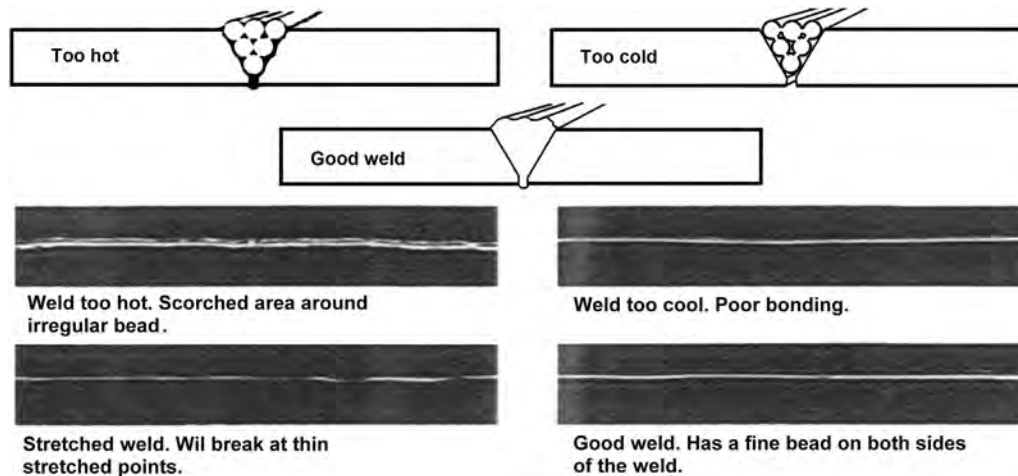


Figure 4.137 Weld quality analysis by its appearance.

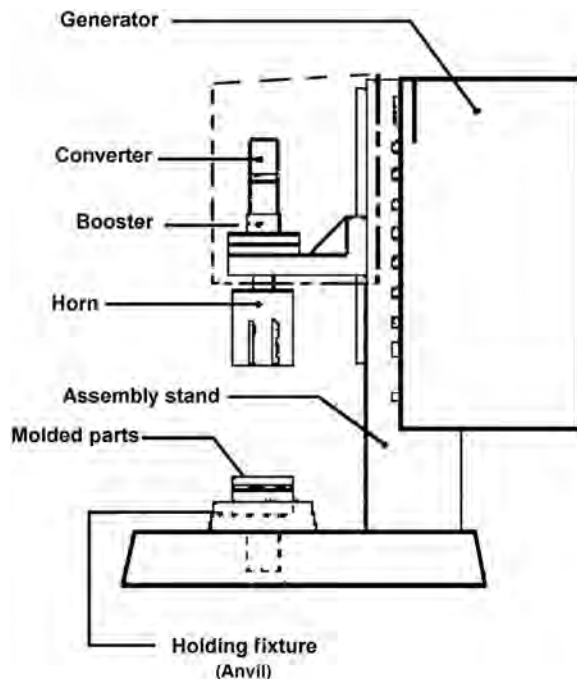


Figure 4.138 Components of an ultrasonic welder.

converter, depending on the amplitude desired for welding, and conveys the vibratory energy to the horn or sonotrode. The horn, made of titanium, steel, or aluminum, can further increase the amplitude of the mechanical vibrations. It contacts one of the parts during welding and transmits vibratory energy to the part. For optimal energy transmission, the end of the horn that contacts the part is designed to mate with the part of the geometry. Fixtures hold the parts in place and apply

pressure during welding. Ultrasonic welding begins after parts have been loaded and a particular force (trigger force) or distance has been reached by the horn [131,132,133].

Ultrasonic vibrations, applied to the part under pressure, generate sinusoidal standing waves throughout the parts being welded at frequencies usually 20–40 kHz (see above). In a viscoelastic material, such as a thermoplastic, this energy produced under sinusoidal strain is dissipated through intermolecular friction, resulting in heat buildup.

Semicrystalline polymers are characterized by regions of ordered molecular structure. A high amount of heat is required to disrupt this ordered arrangement. The melting point is sharp, and resolidification occurs rapidly as soon as the temperature drops slightly. The melt that flows out of the heated region solidifies rapidly. When in the solid state, semicrystalline molecules are spring-like and absorb a large part of the ultrasonic vibrations instead of transmitting them to joint interface, so larger amplitude is necessary to generate sufficient heat for welding [133,134].

4.12.2.4 Spin Welding

Spin welding [135,136,137] is a frictional process in which thermoplastic parts with rotationally symmetrical joining surfaces are rubbed together under pressure using unidirectional circular motion. The heat generated thereby melts the thermoplastic in the joining zone, forming a weld upon cooling.

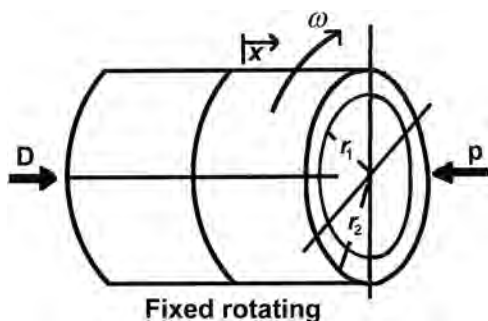


Figure 4.139 Spin welding. One part is fixed, while the other is rotated using rotational motion ω . Pressure is applied axially, along the x -direction. The tubes joined here have inside radius r_1 and outside radius r_2 .

It is a fast, reliable process that requires only minimal, basic equipment but that can be completely automated. After the rotational speed stabilizes, pressure is applied axially, perpendicular to the joining surfaces (see Fig. 4.139). When melting begins, heat is generated through internal friction within the molten material. As the melt thickness increases under pressure, part of the molten material is squeezed out of the bond area into a flash bead around the interface.

The main process parameters for spin welding are the speed of rotation, weld or axial pressure, and weld time. Parameters used depend on the material and the diameter of the joint. In commercial machines, rotational speeds can range from 200 to 14,000 rpm. Weld times may range from a tenth of a second to 20 s; typical values are about 2.0 s, with an actual spin time of 0.5 s, and a cooling time, when pressure is applied but spinning is stopped, of 0.2–0.5 s. Axial pressures range from about 1.0 to 7.0 MPa. The pressure must be high enough to force any contaminants or bubbles out of the joint, and the combination of speed and pressure must be controlled but high enough to cause melting at the interface as opposed to grinding.

4.12.2.5 Infrared Welding

In infrared welding, the joint surfaces of thermoplastic parts are heated to the melting temperature using infrared radiation, at wavelengths 1–15 μm . When melting begins, the parts are brought together

under pressure, forming a weld upon cooling. Infrared welding is a noncontact welding method; the part surfaces are not in direct contact with the heat source but are at distances of up to about 20 mm (0.8 in). Practically all known thermoplastics can be infrared welded, and the high temperatures that can be obtained at short heating times make this method especially suitable for temperature-resistant materials. Infrared welding is similar to hot tool welding.

Rigid clamping devices hold parts and heaters in place, preventing distortion and misalignment during the welding process, and pneumatic actuators can be used to move heaters and parts as necessary during the welding. Hot tool welding equipment is commonly adapted for the use of infrared welding.

4.12.2.6 High Frequency (RF) Welding

High frequency welding or radio-frequency (RF) welding or dielectric welding uses high frequency (13–100 MHz) electromagnetic energy to generate heat in *polar* materials, resulting in melting and weld formation after cooling. A high intensity radio signal is used to impart increased molecular motion in two similar or dissimilar polymers. This causes the materials to rise in temperature, increased polymer chain mobility, and melting. Ultimately, the polymer chains of the two materials penetrate their interface and become entangled, forming a weld. RF welding is frequently used in packaging and sealing applications and is particularly suitable for the medical device industry because it uses no solvents or adhesives, which are possible sources of contamination [138].

The RF welding press has two platens—a movable one, and a fixed one, also called a *bed*. During the process, the press lowers the movable platen and closes the electric circuit. The parts to be welded are placed in a set of metal dies or electrodes, which are usually activated by a compressed air cylinder to apply a preset amount of pressure at the joint area. RF energy flows and the materials melt. The joint cools under pressure, and after an appropriate time the press opens and releases the welded assembly.

Energy used in the RF welding process, typically 27 MHz, is applied to the electrodes, and the resulting alternating current induces a rapidly

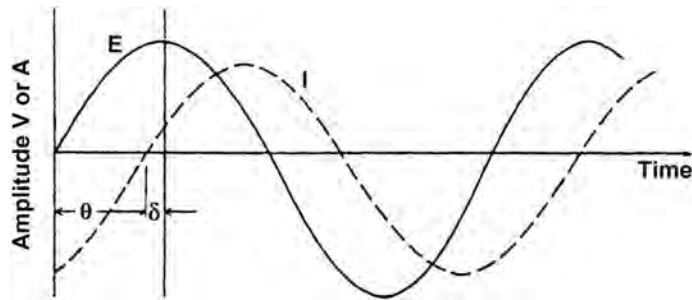


Figure 4.140 Electrical representation of dipole polarization resulting in heat generation due to imperfect alignment.

reversing (several million times per second) electric field around the parts. Polar molecules tend to orient in the field direction, so that the positive (or negative) end of the dipole aligns to the negative (or positive) charges in the electric field, a process called *dipole polarization*. As the dipoles try to align with the rapidly reversing, high frequency electric field, their orientation becomes out of phase. The imperfect alignment causes internal molecular friction and results in the generation of heat. The electrical delay between changes in electric field direction and changes in dipole polarization are represented in Fig. 4.140. An oscillating electric field, E , generates an oscillating current, I , within the dielectric material. At high frequencies, the two curves are out of phase by the phase angle θ , and the loss angle is defined as $90^\circ - \theta$, or δ . The amount of energy absorbed per cycle from the electric field is represented by the power factor and the dissipation factor; the power factor is defined as $\cos \theta$, and the dissipation factor or loss tangent is $\tan \delta$, a ratio of the current dissipated into heat to the current transmitted.

Radio frequency equipment consists of three major components: a radio frequency generator, a press, and a die or electrode. Generators commonly provide power ranging from 1 to 25 kW. Power requirements are determined by the welding area of the electrode and the thickness of the materials to be welded.

4.12.2.7 Vibration Welding

Vibration welding uses heat generated by friction at the interface of materials to produce melting in the interfacial area. The molten materials flow together under pressure and bond, forming a weld upon

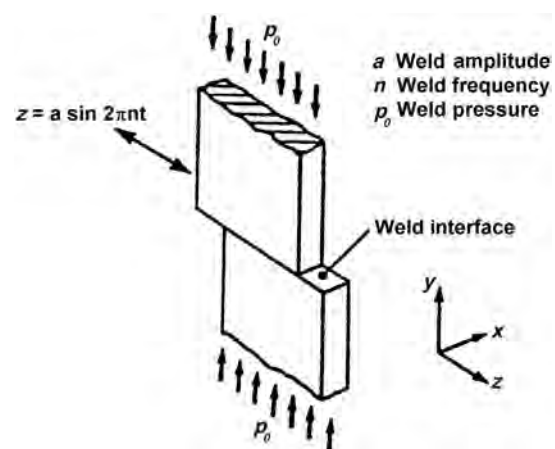


Figure 4.141 Linear vibration welding.

cooling. Vibration welding can be accomplished in a short time (8–10 s cycle time) and is applicable to a variety of thermoplastic parts with planar or slightly curved surfaces. There are two types of vibration welding: *linear*, in which friction is generated by a linear back-and-forth motion; and *orbital*, in which the upper part to be joined is vibrated using circular motion in all directions. Linear welding is most commonly used, but orbital vibration welding makes the welding of irregularly shaped plastic parts possible.

In linear vibration welding, the surfaces to be joined are rubbed together in an oscillating, linear motion under pressure applied at a 90° angle to the vibration. Process parameters are the amplitude and frequency of this motion (weld amplitude and weld frequency), weld pressure, and weld time, all of which affect the strength of the resulting weld (Fig. 4.141).

Most industrial welding machines operate at weld frequencies of 120–240 Hz, although machines

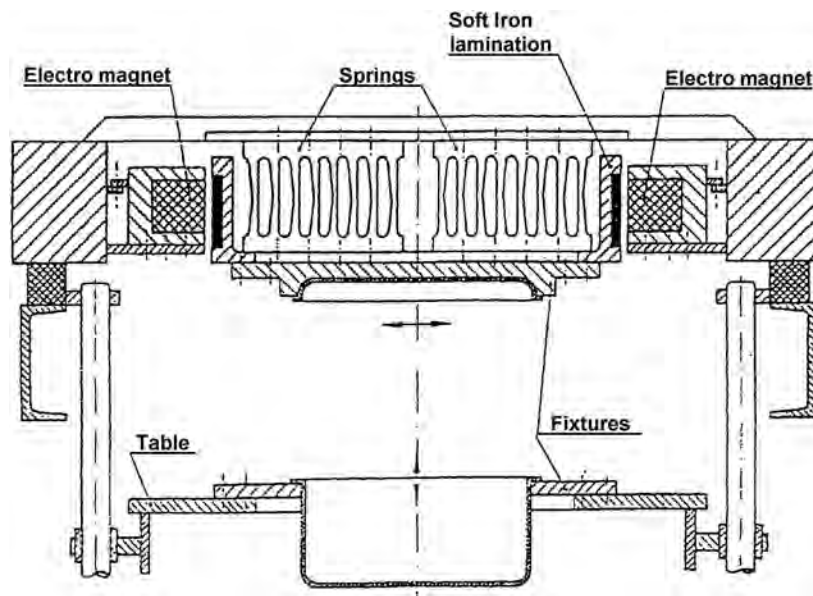


Figure 4.142 Schematic diagram of a vibration welding machine.

with higher frequencies are also available. The amplitude of the vibration produced by exciting a tuned spring-mass system is usually less than 3 mm. Weld times range from 1 to 10 s (typically 1–3 s), with solidification times, after vibratory motion has ceased, usually of 0.5–1.0 s. Typical cycle times range from 6 to 15 s, resulting in 4–10 cycles per minute [139,140].

Weld pressure varies widely (0.5–20 MPa), although usually pressures at the lower end of this range are used. Welding time and pressure depend on the material being welded. Higher pressures decrease the welding time; however, higher strength of the welded parts is usually achieved at lower pressures due to greater melt layer thickness.

Most equipment used in vibration welding produces linear vibratory motion. Equipment is classified as low frequency (120–135 Hz) or high frequency (180–260 Hz) and can be variable frequency or fixed frequency. Most vibration welding systems are electrically driven and consist of three major components: a vibrator assembly suspended on springs, a power supply, and a hydraulic lifting table. A schematic of a vibration welding machine is in Fig. 4.142 [140]. Tooling used in vibration welding equipment is simple, consisting of aluminum plates machined to the contour of the parts at the joint. For complex part geometries,

slides and actuators can be incorporated using polyurethane-poured nests.

4.12.2.8 Induction Welding

Induction welding uses induction heating from high radio-frequency alternating current to magnetically excite ferromagnetic particles embedded in a bonding agent (with a thermoplastic or adhesive matrix) placed at the joint interface of the two parts being welded. The heat released is used to melt and fuse thermoplastics, to heat hot-melt adhesives, or to provide rapid adhesive cures for thermosets. It is a reliable and rapid technique, ranging from fractions of a second for small parts to 30–60 s for parts with long (400 cm, or 160 in) bond lines, and results in structural, hermetic, or high pressure welds [141,142,143].

Induction welding is a type of electromagnetic (EMA) welding, along with radio-frequency welding and microwave welding, that uses electromagnetic energy to heat materials. The three methods differ in the frequencies used for heating: 0.1 kHz to 10 MHz for induction welding, 13–100 MHz for radio-frequency welding, and 2–10 GHz for microwave welding. Induction welding is frequently referred to as electromagnetic welding [138].

Heat in induction welding is generated from interaction of the magnetic field with the

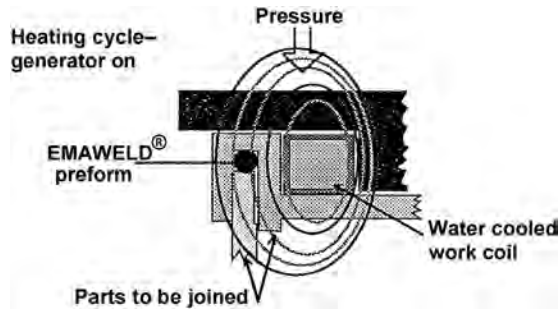


Figure 4.143 The induction welding process.

ferromagnetic material (stainless steel, iron) and from current induced in the metal. The high frequency alternating current moves through a copper coil, generating a rapidly reversing magnetic field. Ferromagnetic materials align with the magnetic field; alignment changes as magnetic field direction changes. Atoms do not return to the initial alignment existing before the magnetic field changed direction but to slightly different alignment; some of the previous alignment is retained. This phenomenon, referred to as *hysteresis*, results in heat losses within the metal, which are transferred to the plastic matrix through conduction. Alternating current also induces voltage within metallic ferromagnetic materials, resulting in internal currents, called *eddy currents*. Eddy currents dissipate as heat, which is also transferred to the thermoplastic matrix.

With higher eddy currents, more current is required in the coil to maintain particular field strength [144].

High frequencies are achieved using an induction generator, which converts a 50–60 Hz supply to frequencies usually 1.8–10 MHz with power 1–5 kW, depending on the application. The magnetic field is formed by passing high frequency current through *work* or *induction coils*, water-cooled copper coils of different sizes and shapes.

In the induction welding of thermoplastic, the *bonding agent*, ferromagnetic particles embedded in a thermoplastic matrix, is placed in the joint before the welding (see Fig. 4.143). Slight pressure (0.1–0.3 MPa) is applied to the parts to be welded, and high frequency current is passed through the coil. Welding can be accomplished in 1–2 s for parts 6.4 mm (0.25 in) or thicker.

Induction welding is less dependent than other welding methods on the properties of the materials being welded. It can be used to weld almost all thermoplastics, crystalline and amorphous.

The equipment for induction welding consists of the induction generator, work or induction coils, and fixtures or nests. Placement nests hold work coils in place; one nest is generally fixed and the other movable. They are made of electrically nonconductive materials in order not to reduce the intensity of the magnetic field. A typical induction welder is shown in Fig. 4.144.

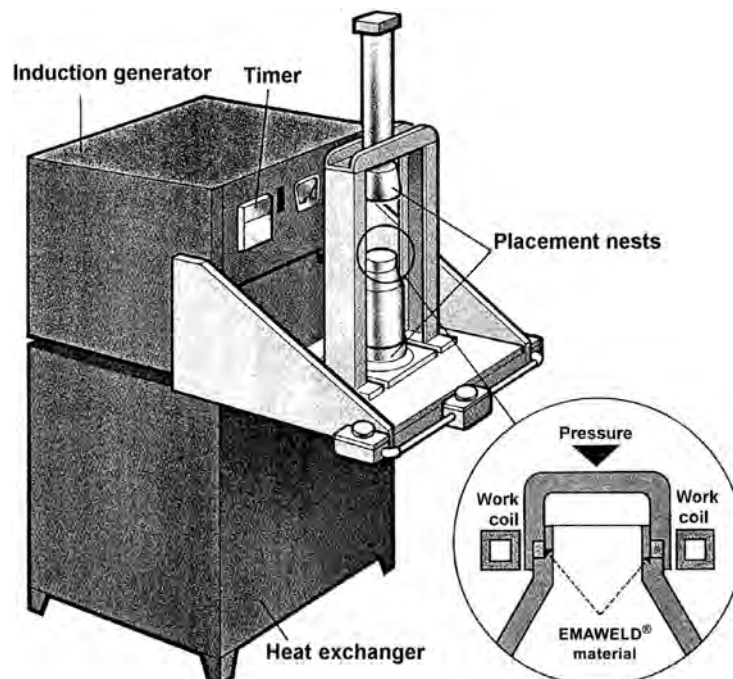


Figure 4.144 A typical induction welder.

4.12.2.9 Microwave Welding

Microwave welding uses high frequency electromagnetic radiation to heat a susceptor material located at the joint interface; the generated heat melts thermoplastic materials, producing a weld upon cooling. The frequencies used for this method are 2–10 MHz, as pointed out earlier (see [Section 4.12.2.8](#)).

The susceptor materials contain polar groups in their molecular structure or are electrically conductive. In an applied electric field, polar groups align in the field direction. In a microwave, the magnitude and direction of the field changes rapidly; polar molecules develop strong oscillations as they continually align with the field, generating heat through friction [145].

Equipment for microwave welding can be as simple as a conventional microwave oven. A more sophisticated, single mode microwave system is shown in [Fig. 4.145](#). The microwave power source has a magnetron generating 3000 W power at a frequency of 2450 MHz. The welding is performed in the double-slotted applicator connected to the tuner. A dummy load connected to the applicator converts transmitted energy into heat; water is used for cooling. This system produces a traveling wave pattern used in adiabatic heating. Connection to a pressure device consisting of a solenoid valve, air cylinder, and relay provides pressure regulation during welding [138,145,146].

4.12.2.10 Other Welding Methods

Resistant welding, also called *resistance implant welding*, is a method in which current is applied to a conductive heating element or implant placed at the joint interface of the parts being welded. The implant

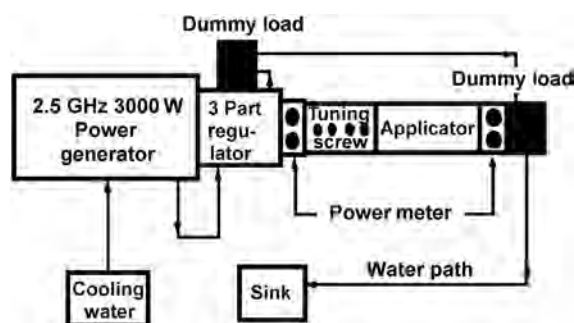


Figure 4.145 A single-mode microwave system.

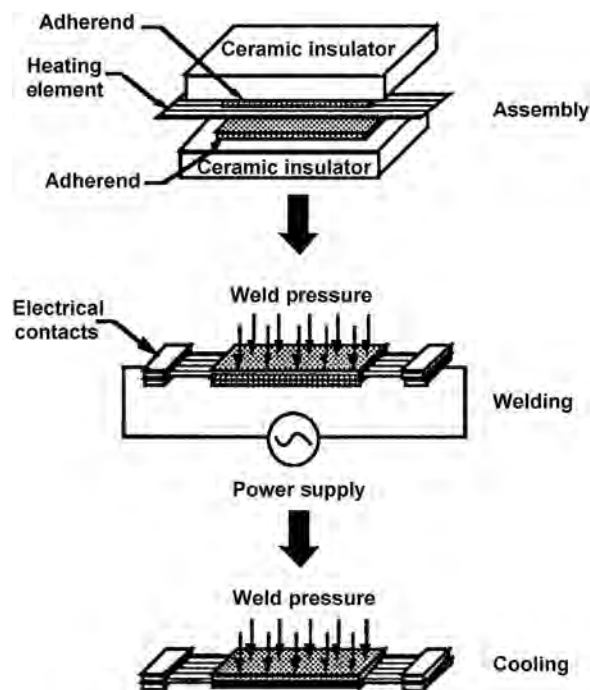


Figure 4.146 The resistance welding process.

is heated through Joule heating, and the surrounding plastic melts and flows together, forming a weld. Heating elements can be carbon fiber prepreps, woven carbon fabric, or stainless steel foil or mesh. Stainless steel heating elements can be used alone in welding thermoplastics. The heating element comprises the innermost portion of the weld stack (see [Fig. 4.146](#)) and is sandwiched between the parts to be joined, referred to as adherends. Insulators on the outermost ends of the weld stack complete the assembly. The weld stack can be autoclaved for consolidation [147,148,149,150,151,152].

Extrusion welding is a reliable technique developed from hot gas welding, in which thermoplastic filler identical to the welded material is extruded into a groove in the preheated weld area. The filler material fills the groove and forms a weld after cooling. Extrusion welding is usually performed manually, but it can be automated.

The extrusion welding for a *V-type seam* is in [Fig. 4.147](#). Cleaned, ground, and scraped parts are positioned in a specific geometry, and the welding area is preheated by hot air from a nozzle that moves along the joint line just before the welding shoe. Both the hot air nozzle and the welding shoe are attached to the welding head, which moves along the joint line at a particular welding speed. Molten extruded thermoplastic material is applied under pressure by the

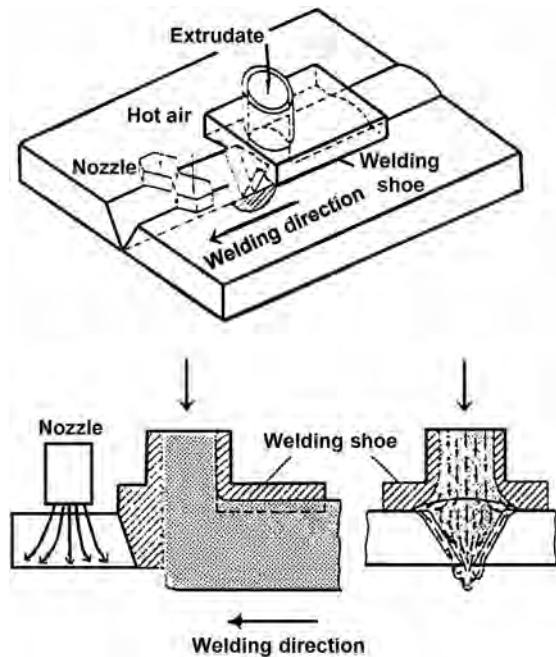


Figure 4.147 Extrusion welding, a V-type seam.

welding shoe, filling the joint area [153,154]. The process for a *lap seam* (Fig. 4.148) used for joining waterproofing membranes is similar, except that the joining pressure is applied to the flat membranes during welding [155].

Preheating of the joint surfaces, in order to form a surface melt layer, is essential for obtaining a good quality weld and is the most important determinant of the mechanical properties of the weld. Parameters that influence the preheating process include hot air temperature, welding velocity, geometry of the air nozzle, and the thickness of the parts being welded. Greater melt thickness produces a weld of greater strength.

Laser welding is a relatively new process, in which a high intensity laser beam is used to increase the temperature at the joint interface of thermoplastic materials to or above the melting temperature. The molten plastics cool down and solidify, forming a weld.

Carbon dioxide and Nd-YAG (neodymium ions in a medium of yttrium aluminum garnet) lasers are predominantly used in industrial applications. Carbon dioxide lasers emit radiation at wavelengths of 9.2–10.8 μm at a range in power from 30 W to 40 kW. The laser beam is transmitted through the air, reflected from mirrors, and focuses using ZnSe lenses. In the Nd-YAG laser, flash lamps excite Nd^{+3} ions in a solid crystal rod, resulting in radiation with

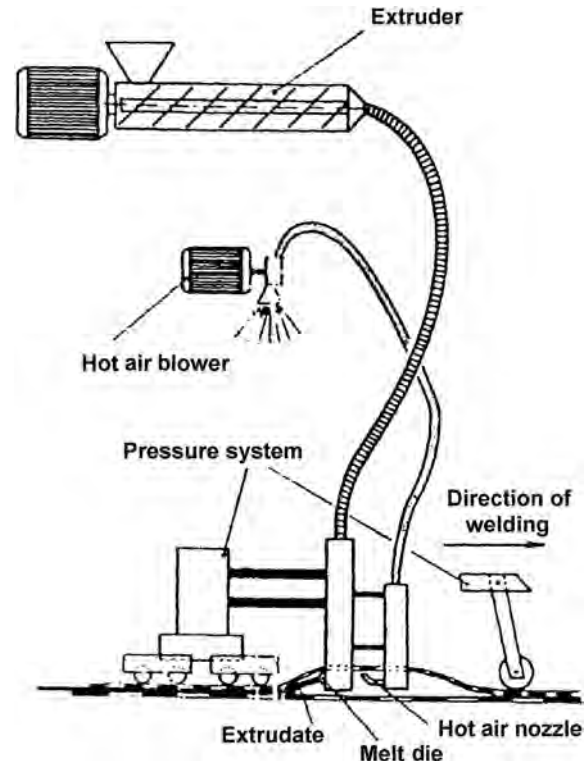


Figure 4.148 Extrusion welding lap seam.

the strongest emission at a wavelength of 1.06 μm . The short-wavelength beam is transmitted through a fiber optic beam delivery system and power ranges from 30 W to 2 kW. Lasers can generate radiation continuously (continuous wave), or it can be emitted in short bursts of microsecond or millisecond duration (pulsed). Carbon dioxide lasers generally operate in a pulsed mode, while either pulsed or continuous wave modes can be used with Nd-YAG lasers [156,157].

In laser welding, parts being joined are clamped onto a moving table. Pressure can be applied throughout the process or may only be applied after heating is terminated. In the presence of shielding gas, the high-intensity laser beam travels at a high speed across the weld interface of the parts being joined. The beam causes heating that is localized near the joint interface, which can rapidly result in melting, degradation, and vaporization of the polymer in the weld interface. Degraded material in the joint interface, which has a negative effect on joint strength, is pushed out of the weld due to external pressure, forming flash on top and bottom surfaces, and is vaporized due to the high-intensity beam. Molten material flows together at the joint interface and forms a weld after cooling is complete [158,159].

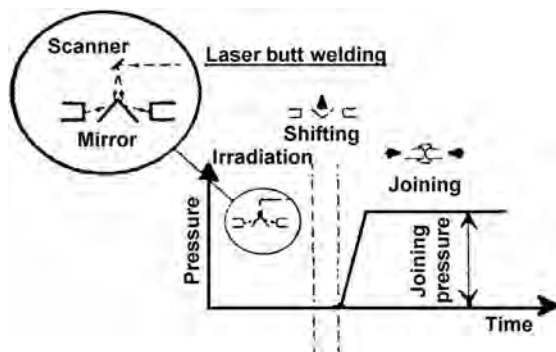


Figure 4.149 The laser welding process.

Radiation reaching the joint surface can be reflected, transmitted, or absorbed. Reflected radiation hits the part surface and bounces off, while transmitted radiation travels through the part unaffected. Reflection from all plastics is low (5–10%). Laser radiation can be absorbed at the surface of the material or can penetrate to various depths depending on the wavelength of the incident beam and the amount and type of pigment, filler, or reinforcing additives in the plastic material. Absorption results in heat generation within the plastic. The laser welding process is depicted in Fig. 4.149. A detailed description of laser welding is in Refs [156] and [157,158,159].

4.12.3 Adhesive Bonding

The majority of thermoplastics can be bonded by adhesives. Some of them can be joined without any surface treatment; others require surface treatment to achieve a sufficient adhesion.

4.12.3.1 Principles of Adhesive Bonding

An adhesive is a substance capable of holding materials together by surface attachment. There are many types of adhesives available; they may be classified in several ways, including the mode of application, chemical composition, suitability for certain substrates, and cost.

Essentially, an adhesive must be applied to the *substrate* (or *adherend*) in a fluid form to wet the surface completely and leave no voids, even if the surface is rough. To meet these requirements, it has to have a low viscosity at the time of application. In order to create a strong bond, the adhesive layer has to exhibit a high *cohesive strength*, that is, it has to set. This usually happens by the removal of the

solvent or water, by solidification, crystallization, polymerization, and/or cross-linking.

Wetting of a surface and spreading of a liquid depends primarily on the nature of the surface of the substrate and on the *surface tension* of the liquid. The wettability of a solid surface depends on its *surface energy*, expressed by its *critical surface tension*. The critical surface tension indicates the maximum surface tension permissible in a liquid (i.e., adhesive) for a particular substrate. To assure spreading and wetting, the liquid adhesive should have a surface tension *no higher* than the critical surface tension of the substrate (i.e., solid adherend). When the substrate is organic and not too polar, *solubility parameter* (δ) is a quantity useful in the selection of a suitable adhesive to it. The solubility parameter is defined [160] as:

$$\delta = (\Delta E/V)^{1/2} \quad (4.7)$$

where ΔE is the energy of vaporization, and V is the molar volume. The term $\Delta E/V$ is referred to as *cohesive energy density*. The values of solubility parameter and critical surface tension are related [161]. Examples for selected polymers are in Table 4.37.

The degree of wetting and spreading is quantitatively expressed in terms of the *contact angle* [162]. Contact angle (θ) is the angle (in the liquid) between the air–liquid and liquid–solid interface (see Fig. 4.150), resulting as a mechanical equilibrium of a drop resting on a plane solid surface under the action of three surface tensions: γ_{LV} at the interface of the liquid and vapor phases, γ_{SL} at the interface of the solid and the liquid, and γ_{SV} at the interface of solid and vapor. Hence,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos \theta \quad (4.8)$$

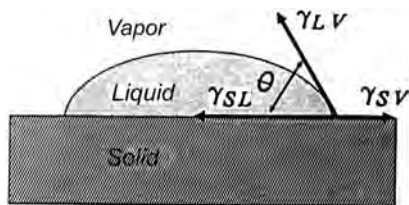
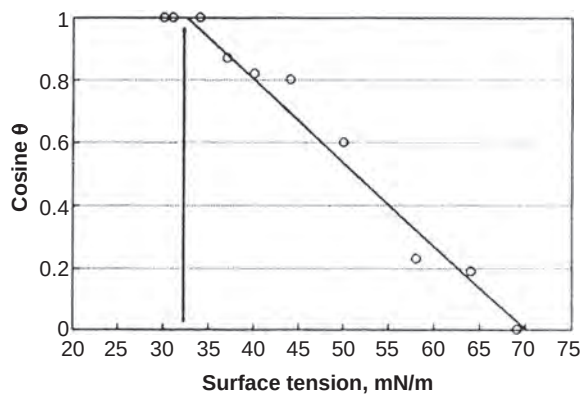
From this relation, the critical surface tension, γ_c , is derived for an individual substrate by measuring contact angles of a homologous series of liquids with known surface tension values on it, and the results are plotted as shown in Fig. 4.151 (often referred to as the *Zisman plot*). Extrapolating to a zero contact angle (i.e., $\cos \theta = 0$) and extending the intercept to the surface tension axis gives the critical surface tension of the solid surface [163].

If the contact angle is near zero degrees, the liquid spreads and wets the substrate completely. Larger values of the contact angle indicate a poorer wetting. An extreme case is when θ is 180° ; then there is

Table 4.37 Solubility Parameters and Critical Surface Tensions for Selected Polymers

Polymer	Solubility Parameter, δ Hildebrands	Critical Surface Tension, γ_c dynes/cm
Polytetrafluoroethylene	6.2	18.5
Silicone, polydimethyl	7.6	24
Butyl rubber	7.7	27
Polyethylene	7.9	31
Natural rubber	7.9–8.3	—
Polyisoprene, cis	7.9–8.3	31
Styrene-butadiene rubber	8.1–8.5	—
Polyisobutylene	8.0	—
Polybutadiene, cis	8.1–8.6	32
Polystyrene	9.1	32.8
Poly(methyl methacrylate)	9.3	39
Poly(vinyl chloride)	9.5–9.7	39
Poly(ethylene terephthalate)	10.7	43
Poly(vinylidene chloride)	12.2	40
Polyamide 6,6	13.6	43
Polyacrylonitrile	15.4	44

Ref. [160].

**Figure 4.150** Contact angle of a sessile drop.**Figure 4.151** Determination of the critical surface tension.

absolutely no wetting of the substrate. Detailed discussion of wetting and spreading of liquids on solids are in Refs [162] and [163].

4.12.3.2 Methods of Surface Treatment

The surfaces to be bonded, regardless of the bonding method or the type of adhesive, have to be clean. Often it is sufficient to wash them with solvents to remove contaminants such as oils; sometimes grinding the surface cleans them and the roughness improves the bonding by virtue of providing a greater surface area.

However, if the surface of the polymer to be bonded by adhesive has a too low surface energy, it has to be treated in order to increase the surface energy, which improves the wetting by the adhesive. The three methods used for most frequently for this are flame, corona, and plasma treatment.

Flame treatment is a commercial process to render polyolefins and polyethylene terephthalate receptive to adhesives, coatings, and printing inks. The polymer article (e.g., film) is passed over an oxidizing flame formed by an oxygen-rich (relative to

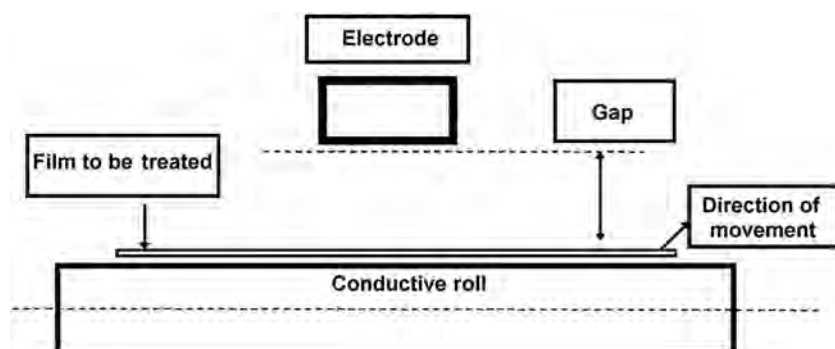


Figure 4.152 Conceptual schematic diagram of a film corona treatment system.

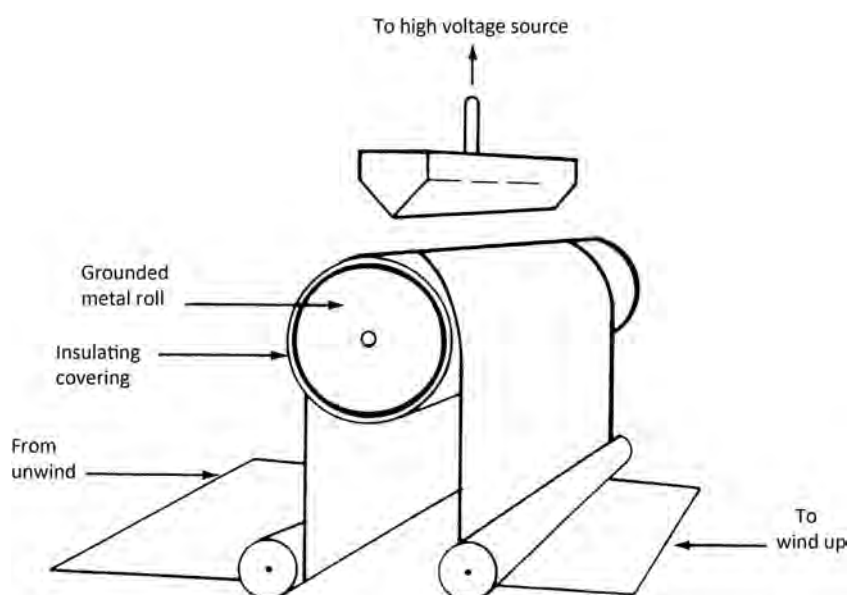


Figure 4.153 A typical single side corona treatment machine.

stoichiometry) mixture of hydrocarbon gas. The gas flame contains excited fragments and species such as atomic oxygen (O), NO, OH, and others that can abstract hydrogen from the surface of the polymer, which is then replaced by oxygenated functional groups (mostly —C=O and —OH).

Corona discharge treatment takes place at atmospheric pressure in contrast to low temperature (cold) plasma (see below) that requires vacuum. Corona is a stream of charged particles such as electrons and ions that is accelerated by an electric field. It is generated when a space gap filled with air or other gas is subjected to a sufficiently high voltage to set up a chain reaction of high-velocity particle collisions with neutral molecules resulting in the generation of more ions. The treated surface

has higher surface energy and can be therefore readily wetted. One of the widely used configurations (Fig. 4.152) uses corona discharge produced by high-frequency high-voltage alternating current [164]. The main parameters for the control of this treatment process include the voltage, width of the air gap, film/web speed, and the width of the electrodes. Most machines allow treatment on one side of the web (see Fig. 4.153) and require two passes for two-sided treatment.

Plasma (glow discharge) is produced by exciting a gas with electrical energy (Fig. 4.154). It is a collection of charged particles containing positive and negative ions [165]. Other types of fragments, such as free radicals, atoms, and molecules, may also be present. Plasma is electrically conductive and is

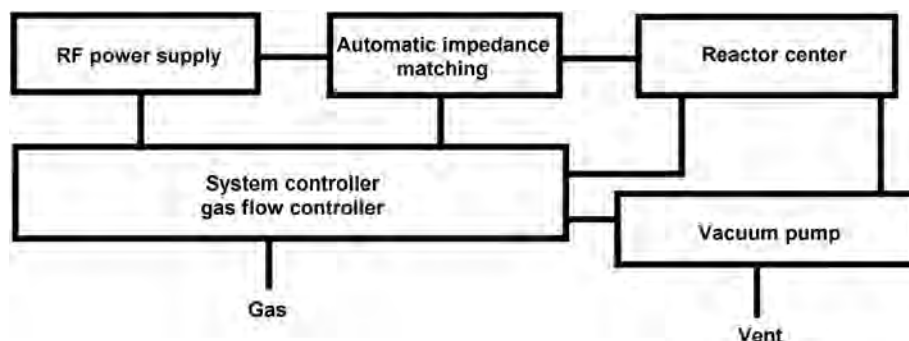


Figure 4.154 Schematic diagram of a plasma system.

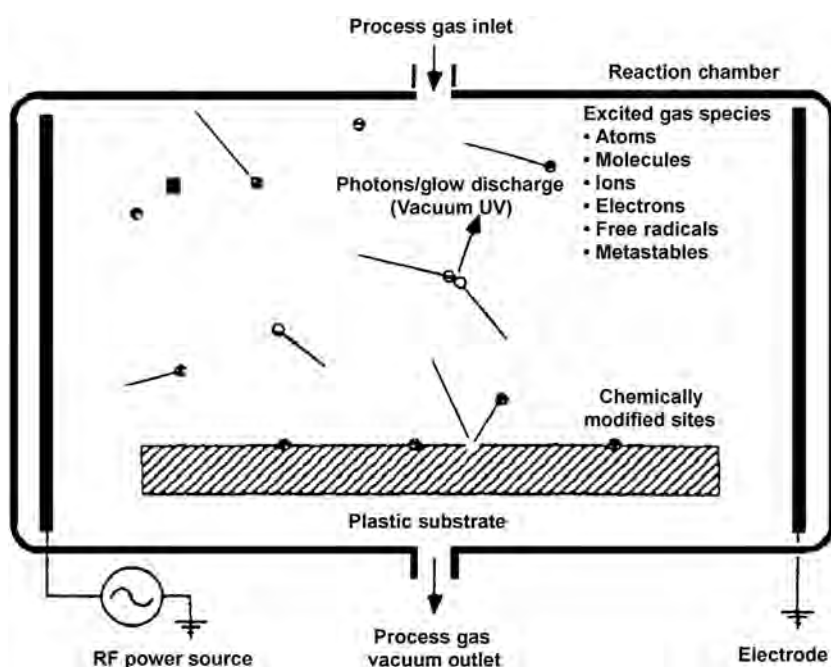


Figure 4.155 Schematic diagram of the surface modification of plastics in a gas plasma reactor.

influenced by magnetic field. It is intensely reactive, which is the reason why it can modify surfaces of plastics [166,167]. It can be used to treat parts to make their surfaces harder, rougher, more wettable, less wettable, and easier to adhere to. Plasma treatment can be carried out on a variety of plastic parts and even on powder additives like pigments and fillers.

The plasma used for treating surfaces of materials is called *cold plasma*, which means its temperature is about room temperature. Cold plasma is created by introducing the desired gas into a vacuum chamber (Fig. 4.155), followed by radio frequency

(13.56 MHz) or microwave (2450 MHz) excitation of the gas [167]. As pointed out earlier, the energy dissociates the gas into electrons, ions, free radicals, and metastable products. Practically any gas may be used for plasma treatment, but oxygen is the most common. The electrons and free radicals created in the plasma collide with the polymer surface and rupture covalent bonds, thus creating free radicals on the surface of the polymer.

Other methods of surface treatment include: *etching and oxidation* using chromic acid and other strong oxidizing compounds; *thermal treatment*, which is done by a blast of hot air ($\sim 500^\circ\text{C}$ or

932 °F) [168,169], and *surface grafting* that is performed by irradiating the substrate by electron beam in the presence of acrylic acid [170]. *Laser treatment* is done by XeCl, ArF, and KrF lasers and introduces oxygenated functional groups to the surface and removes surface contaminants [171].

Primers are reactive compounds that are applied to the substrate surface before the application of the adhesive. They form a chemical bridge between the substrate and adhesive through multifunctional groups that react preferentially with either adhesive or substrate [172].

Methods of surface treatment of materials for adhesive bonding are covered thoroughly in Refs [173] and [174].

4.12.3.2.1 Evaluation of the Level of the Surface Treatment

There are several ways to test the level of any of the above treatments. One common method involves using solutions made from two chemical compounds that produce liquids (“dyne liquids”) with surface tensions in the range 30–70 dynes/cm. The test consists of placing droplets of the various dyne liquids on the treated surface and observing the spreading of the drops in 2 s. Successive liquids with different surface tensions allow narrowing of the surface tension range of the web. This method is subjective, but it provides a rapid means of assessment of the treatment level. There are also pens operating in a similar fashion as the dyne liquids. A more quantitative approach is the measurement of contact angle, which decreases with the increase of the treatment level [175].

4.12.3.3 The Types of Polymeric Adhesives

As pointed out earlier, polymer-based adhesives can be classified in several different ways. They may be liquids of different viscosity, represented by *solvent-based adhesives*, *aqueous dispersions* or *emulsions*, and *latexes*, *monomers*, or *oligomers*. In all cases the main component is an organic compound, such as a polymer (dispersions, emulsions, and latexes), or a monomer or oligomer that forms the adhesive film. Polymers used in adhesives are mainly thermoplastics or elastomers that often are combined with tackifying resins. Monomers and oligomers have to polymerize in order to form

a strong enough film. In some cases all these adhesive substances may be cross-linked in order to further increase the cohesive strength, heat resistance, and chemical resistance of the bond.

Contact adhesives are mainly solvent-based or water-based adhesives, most frequently containing elastomers combined with tackifiers and exhibiting an aggressive tack. Once the components coated with contact adhesives are joined, the bond is strong and permanent.

Hot-melt adhesives are 100% nonvolatile materials, i.e., containing no solvents or water or other volatile carriers. They are solid at room temperature but fluid at elevated temperatures. Hot melt adhesives are applied in the molten state with special equipment, often as beads or stripes. After application, bonding, and cooling, hot-melt adhesives return to the solid state and develop their ultimate strength.

Heat-activated assembly adhesives are solution-based adhesives that are applied to the surfaces of two substrates and dried. Then, prior to assembly, the coated surfaces are heated to a sufficiently high temperature and then pressed together.

Two-part adhesives consist of two components, kept packaged separately, which are mixed just prior to use. After these two components are mixed, they start to react. As the reaction proceeds, the adhesive layer becomes stronger. The reaction is most widely a polymerization (polyaddition, polycondensation, etc.). The reaction may be completed in short times (minutes), but it may take hours or days, depending on the system.

Moisture-cure adhesives are based on compounds that cure by the exposure to moisture. They are kept in impermeable packaging until they are applied onto the substrate. The reaction usually takes days to be completed since it depends on diffusion of moisture through the applied layer.

Anaerobic adhesives are single-component liquids that can be stored at ordinary temperatures in the presence of oxygen and then polymerize rapidly to solids on being confined between two surfaces that exclude air.

As for the chemical nature, there are many polymers used in adhesives. A detailed list is beyond the scope of this work, so only the most widely used polymers, monomers, and oligomers will be listed.

Elastomers are widely used in solvent-based, water-based (latexes), contact, pressure-sensitive, and hot-melt adhesives. Elastomer-based adhesives may contain a wide variety of component materials,

such as resins, tackifiers, fillers, plasticizers, antioxidants, curing agents, etc. Solvent-based adhesives are prepared by simply dissolving the rubber compound in a suitable volatile solvent. Elastomer-based hot melts are generally mixtures of the base elastomer and a tackifying resin and other ingredients that affect its melting and melt viscosity. No volatile ingredients are present in hot melts, as pointed out earlier. Latex-based elastomeric adhesives contain a variety of other materials, such as protective colloids, emulsifiers, surfactants, thickeners, and emulsion stabilizers.

The following elastomers are typically used in most commercial adhesives: natural rubber, polyisoprene, styrene-butadiene rubber, polybutadiene rubber, acrylonitrile rubber, polychloroprene, acrylate rubber, polyurethane rubber, polysulfide rubber, silicone rubber, carboxylic elastomers, and copolymers of ethylene and vinyl acetate.

Thermoplastic elastomers such as SBS, SIS and TPU are most widely used in hot-melt, pressure-sensitive, contact, and heat-activated adhesives alone or in blends with other elastomers and resins.

Epoxy resins are mostly employed in two-part adhesive systems with different curing times and with different bond characteristics.

Polyurethane- and isocyanate-based adhesives: Certain types of polyurethane adhesives are two-part systems, consisting of a polyol (often an oligomeric polyol) and a polyisocyanate, which are kept separately and mixed only prior to use. The bond strength develops rather rapidly. Other polyurethane adhesive systems include thermoplastic polyurethanes used in hot melts, polyurethane aqueous dispersions, powders, and films. Isocyanates alone are used as primers [176] or as cross-linking agents in certain elastomeric adhesives prepared with thoroughly dried inert solvents [176].

Silicones: Silicones can be used in two-part systems and also as single-package moisture curing adhesives and sealants.

Cyanoacrylates: Cyanoacrylate adhesives form a strong adhesive bond rapidly, typically in less than a minute. This is the result of an anionic polymerization initiated by weakly basic species, such as water or alcohol, at ambient temperatures [177].

Other polymers used for adhesives are: ethylene-vinyl acetate copolymers, polyvinyl acetal, polyamides, polyimides, polybenzimidazoles, polybenzotriazoles, and others used for specialized applications.

The reader can find more on the subject in Ref. [178].

4.12.3.4 Application of Adhesives

Most of the adhesives are applied in liquid form. The commonly used methods of application are:

- Brushing
- Spraying
- Dipping
- Curtain coating
- Application by roll
- Application of a bead or stripe of a hot melt

4.12.3.5 Formation of an Adhesive Bond

When an adhesive is applied as a solution in a volatile solvent or as an aqueous dispersion or emulsion, the solvent or water has to be evaporated. In most cases this happens over a relatively short time at ambient temperature. Sometimes the drying time can be reduced by applying hot air to the surface of the parts to be joined or by using infrared heaters.

The assembly of the joint has to take place while the adhesive layer has a sufficient tack. So each type of adhesive has a specific *open time*. Open time or *bonding range* is the maximum time two surfaces coated with an adhesive may be allowed to dry (or cool down if applied in molten state) before bonding and still have satisfactory adhesion. It depends on the specific application and can vary from less than 1 min to more than 24 h.

The adhesive joint can be formed by pressing the two adherends together. If the adhesive has a high tack (e.g., a contact adhesive), no additional pressure is required. Similarly, the bond formed by hot melts requires a brief application of pressure until the melt solidifies. In other cases pressure has to be applied for a certain period of time by placing the joint between platens of a press or into a specialized fixture that holds the joined parts together until the bond is sufficiently strong. The same applies to adhesive bonds that become stronger due to a chemical reaction. Occasionally, heating of such joints is used to reduce the time for a sufficiently strong bond or to achieve considerably higher bond strength.

4.12.3.6 Measurement of the Bond Strength

There are many tests of measuring the strength of the bond between an adhesive and a substrate. They are used for five main purposes [179]:

1. To check the quality of an adhesive to see if it falls within well-defined limits;
2. To determine the effectiveness of the surface treatment;
3. To gather data for the prediction of the performance of the adhesive joint;
4. To select an adhesive from a group for a specific application;
5. To evaluate the effect of aging on the performance of the joint.

The most common test configurations are:

- Tensile
- Shear
- Peel

Shear tests are the most commonly used tests for a quick assessment of adhesion between two rigid substrates. The simplest test configuration is the *lap shear test* using two principal forms of test pieces, the single lap joint (Fig. 4.156) [180], and the double lap joint (Fig. 4.157) [181]. The advantage of the lap joint is that it can be easily manufactured and quickly tested. After the test piece is ready for the test, it is pulled apart in the axis of the bond and the failure load is then calculated. The test results are of restricted value in the design of adhesively bonded components because of its complex stress distribution [182]. However, in spite of that, this test provides a rapid assessment of the shear stress of the adhesive

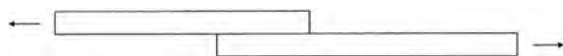


Figure 4.156 Single lap joint.

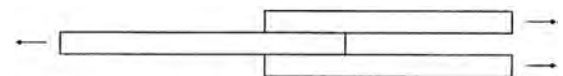


Figure 4.157 Double lap joint.

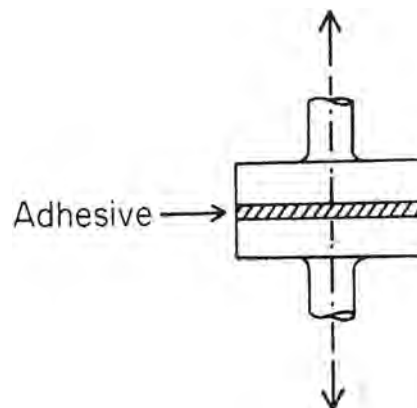


Figure 4.158 Adhesion tensile test piece.

and may serve as a good method of screening adhesives for a specific application.

The test piece for the adhesive *tensile test* can take several forms; one simple configuration consists of two cylinders (Fig. 4.158) that are bonded together at their ends. The joint is loaded to failure at right angles to the plane of the adhesive, and the failure stress is determined by dividing the failure load by the loaded area [183]. The tensile test pieces are widely used for testing the strength of bonds of rubber and plastics to metals.

Peel tests are generally used for elastomeric adhesives. A typical version is the *T-peel test*, in which two strips of substrate bonded together face to face are peeled, and the force required to pull them apart is recorded. The peeling can be done at a 90° angle, typically for two flexible substrates (Fig. 4.159) [184] or at a 180° angle for peeling of a flexible substrate from a rigid substrate (Fig. 4.160) [185].

Other adhesive tests, such as wedge test, cleavage strength test, impact strength test, and fatigue strength test [178], are designed for specific applications and service conditions.

4.12.4 Mechanical Fastening

Mechanical fastening is a simple and versatile joining method. Mechanical fasteners are made from plastics, metals, or a combination of the two materials and can be periodically removed and replaced or reused when servicing of the part is necessary. Screws, nuts, and inserts can be made from plastics or metals; rivets are generally made from metals. Plastic fasteners are lightweight, corrosion resistant, and impact resistant. They do not freeze on threads of

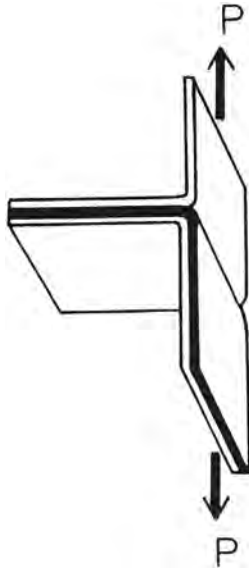


Figure 4.159 90° peel test.

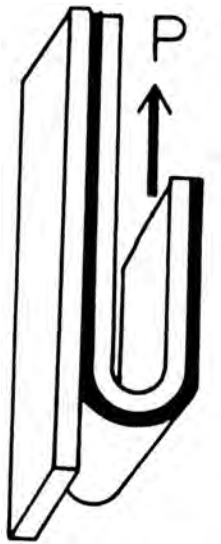


Figure 4.160 180° peel test.

screws and require no lubrication. Metal fasteners provide high strength and are not affected by exposure to extreme temperatures [186].

Screws, nuts, washers, pins, rivets, and snap-type fasteners are examples of nonintegral attachments, in which the attachment feature is a separate part. Use of separate fasteners requires plastic materials that can withstand the strain of fastener insertion and the resulting high stress near the fasteners. Snap-fits are examples of integral attachments, attachment features that are molded directly into the part. Strong plastics that can withstand assembly strain, service

load, and possible repeated use are required for nonintegral attachments. Separate fasteners add to product cost due to increased assembly time and use of additional material and can be difficult to handle and insert; as a result, use of integral attachment features is increasing [187,188,189].

For more detailed discussion of the subject of joining plastics, see Refs [190], [191], and [192].

4.12.5 Decorating

Plastics decorating involves the modification of a plastics surface, using a coating or impression, by the application of heat, pressure, or a combination of both.

4.12.5.1 Appliqués

Appliqués are surface coverings applied using heat and pressure for a specific period of time; they may be applied as decals, during molding, or by hot stamping, hot transfer, or water transfer [192].

4.12.5.2 Painting

Parts may be painted to provide color for color matching, a high gloss or matte finish, a wood grain, luminescent or metal flake appearance, a textured appearance, or coverage of surface imperfections. Paints and coatings can also provide enhanced performance properties such as improved chemical, abrasion or weathering resistance, and electrical conductivity. Painting requires clean surfaces, and the paint should be compatible with the substrate. Parts should have uniform walls, and molding should be stress-free [192].

4.12.5.3 In-Mold Decorating

Parts can be decorated during molding by the placement of a pre-decorated carrier into the mold; the molten plastic then fuses with the film during processing. They must have good thermal stability due to the high temperatures encountered during the molding process. There should not be sharp edges, and complex surfaces may result in problems caused by air entrapment or stretching the film.

4.12.5.4 Metallization

Plastic surfaces are metallized to give the material surface a metallic appearance and make its properties more similar to that of metal. Conductive paints composed of pigments and conductive particles (nickel, copper, silver, graphite) can be applied to the part with air atomizing or airless spray equipment.

Vacuum metallization (or physical vapor deposition) is a process in which the metal used for the application to the surface of the plastic (very often aluminum, although other metals are also used) is heated in a vacuum chamber and to its vaporization point, which is lower than the melting point of the plastic material. The metal vapor then condenses on the cooler plastic surface. The parts to be metallized are held in an appropriate fixture that can rotate to expose all surfaces to be metallized. Several power sources are used for metal evaporation, such as resistance heating, induction evaporation, electron beam guns, or vacuum arc. Resistance-heated tungsten filaments are most often used. Aluminum chips or staples are placed on the filaments or into a thermally heated boat or crucible.

Frequently, the thin metal layer is coated by a transparent topcoat to improve its abrasion resistance and to protect it against environmental influences, such as humidity.

Flame and/or arc spraying are easy, low-cost metallization processes, where a handheld or automated pistol is used to spray liquid metal onto a part. The metal layer produced is thick compared to other metallization techniques, and the deposition rate is high. However, the coatings prepared by these two methods are quite porous, coating adhesion is lower, and the surface roughness is relatively high. In flame spraying, a metal powder or wire is heated and propelled onto the plastic surface by a stream of hot gases. Arc spraying is comparable to flame spraying, but in arc spraying a direct current electric arc is used. The arc is struck between two continuous consumable wire electrodes that form the spray material.

Sputtering is a process in which metal atoms are dislodged with inert gas plasma instead of heating the metal. In cathode sputtering, the metal is attached to the cathode, with the plastic acting as the anode. An electron beam dislodges positively charged metal ions, which then condense on the plastic surface. Sputter coatings have a better adhesion and are more resistant to abrasion than vapor deposition coatings, due to a higher kinetic energy of the deposited metal atoms.

Also, sputter coatings can be easily applied over large surface areas with a uniform layer thickness.

Sputter coating can be done batch-wise or in line with the injection molding process. Examples are compact disks produced in-line with an injection molding machine with sputter coating cycles of less than 2 s.

Plating processes of plastic materials can be divided into an electroless plating process, without a galvanic electric current, and electroplating, where electric current is used in a galvanic process. Plating in general yields better adhesion than vacuum metallization, but the process is less environmentally friendly, less safe, and also expensive.

In *electroless plating* a metallic coating is deposited onto electrically nonconductive plastics. Nickel and copper are most frequently deposited this way. The surface of the part to be plated is first etched with a strong oxidizing solution. After etching, the part is immersed in a solution, and a metallic coating is formed in a chemical reaction between the reducing agent present in the solution and the metal ions.

Electrolytic plating is the deposition of a metal on a conductor using an electric current. A plastic surface must first be made conductive in order to be electrolytically plated. The process is essentially comprised of three steps: activation or treatment of the surface of the plastic, sensitization, and coating. Stannous chloride is frequently used as sensitizer. Electric current is then used to deposit metals onto the prepared substrate from metal salt solutions. The anode is usually made from the same metal and dissolves during the plating process, replenishing the plating bath.

Metallizing makes surface flaws more apparent, and the physical characteristics of the resin may change. Clean surfaces are required, with no mold release agents present, and precleaning processes should be checked for compatibility. Design considerations include [193]:

- Uniform wall sections
- Radiuses sharp edges (0.5 mm or 0.020 in minimum)
- Avoidance of deep vertical walls
- Gradual wall transitions
- Minimal amount of projections
- Avoidance of flat areas
- Hole depth of a diameter ratio less than 5 to 1

- Recesses less than 51 mm (2 in) with greater than 5° draft
- Minimum wall thickness about 2 mm (0.080 in)
- Maximum walls ranging to 4.8 mm (0.190 in)

4.12.5.5 Printing

In printing, a mark or impression is made on a plastic surface. Printing processes include pad transfer, screen printing, laser printing, dyeing, and fill and wipe.

Pad transfer is used to print on flat and irregular surfaces. A metal plate with an etched pattern is covered with ink, and a soft silicone rubber pad is pressed onto it. The pad picks up the ink pattern (in reverse) and is pressed against the part. The pad can wrap 180° around a small part (360° with specialized equipment), and coverage is excellent. Parts for pad transfer decorating should be designed with smooth and even transitions, and sharp edges should be avoided. The surface finish affects sharp line intersections, and thickness can be inconsistent in large print areas. The size of the printing area should be minimized [193].

In *screen printing*, a pattern is produced by selectively sealing holes in a fine mesh screen. The mesh is then placed on the part, and a squeegee is used to force ink through the open holes onto the part surface. Parts should be designed with smooth and even transitions, with all coverage areas in one plane, and points and projections should be avoided.

In *diffusion process* (wet or dry), dry solids are transferred below the surface of a plastic (to a depth of 0.025–0.100 mm or 0.001–0.004 in) using heat or heat and pressure. Inks used in this process undergo sublimation—they change from a solid to a gas and back without passing through the liquid phase. In wet diffusion, pad transfer methods are used to transfer the inks from a solvent suspension, which evaporates after exposure to heat, to the plastic substrate. Dry diffusion is similar to hot stamping; designs are reverse printed on a carrier, then applied to the surface by heat and pressure over a period of time. Wet diffusion is more economical; however, dry diffusion can transfer multiple colors in one operation [193]. Since dye inks are translucent, diffusion is appropriate only to parts that have planar or slightly curved surfaces, and the surface finish affects sharp line intersections. Wall sections should be thick enough to be stable during the heating process of dry diffusion.

Laser printing uses a CO₂ or YAG laser to produce marks on the surface. The laser beam vaporizes the plastic surface, changing the color. It is useful for placing permanent lettering (e.g., codes) on parts too small for conventional printing. Pulse power, rate, and marking speed control the depth of etching; the amount of contrast produced is important in determining the quality of the finish. Design considerations include gradual wall transitions and a minimization of sink marks.

In *fill and wipe* processes, the part is etched, and the ink is used to fill the recesses. Excess ink is then wiped away. For sharp detail, the surrounding surface should be very smooth, and edges should be sharp. Adjacent surfaces should be polished. Thick, rather than thin borders should be used, and inside corners should be radiused. Recesses should be 0.38–0.76 mm (0.015–0.030 in) deep; small character openings may not be filled in [193].

4.12.5.6 Other Decorating Processes

Textures and lettering can frequently be molded into the surface of the part, in order to hide surface imperfections and provide decoration at no additional cost. Additional draft is required to eject a part with textured sides. Surfaces with molded-in texture do not usually maintain optical clarity [193].

Another special process is *flocking*, in which the surface is coated with an adhesive and exposed to an electrostatic charge. Short textile fibers are then blown onto the surface and stand on end due to the charge. As in other processes, flocking requires clean surfaces, with a minimal amount of sink marks, wall transitions, and projections. Sharp corners should be broken to a minimum of 0.5 mm (0.020 in) [194].

4.12.6 Cross-linking

Typically, thermoplastic materials are not subjected to cross-linking. However, in some cases cross-linking is used to improve mechanical properties and affect the flow of the material [195]; it increases heat resistance and reduces swelling in oils and solvents and eliminates dissolution of the polymer in oils and solvents. An example is the use in wire and cable insulation where cross-linking improves resistance to abrasion and cut-through as well as the heat resistance. Another application is in the production of foams, where partial cross-linking increases the melt strength of the polymer required for the proper

behavior during the foam expansion. Cross-linking is also used for the manufacture of heat-shrinkable films and sheets. Although chemical methods of cross-linking of many thermoplastics are possible, irradiation by electron beam is the most widely used method in the industrial practice where relatively thin layers are handled in a continuous process and in large volumes. Two distinct advantages of cross-linking by electron beam are that the depth of penetration of the beam can be controlled by the accelerating voltage and the degree of cross-linking by the radiation dose [196]. In some cases, an addition of a radiation promoter (prorad) is required to improve the process efficiency. Many thermoplastics can be cross-linked by electron beam, but there are some that are either degraded by electron beam or resistant to the effects of irradiation [195].

4.13 General Processing Technology of Thermoplastic Elastomers

The ability of thermoplastic elastomers to exhibit good flow properties upon heating and then solidifying upon cooling allows manufacturers to use highly productive thermoplastic melt processing equipment, such as injection molding, extrusion, and blow molding (described in previous sections) for the production of elastomeric articles. This represents a substantial saving when compared with multistep fabrication of rubber articles from thermoset elastomers. Vulcanization (cross-linking) of thermoset elastomers alone requires long times (minutes to hours) and consumes a great deal of energy as opposed to short cycles (minutes or less) used in melt processing techniques.

4.13.1 Compounding of Thermoplastic Elastomers

Traditional processing involves the use of a large number of ingredients, such as fillers, plasticizers, resins, curing agents, accelerators, activators, etc., requires intensive mixing that consumes great amounts of energy, and is labor intensive. In general, thermoplastic elastomers may be used without additives, but in many cases they are blended with other polymers, and they may be mixed with fillers, oils, and resins to achieve required processing

characteristics and/or properties. In such cases the final compound may contain less than 50% of the original polymer [197]. Not only is the volume of the added ingredients important but also their distribution. In block copolymers, the added materials can accumulate in the soft phase or in the hard phase, in both phases, or may form an entirely separate phase.

If the additive accumulates in the hard phase, it increases its relative volume and the material becomes harder. If the additive is a polymeric material, its glass transition temperature must be higher than that of the hard phase; otherwise, it reduces the high temperature performance of the block copolymer.

If the additive accumulates in the elastomeric phase, it increases its relative volume and makes the material softer. It may change the glass transition temperature of the elastomeric phase, which may in turn affect some end use properties such as low temperature flexibility and tack.

If the additive forms a separate phase, it depends on its molecular weight. Low-molecular-weight additives, such as oils and resins, are often compatible with both phases. Polymeric additives with sufficiently high molecular weight usually form a separate third phase, which is co-continuous with the block copolymer and affects the properties of the finished product.

If the additive goes into both phases, it will reduce the degree of phase separation and consequently weaken the product. For that reason, such a situation should be avoided.

The choice of mixing equipment is determined by the overall volume of the compounds to be mixed and their assortment. In such cases, where a small number of very large volume compounds are mixed, large equipment, such as an internal mixer, is suitable since it is capable of mixing large-sized batches in short times. However, equipment of this type represents a large capital investment.

Other choices are single-screw extruders, twin-screw extruders, and reciprocated single-screw extruders (e.g., Buss Kneader); the selection depends mainly on the type and volumes of materials being mixed.

Twin-screw extruders used for TPE compounding typically have L/D ratios from 36:1 to 41:1, depending on the number of process tasks involved [198]. Operating conditions are greatly dependent on the type of TPE being processed. For SBC, TPU, and COPE, the main compounding concern is to

maintain the material integrity and obtain proper blending of components. TPU in particular is sensitive to both moisture and shear. TPU compounding process design is critical since “overwork” can lead to a catastrophic molecular weight reduction [198].

TPV are generally robust materials that can be processed under a wide range of temperatures and mixing speeds; however, the challenge here is to obtain homogeneity in a system containing a cured rubber phase that does not accept color or other additives as well as the thermoplastic phase. Additional challenge in compounding of TPVs is keeping the balance between the cross-linking process and the mixing process. Mixing polypropylene and the elastomer (most commonly EPDM) is not easy because the polymer viscosities are very different and because the viscosity changes during the cross-linking. The degree of cross-linking determines most of the mechanical properties and flow behavior during subsequent processing operations. The most common mixing procedure has two steps: EPDM and polypropylene are premixed in an internal mixer and the dynamic vulcanization takes place in an extruder. However, a single step of preparing a TPV in an extruder has been patented [199]. The single step has the advantage of eliminating batch-to-batch variation, but the longer extruder needed for this process can limit the throughput [198].

Direct extrusion, in which the raw materials are compounded and then made directly into a sheet or profile, eliminates the pelletizing step and has been used in some cases, mainly for TPOs. The equipment used, a standard compounding extruder, has to be lengthened by approximately 8 L/D and the screw has to be modified [198].

4.13.2 Injection Molding

The injection molding process is adapted to TPEs rather readily. The various classes of TPEs will generally mold well. Historically, the thermoplastic urethanes were the exception due to their high viscosity, but in recent years TPU grades that injection mold well have been commercialized. In order to process TPEs, the key process variables, including melt temperature, melt viscosity, and shrink rate, have to be set to accommodate the particular properties of any given class of TPE.

The TPVs represent a special case since the structure does not consist of a single polymer type. TPVs have a cross-linked rubber phase dispersed in a thermoplastic phase. This morphological structure makes them very shear dependent such that the viscosity is quite low at the high shear rates used during injection molding (1000 to 100,000 s⁻¹). Then at very low shear (and when static) the viscosity is quite high, giving the TPV melt a relatively high stiffness. The grades of TPVs commercially available also vary widely in their suitability for injection molding. Some are highly tailored to injection molding and work extremely well. These molding grade TPVs work better in thin and difficult-to-mold parts [200]. Typical injection molding parameters for commercial TPEs are in Table 4.38 and typical temperature settings in Table 4.39.

4.13.2.1 Overmolding

There are many reasons to use “soft-touch” materials over rigid parts for industrial and consumer goods. Rigid components, such as plastics and metals, provide the required strength, stiffness, and

Table 4.38 Typical Injection Molding Parameters for Commercial TPEs

TPE Class	Typical Melt Temperature, °C	Typical Injection Pressure, MPa	Typical Shrinkage Rate, %
SBC	190–200	1.0–5.5	0.3–0.5
TPO blend	175–205	1.0–10.0	0.8–1.8
EPDM TPV	190–230	1.0–10.0	0.5–4.7
NBR TPV	190–230	1.0–10.0	1.0–2.2
MPR	199–255	1.0–5.5	1.1–1.9
TPU	175–205	1.0–7.0	0.5–2.5
COPE	180–260	2.0–10.0	0.5–1.6

Table 4.39 Typical Injection Molding Temperature Setting for Commercial TPEs

TPE	SBS	TPO	TPV	MPR	TPU	COPE
Zone	Temperature, °C	Temperature, °C	Temperature, °C	Temperature, °C	Temperature, °C	Temperature, °C
Feed/Rear barrel	120–150	185–200	170–190	171–177	160–182	200–215
Center barrel	170–182	190–210	170–190	171–177	177–199	205–235
Front barrel	185–195	200–220	170–190	171–177	188–210	210–235
Nozzle	190–200	200–220	170–210	171–177	190–210	215–240
Melt	190–200	207–216	185–205	171–177	185–210	220–245
Mold	22–32	10–50	10–80	21–49	38–60	20–50

structural integrity, and the soft materials applied over them provide improved aesthetics, better tactile properties, and enhance grip of products while absorbing vibrations transmitted to the hand. Products are more durable and comfortable to use. Typical overmolding applications are in automotive interiors, housewares, personal care items, appliances, hand tools, calculator and computer keys, sporting goods, and lawn care products.

Traditional joining techniques, such as snap-fit designs, mechanical fasteners, and adhesion and welding techniques (ultrasonic and heat) are still being used. These usually involve labor-intensive secondary assembly steps, which increase costs and limit control over product integrity.

Processing techniques such as co-injection, two-shot molding, and insert molding have been used with increasing frequency since they offer significant cost and performance advantages.

Co-injection molding provides the greatest adhesion between the rigid substrate and the soft TPE compound, but it is difficult to control and expensive. In this method the substrate and the TPE are injected simultaneously, and the TPE migrates into the proper position [201].

Two-shot molding uses a complex mold with several gates and activated slides. The rigid substrate is injected first, and then the mold is indexed to another barrel, and the TPE compound is injected onto the rigid substrate.

Insert molding is a method in which the thermoplastic elastomer compound is injected and overmolded onto the rigid part that has been molded in a separate process. The TPE provides the formation of a joint through melt flow or chemical bond.

Specific processing conditions for all applicable techniques described in this chapter are discussed in more detail in chapters covering individual TPEs.

4.14 Process Simulation

At the heart of every decision is an understanding of the relationship between the decision variables to the expected outcomes. Since such knowledge is so significant in product design and manufacturing process development, phenomenological simulation and numerical analysis is a continuous activity. The act of developing these simulations provides significant insight into the process physics, and the results are very useful for integrated product and process design.

The development of aerospace, automobile, and high-technology industries requires the development of advanced plastic processing technologies in order to manufacture parts with light weight, high strength, high precision, high efficiency, and at low cost, within a short period and a friendly environment, and with intellectualization and digitization. There are key problems urgently to be solved in the research and development of advanced plastic processing technologies, and FEM numerical simulation in combination with physical modeling and theoretical analysis has been playing an increasingly important role in this field.

There are several major resources for process simulation. *Moldflow* [202] is software that simulates the injection-molding process, trying out any shape of mold that the designer can imagine. It displays color-coded pictures of the way molten plastic will flow into the mold and how the plastic will shrink or warp when it cools. This information can be used to design a mold, to add extra cooling channels into the mold if needed, and to beef up plastic sections that might warp. The toolmaker uses the computer-generated design to make the mold.

Compuplast [203] specializes in offering the computer simulation tools for the analysis and design of almost any extrusion-related process including sheet and film extrusion, cast film process, blown film extrusion, pipe and profile extrusion, wire and cable coating, and extrusion blow molding. Separate software packages are available for injection molding and thermoforming.

4.15 3D Printing

Additive manufacturing or 3D printing is a process of making a three-dimensional solid object of virtually any shape from a digital model. 3D printing is achieved using an *additive process*, where successive layers of material are laid down in different shapes. 3D printing is also considered distinct from traditional machining techniques, which mostly rely on the removal of material by methods such as cutting or drilling (*subtractive processes*). A 3D printer is a limited type of industrial robot that is capable of carrying out an additive process under computer control.

The 3D printing technology is used for both prototyping and distributed manufacturing, with applications in architecture, construction, industrial design, automotive, aerospace, military, engineering,

civil engineering, dental and medical industries, biotech (human tissue replacement), fashion, footwear, jewelry, eyewear, education, geographic information systems, food, and many other fields. One study has found that open source 3D printing could become a mass market item because domestic 3D printers can offset their capital costs by enabling consumers to avoid costs associated with purchasing common household objects [204]. The raft of technologies covered by the name is limited, however, in terms of material compatibilities and ultimately, therefore, in the mechanical properties that can be achieved.

4.16 Product Development and Testing

Development of new products and processes as well as their improvement are important factors in growing any business based on manufacturing products. There are essentially two ways to develop ideas for new products and processes [205]:

1. R&D can make technological forecast of new developments in basic and applied research leading to new products and/or processes.
2. At the same time, marketing and sales employ the tools of market research to identify unfilled needs in the marketplace or opportunities to compete with other products or applications.

The financial success of any new product is assured when there is demand for it in the marketplace and when it can be manufactured in a cost-effective manner. When a product is properly designed, it has the following key features:

- Unique performance properties that demand a premium in the marketplace or at least provide a competitive alternative to existing materials and products.
- Can be manufactured to a specified consistency and in a cost-effective manner.
- Does not require alteration during and after production, which can increase the chance of inconsistency.
- Performs to the expectations and claims of the manufacturer under the environmental conditions for which it was intended to be used.

It is fair to say that product design has a direct bearing on product quality. A poorly designed product that is made from inferior or improper material and/or by improper process will not perform to the customer expectations and will ultimately fail in the marketplace.

There are many factors that contribute to the success and failure of product development products, such as:

- R&D philosophy of the company
- Management support
- Technical aspects of synthesis and product testing

Specific attributes used typically for evaluating products based on polymers are:

- Physical and mechanical properties
- Processing (rheological) properties
- Chemical nature and aging
- Methods of quality control (probability and statistics)

Thus, it is extremely important to understand not only the principal methods of testing but also the regression and statistical approaches in planning the experiments and in evaluation of the test results.

In some organizations the development process is performed in a sequence, where specialists contribute to each phase of product development effort, passing from one function to the next. Each functional group makes its major contribution to the product development effort, passing it from one function to the next.

Each functional group makes its major contribution to the product only once, and there is little dialogue between them.

In a completely different, parallel approach, everyone responsible for any aspect of the development is brought in to formulate the development strategy. All participants continue to interact throughout the process. Typically, members of the development department, marketing, production, and quality assurance work together. The parallel approach brings together a broad range of talent for trying things out, learning from each attempt, and then trying again. Through recycling and an interactive approach, this enables more reliable products to be developed in a shorter time [205].

A typical product development starts with the selection of the material to be used. It may be a polymer, blend of polymers, or a compound containing a variety of components. The initial series of candidate materials is evaluated as to their rheology, physical, and mechanical properties, and sometimes for aging on the laboratory scale. If the project is rather involved, consisting of a large number of experiments, a systematic approach, such as design of experiments, should be used [206]. In the first step (screening stage), the independent variables within the relevant range are identified. The next phase (response surface defined), will allow some interpolation and leads to the phase that allows scale-up prediction [205]. This method is suited to both material and process development and optimization.

Once the best candidate material is found, it is evaluated on pilot equipment that in most cases is similar to that used in production. In this stage the experimental procedure involves process optimization resulting in optimum process parameters. The next stage is a scale-up from pilot to production equipment, usually for a short run. This may include mixing and processing into the final product. Often some adjustments are needed to achieve a smooth run. The first products are then frequently subjected to field testing. The type and duration of the field tests depend on the type of products and expected service conditions. The transition to full-scale production occurs after a thorough analysis of the short run and the results of field tests. The initial production run requires a close monitoring and statistical analysis [206] to assure a uniform quality of products.

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9 Thermoplastic Polyurethane Elastomers

9.1 Introduction

Polyurethanes represent a large segment of polymers used in high-performance materials, such as films, coatings, adhesives, fibers, and elastomers. They are formed by a simple polyaddition reaction but, because many different compounds can be used to produce polyurethanes, there is a large number of possible final products. This also opens up the possibility to produce materials with tailor-made properties.

Thermoplastic polyurethane elastomers (TPUs) were the first homogeneous elastomeric materials that could be processed via methods commonly used for the processing of thermoplastics. Their growth contributes to the overall rapid growth of thermoplastic elastomers.

The credit for the discovery of polyurethanes belongs to the group led by Otto Bayer at the I.G. Farbenindustrie in Germany (now known as Bayer A.G.). The original work concentrated on the duplication or improvement of synthetic polyamide fibers [1]. The first patent issued to this group was issued in 1937 [2]. Subsequent patents covering elastomeric properties of polyurethanes were issued to DuPont [3] and ICI [4]. The first polyurethane elastomer, dubbed “I-Rubber”, had very poor properties [1]. Additional development work led to products that had considerably improved properties. The commercial products developed during that period were Vulkollan® (Bayer), Chemigum SL® (Goodyear Tire and Rubber Co.), and Adiprene® (DuPont) [5,6]. The early polyurethane elastomers consisted of three basic components [1]:

- A polyester or polyether high-molecular-weight diol
- A chain extender (water, low-molecular-weight diol)
- A bulky diisocyanate, such as naphthalene-1,5-diisocyanate (NDI)

These polyurethane elastomers were not true thermoplastics, because their melting temperatures

were higher than the decomposition temperature of the urethane linkages [1]. A major breakthrough was achieved when NDI in these systems was replaced by diphenylmethane-4,4-diisocyanate (MDI). The first records of true TPUs are from 1958 [7]. Today, it is well established that the elastomeric properties of TPUs are a result of *multiblock structure of phase-separated systems* [1].

The *hard segment* is formed by the addition of the chain extender, such as butadiene diol, to the isocyanate (in most cases, MDI). The *soft segment* consists of the flexible polyether or polyester chains that connect the two hard segments (see Fig. 9.1).

The two segments are incompatible at room temperature, which results in micro-phase separation. The driving force for the separation is to a degree the development of crystallinity in the hard segments. Additional factors are the difference in melting points and polarity of the two segments. The hard segments have a much higher melting point and polarity than the much less polar and low melting soft segments.

When the material is heated above the melting temperature of the hard segments, the polymer becomes a homogeneous viscous melt that can be processed by usual methods used for plastics, such as extrusion, injection molding, blow molding, etc. Cooling of the melt results again in phase separation due to the recovery of hard and soft segments, and the polymer develops its elastic properties.

The soft segments form an elastomeric matrix responsible for most of the elastic properties of

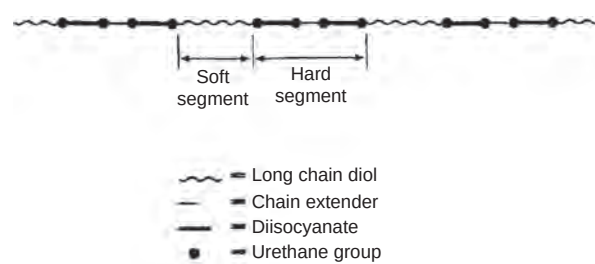
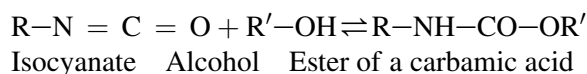


Figure 9.1 Schematic representation of thermoplastic polyurethane elastomer composed from diisocyanate, long chain diol, and chain extender.

TPUs, and the hard segments act as multifunctional tie points, functioning as both cross-links and reinforcing fillers. These cross-links can be removed by heat or by the use of solvents [8]. The TPU network can be recovered by cooling, as mentioned earlier, or by evaporation of the solvent. In order to obtain thermoplasticity, the average functionalities of the starting materials should be close to 2.00; that is, each prepolymer and monomer unit should have two terminal groups. This ensures the formation of high-molecular-weight linear chains with no or only few branch points [9–11a,11b].

9.2 Synthesis of TPUs

The basic reaction of the polyurethane chemistry is that between an isocyanate and a compound containing a hydroxyl:



The resulting compound is an ester of a carbamic acid. The trivial name *urethane*, which is used for the compound ethyl carbamate, gave the polyurethane chemistry its name: polyisocyanates and polyols form polyurethanes [12]. There are many other possible reactions of the isocyanate group, the most common are those with compounds containing groups with active hydrogen, such as $-\text{NH}_2$, $-\text{NH}-$, $-\text{COOH}$, $-\text{CONH}_2$, and, of course, with water.

The reactions that are of importance for the preparation of TPUs are those between diisocyanates and a variety of compounds containing terminal hydroxyl groups, such as diols. Clearly, isocyanates and diols form linear polyurethanes.

In general, TPUs are prepared from long-chain polyols with the average molecular weight in the range from 600 to 4000, chain extenders with molecular weights in the range of 61 to 400, and a polyisocyanate. The choice of the components of the reaction mixture and their ratio determine the properties of the final product, which may range from soft and flexible to hard, high modulus material.

9.2.1 Raw Materials for TPUs

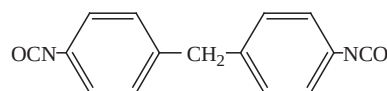
9.2.1.1 Raw Materials for Soft Segments

The soft segments of a TPU are long and flexible and control the low-temperature

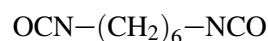
properties, the resistance to solvents, and the resistance to weather. The main raw materials for soft segments are hydroxyl-terminated polyesters and polyethers. Generally, more polyesters than polyethers are used for the polyol component [13]. Typical examples of polyesters are adipates, polycaprolactones, and aliphatic polycarbonates [14]. Typical examples of polyethers used on a large scale are poly(oxypropylene) diols and the poly(oxytetramethylene) diols. Mixtures of polyethers and polyesters are sometimes used and yield a very useful combination of properties at an attractive cost [15,16]. General trends in properties produced by the commonly used polyols are shown in Table 9.1.

9.2.1.2 Raw Materials for Hard Segments

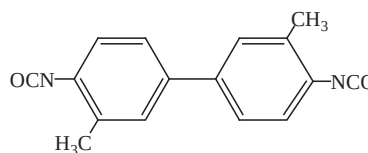
As pointed out earlier, the raw materials used for hard segments are isocyanates and chain extenders. From the commercially available polyisocyanates, only a very few are being used for the manufacture of thermoplastic polyurethanes [17]. The most widely used is MDI:



Other isocyanates used for TPUs are hexamethylene diisocyanate (HDI):



and 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI) [18]:



The most widely used chain extenders are linear low-molecular-weight diols, such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and hydroquinone bis(2-hydroxyethyl) ether, and these are the most suitable for TPUs.

Table 9.1 Important Polyols^a and Corresponding Thermoplastic Polyurethane Elastomers^b

Polyol Nomenclature	Polyols		Elastomers	
	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$	$T_g, ^\circ\text{C}$	Hydrolytic Stability
Poly(ethylene adipate) glycol	-46	52	-25	Fair
Poly(butylene-1,4-adipate) glycol	-71	56	-40	Good
Poly(ethylene butylene-1,4-adipate) glycol	-60	17	-30	Fair/good
Poly(hexamethylene-2,2-dimethylpropylene adipate) glycol	-57	27	-30	Good
Polycaprolactone glycol	-72	59	-40	Good
Poly(diethylene glycol adipate) glycol	-53	/	-30	Poor
Poly(hexadiol-1,6 carbonate) diol	-62	49	-30	Very good
Poly(oxytetramethylene) glycol	-100	32	-80	Very good

T_g : Lower end of glass transition range.

^aMolecular weight 2000.

^bHardness approx. 85 Shore A.

9.2.1.3 Other Raw Materials

Other materials used widely in the thermoplastic polyurethanes are:

- *Mold release agents* are useful for fast and economical cycle times. These are either derivatives of fatty acids, or silicones, or certain fluoroplastics. They are added in amounts 0.1–0.2% by weight.
- *Antidegradants*, such as aromatic carbodiimides, are added to polyester-based TPUs to reduce their hydrolytic degradation, in amounts typically 1–2% by weight. Sterically hindered phenols and certain amines reduce the degradation by heat and oxidation.
- *Ultraviolet (UV) absorbers*, such as benzophenones or benzotriazols, combined with sterically hindered amines (HALS) stabilize the TPU materials against discoloration by UV light [19].
- *Mineral fillers*, such as calcium carbonate, talc, and silica fillers, are added for better release in molding and in film production. They often act as nucleating agents (to promote crystallization) or produce a rough surface.
- *Reinforcing fillers* (mica, glass fibers, organic fibers) are used to reinforce TPU materials.
- *Lubricants*, such as graphite, molybdenum sulfide, PTFE micropowders, or silicone oil, are used to reduce the coefficient of friction.

- *Plasticizers* are used to produce soft grades of thermoplastic polyurethanes and are added in amounts up to 30% by weight [20].

The isocyanate-to-hydroxyl ratio is critical to the molecular weight control of the TPU products. The initial molecular weights of the products decrease with the increase or decrease of NCO:OH ratios from the equivalence point, that is, where $\text{NCO:OH} = 1$ (see Fig. 9.2). However, the molecular weights of the products synthesized above the equivalence point

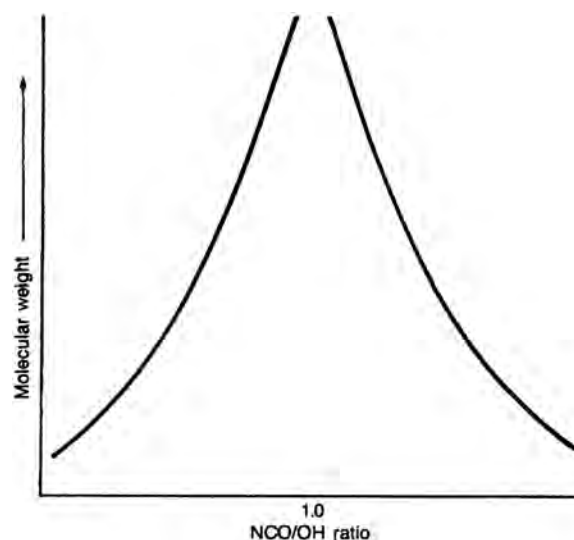


Figure 9.2 The relationship of the initial molecular weight of thermoplastic polyurethane elastomer and the NCO/OH ratio.

ultimately will increase because of the reaction of excess isocyanate with moisture, urethane, and urea groups, to give urea, allophanate, and biuret, respectively.

The reaction components are mixed and heated to temperatures above 80 °C (176 °F). To achieve optimum results, the ratio of isocyanate groups to the sum of the groups reacting with them should be close to 1.0. If this ratio is lower than 0.96, polymers with insufficiently low molecular weight are obtained, and if it is higher than 1.1, cross-linking and other reactions occur (see earlier), which yield products that are difficult to process by thermoplastic processing methods. An average molecular weight (M_n) of 40,000 is sufficient for the development of satisfactory properties, and this can be achieved if the ratio of the reacting groups is 0.98 and higher.

There are several ways to carry out the reaction. In the *one-shot method*, all the reactants are mixed together. In the *prepolymer method*, the isocyanate is first reacted with the polyol. This produces a prepolymer, which is then reacted with the chain extender. The polymer can be produced in a batch process [21] or continuously in a mixing chamber or a reaction extruder [22a,22b–24].

For large-scale industrial production, two methods are commonly used: the belt process and the reaction extruder process. In the *belt process* all ingredients are mixed together and poured onto a belt. The product solidifies on the surface of the belt, forming a slab. The slab is then converted into granules. The granules may be used as such but they are often fed into an extruder and extruded into pellets that are more uniform in size. In the *reaction extruder process*, the reaction is almost complete at the end of the extruder and the product is immediately extruded into pellets.

The heat history during the production of TPUs is very important because the phase separation of the soft and hard segments is temperature dependent. Another factor is the shear conditions during the build-up of the molecular weight. In the belt process, the reacting melt does not experience any shear after leaving the mixing chamber whereas during reactive extrusion the melt is subjected to a significant shearing stress all the time. Typically, TPUs produced by reactive extrusion show a less pronounced phase separation resulting in lower crystallinity [25].

Because the phase separation determines essentially the properties of the TPU, it is possible that

even when starting from the same reaction mixture, the physical properties of the resulting polymers will be very different [26–33].

9.3 Morphology

The morphology of the multiphase system is an important factor in determining the final properties of the polymer. In general, desired properties of a material can be obtained by controlled variation of the morphology. For that reason, a very good knowledge of the morphology is essential for the understanding of structure–property relationship. In the case of urethane block copolymers, this became a formidable challenge because of complications due to physical phenomena such as crystallization, phase mixing, hydrogen bonding in both segments, and dependence of properties on thermal history. In general, a higher degree of phase separation is expected for a copolymer system where one component is crystallizable. In polyurethanes, both the soft and hard phases may be amorphous or partially crystalline [34].

The chemical composition and the molecular weight of the long-chain diols have a major effect on the extent of phase separation of the TPU. Because of stronger hydrogen bonding, the phase mixing of a polyester-based TPU is generally greater than that of a polyether-based TPU. The phase separation is determined by the molecular weight of the long-chain diols; the higher their molecular weight, the better is phase separation [35].

9.3.1 Morphology of Hard Segments

Extensive studies were performed to elucidate the nature of the hard-segment domains, using wide-angle X-ray scattering [36], small-angle X-ray scattering (SAXS) [37–42], and X-ray diffraction [43,44]. Hard segments formed by the reaction of linear glycols and polyisocyanate (MDI) would be expected to be crystalline. However, under normal conditions, crystallinity appears to be inhibited [36]. The ordered state of the hard segments has been referred to as *paracrystalline* [37], and a suitable heat treatment was reported to transform the structure from paracrystalline to crystalline [38]. Relatively high temperatures and long annealing times (190 °C, 12 h) are reportedly required to produce a significant hard-segment crystallinity [45].

9.4 Thermal Transitions

Thermal transitions, such as melting, glass transitions, and phase segregation, have been studied by several investigators. A study analyzed the thermal response of a TPU based on a polyesterdiol, butanediol (BDO), and MDI with respect to engineering properties using differential scanning calorimetry (DSC) [46]. With increasing hard segment content, the glass transition is broadened and shifted toward higher temperatures. The observed glass transition shift may be explained by an increasing amount of hard segments that are “dissolved” in the soft matrix. It was postulated that a concentration gradient of hard segments exists near the phase interface.

The kinetics of phase separation has been studied and reported in [47,48]. Polyester TPUs were quickly heated and then rapidly quenched to room temperature. Changes in phase separation were monitored by SAXS and DSC as a function of time. It was shown that it took as much as several days to regain equilibrium as a result of kinetic and viscous effects.

Interphase mixing phenomena, as studied by thermal analysis and SAXS, have been explained in terms of the hydrogen bonding ability of soft segments [41,42,49]. Other, more-involved studies on specific systems using DSC [50,51], thermo-mechanical studies, DSC, X-ray scattering, and infrared analysis [51–55] were performed to elucidate their structural organization and thermal transitions. A similar study is described in Senich and MacKnight [56].

In general, it can be concluded that the glass transition temperature of the soft segments is a sensitive measure of the degree of phase separation. As the hardness of the TPU is increased by the increasing proportion of hard segments, the extent of phase mixing also increases, resulting in a decrease of low temperature flexibility. This can be offset by incorporating soft segments with a higher molecular weight or by the use of preextended polyols [57].

9.5 Properties

As pointed out earlier, TPUs were the first polymeric materials to combine both rubber elasticity and thermoplastic characteristics. The proportion of hard segments (formed by the diisocyanate and the short-chain diol) is the factor determining the majority of properties of the resulting material, such as hardness, modulus, tear strength, and upper use temperature. The proportion of soft segments determines the elastic and low-temperature properties. Typically, the molar ratios of polyol:chain extender:diisocyanate range from 1:0.5:1.5 for soft grades (Shore A hardness about 60) up to 1:20:21 for harder grades (Shore D values higher than 70) without the use of plasticizers or reinforcing agents. With Young moduli values ranging from 5 to 2000 MPa [58,59], TPUs are virtually bridging the gap between elastomers and plastics (see Fig. 9.3). The stiffness of a given TPU can be further increased with inorganic and organic fillers, especially glass fibers [60]. The exceptional

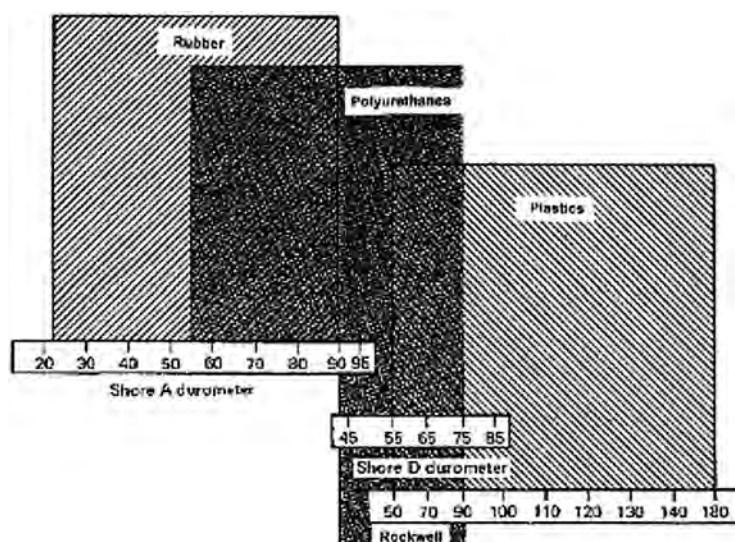


Figure 9.3 Thermoplastic polyurethane elastomers bridging the gap between elastomers and plastics.

flexibility of the chemistry used in the synthesis of TPUs accounts for the numerous products available commercially.

9.5.1 Mechanical Properties

TPUs exhibit high tensile strength and ultimate elongation (see Fig. 9.4). Additional valuable attributes are an exceptional resistance to tear propagation and abrasion. The properties are dependent on temperature (see Figs 9.5 and 9.6) and on hardness (compare Figs 9.5 and 9.7). Most commercial TPUs are ester based, and the mechanical properties of these grades are superior to those of TPUs made from the more expensive poly(oxytetramethylene) diol. These polyether-based materials are well suited for situations where high resistance against hydrolysis or microbial deterioration and/or improved low-temperature flexibility is required [61]. Poly(oxypropylene) diols are used mainly in mixture with polyester glycols, and such hybrid products are a good compromise having properties and cost between those of ether- and ester-based TPUs. Further advantages are often gained when preparing ether-ester TPUs via a special synthesis procedure [16].

The properties of TPUs are strongly affected by domain morphology, as pointed out earlier. Phase

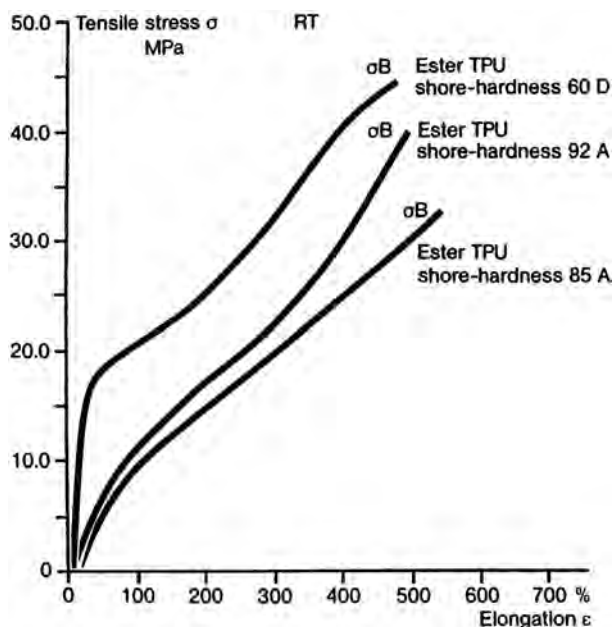


Figure 9.4 Stress–strain curves of three thermoplastic polyurethane elastomers (TPUs) with different hardness values.

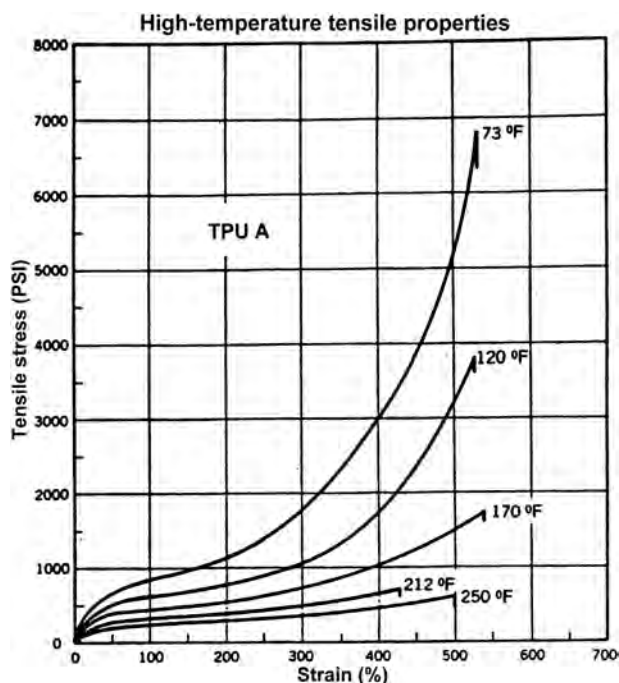


Figure 9.5 Effect of high temperatures on the stress–strain curve of thermoplastic polyurethane elastomer TPU A (hardness 85 Shore A).

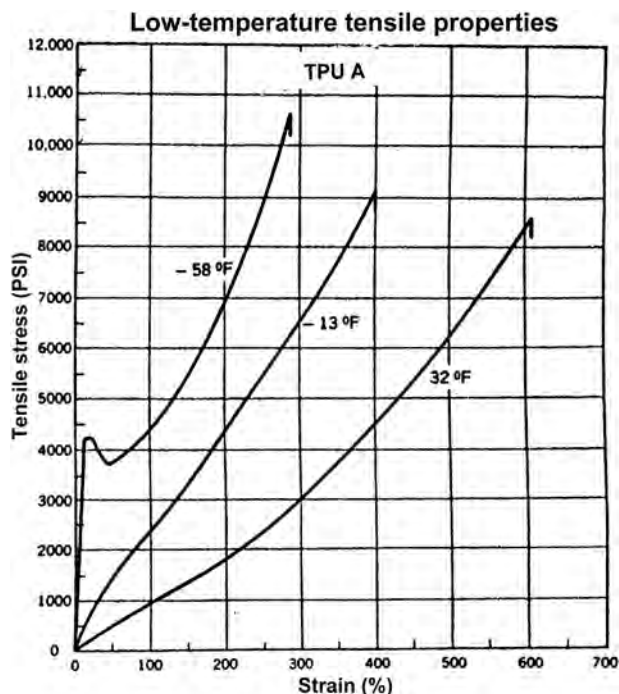


Figure 9.6 Effect of low temperatures on the stress–strain curve of thermoplastic polyurethane elastomer TPU A (hardness 85 Shore A).

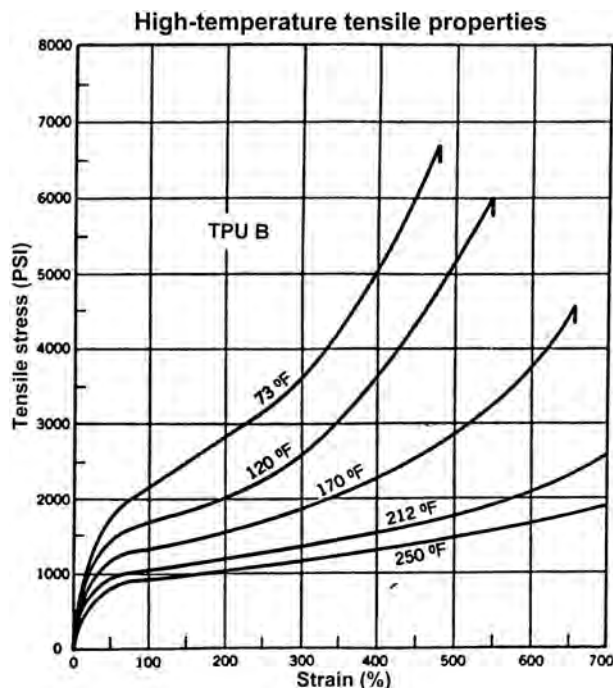


Figure 9.7 Effect of high temperature on the stress–strain curve of a thermoplastic polyurethane elastomer TPU B (hardness 55 Shore D).

mixing takes place during the heat processing or treatment of the TPU, while phase separation occurs on rapid cooling. Several studies showed that the mechanical properties of TPUs are strongly related to the time-dependent formation of domain morphology [48,62–64]. Therefore, to obtain optimum properties, postcuring is recommended after thermal formation. Postcuring conditions vary with the type of TPU material. Often it is sufficient to store it at ambient temperature for 2–3 weeks. If it is necessary to attain ultimate physical properties on TPU parts immediately after fabrication, a postcure in a circulating hot air oven for 8–16 h at 230 °F (110 °C) is usually sufficient [65]. Because postcuring is time consuming and means additional work, most production parts are not subjected to a postcuring cycle. Postcuring is used mainly in cases where improvement of compression set is desired [66].

9.5.1.1 Stress–Strain Properties

TPUs offer high tensile strength and elongation. Depending on their chemical structures and hardness, tensile strength values of TPUs range typically from 25 to 75 MPa (3600–10,000 psi) (see Fig. 9.4). The stress–strain curve of TPU is generally believed to

be affected by the hard segment-to-soft segment ratio, soft segment length, hard segment crystallinity, and susceptibility of the hard segment to reorientation and alignment. Because this reorientation is time dependent, the stress–strain curve is affected by the extension rate [67]. Temperature also affects the stress–strain curve of TPUs as pointed out earlier (see Figs 9.5 and 9.7). This is explained by the finding that the moduli at fixed strain decrease with increasing temperature [67].

9.5.1.2 Compression Set

The compression set is an elastic recovery behavior under a specific loading or a specific deflection at various times and temperatures. The usual method is ASTM D 395, Method B that includes 22-h loading at a constant deflection of 25%. Typical values for TPUs measured at room temperature range from 10% to 50% depending on the polymer and conditioning cycle [68]. When measured under a 25% deflection at 70 °C (158 °F) for 22 h, the values are typically in the range from 60% to 80% without postcuring and 25% to 50% with postcuring. Slightly cross-linked TPUs give lower compression set values [69].

9.5.1.3 Hardness

Hardness of a material is its ability to resist deformation, indentation, or scratching. Shore A and Shore D tests (ASTM D2240 or ISO 868) are most commonly used to measure the hardness of TPUs. The softer materials are measured by Shore A and the harder ones by Shore D. Because of their block copolymer nature, TPU with hardness values between Shore 70 A and about Shore 80 D can be obtained by varying the ratios of hard segment to soft segment. The hardness, along with modulus, load-bearing capacity (compressive stress), tear strength, and specific gravity of a TPU normally increases with increasing hard segment content.

9.5.1.4 Stiffness

The stiffness is expressed by the flexural modulus, which is determined during the initial bending of a test specimen. It is obtained from test according to ASTM D 790. Although hardness of a TPU is related to its flexibility, it is not directly indicative of its stiffness.

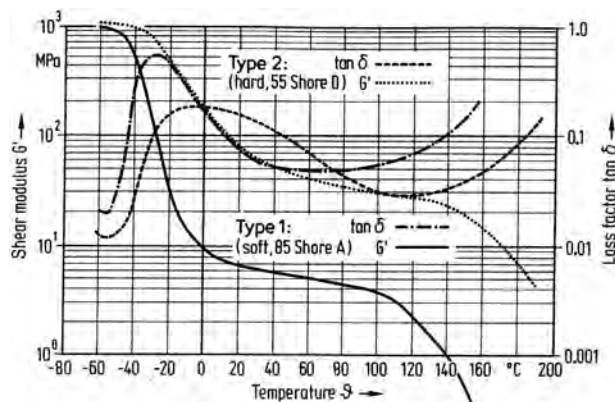


Figure 9.8 Mechanical loss factor ($\tan \delta$) and storage (shear) moduli vs temperature for thermoplastic polyurethane elastomers of different hardnesses.

9.5.1.5 Dynamic Properties

TPUs have higher mechanical damping than most elastomeric materials [70]. The mechanical loss factor, $\tan \delta$, the ratio of loss modulus and storage modulus (G''/G'), and its dependence on temperature are shown in Fig. 9.8 for two TPUs with different hardnesses. It is lower in the softer grades at room temperature. The temperature rise is also lower at equivalent deformation. Fig. 9.8 also depicts the temperature dependence of the storage (shear) modulus (G').

Because TPU is a poor thermal conductor, the heat resulting from dynamic loading is dissipated slowly. The heat buildup is a function of both frequency and force applied. Therefore, parts, such as solid wheels or rollers made from TPU should not run at high speeds or overloaded. The choice of a suitable TPU for dynamic application depends on modulus. The higher is the stiffness, the lower is the deformation under comparable load.

9.5.2 Thermal Properties

Thermoplastic urethanes can be used from $-40\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ (-40 to $176\text{ }^{\circ}\text{F}$) for long-term use and up to $120\text{ }^{\circ}\text{C}$ ($248\text{ }^{\circ}\text{F}$) for short-term exposure. In some cases, even higher temperatures can be tolerated [71].

The following factors contribute to higher service temperature [72]:

- Proportion of hard segments
- Type and amount of chain extender
- Type of diisocyanate

The harder the product (more isocyanate and chain extender), the higher is the service temperature.

Mechanical properties, including stiffness and elasticity, also depend on temperature, and hardness shows similar dependence on temperature.

Most of the changes described here occur due to the change in morphology (e.g., melting of the hard segments) and are related to the thermoplastic nature of the TPU materials. This process is reversible.

The other process, taking place at higher temperatures, is chemical degradation, a destructive change in chemical structure. The thermal stability of a TPU is strongly dependent on the structures of the isocyanates and chain extenders used for its synthesis [73,74]. The majority of TPUs decompose slowly at $150\text{--}200\text{ }^{\circ}\text{C}$ ($302\text{--}398\text{ }^{\circ}\text{F}$) and at a measurable rate at $200\text{--}250\text{ }^{\circ}\text{C}$ ($398\text{--}482\text{ }^{\circ}\text{F}$) [65]. Several studies indicate that the thermal decomposition of ether-based TPUs is predominantly an oxidative process. The ester-based TPUs normally exhibit considerably better thermal and oxidative stability than the ether-based ones [75].

Other thermal properties, such as thermal conductivity, specific heat, heat of fusion, and coefficient of linear expansion (in US units), are shown in Table 9.2.

Table 9.2 Typical Thermal Properties of Thermoplastic Polyurethane Elastomers

Property	Test	Unit	Value
Thermal conductivity	ASTM D2214 Cenco-Fitch	BTU/(ft ²) (hr) (°F/in)	1.5–2.5
Specific heat (at 212 °F)	DTA	BTU/(lb) (°F)	0.40–0.45
Heat of fusion	DTA	BTU/(lb)	1.8–6.6
Coefficient of linear thermal expansion	ASTM D696	$10^{-5}/^{\circ}\text{F}$	6.5–9.5

Ref. [65,76], p. 233.

9.5.3 Hydrolytic Stability

TPUs contain ester (and/or ether) urethane linkages, so some degree of hydrolysis will inevitably occur. From published data [76], the hydrolytic stability of TPUs based on three different long-chain diols is as follows:

Polyether > Polycaprolactone > Polyester

Although the urethane linkage can be hydrolyzed, the cleavage of ester linkage is the primary route for hydrolytic degradation of the ester-based TPUs [76]. Acids present in the TPUs tend to catalyze the cleavage of carboxylic esters. This can be prevented by the addition of carbodiimides that act as acid scavengers [76,77]. The hydrolysis of urethane linkages is the major way of the decomposition of ether-based TPUs. It is believed to cause chain cleavage that leads to the reduction of average molecular weight. When the molecular weight is reduced to a critical value, cracks will develop on the surface of the material [78]. With increasing hardness, the materials become more resistant to hydrolysis because of the hydrophobic nature of the hard segments.

9.5.4 Chemical Resistance

In general, TPUs are resistant to pure mineral oils, diesel oils, and greases. However, some additives in these media may adversely affect the resistance of the TPU material. TPUs generally resist well to gasoline and other petroleum fuels if they do not contain alcohol. Such fuels containing alcohols and aromatics cause a reversible swelling of the TPU material. The extent of such swelling is proportional to the content of such ingredients [79].

Nonpolar solvents, such as hexane or heptanes, have practically no effect on TPUs. On the other hand, chlorinated hydrocarbons and aromatic hydrocarbons cause a very severe swelling [80]. The degree of swelling depends on the structure of the TPU; soft TPUs swell more than hard ones. The ether types of TPU swell more than do the polyester types.

Polar solvents, including dimethylformamide, tetrahydrofuran, *N*-methyl pyrrolidone, dimethylacetamide, and dimethylsulfoxide, are considered good solvents for TPUs [81]. Soft linear polyurethanes can be dissolved in the mixtures of methyl ethyl ketone and acetone and applied as adhesives. Harder linear polyurethanes are dissolved and

applied as coatings on textile, leather, and other substrates [82].

TPUs are sensitive to acids and bases and attacked even by diluted acids and bases at room temperature. At higher temperatures, they cannot withstand concentrated acids and alkali [82]. However, the effect of solutions of weak acids or bases (pH 5.5–8) can be considered similar to that of water [78].

9.5.5 Abrasion Resistance

TPUs exhibit an excellent resistance to abrasive wear. However, the abrasion of a lubricated TPU during the test is believed to be related to the coefficient of friction, stress loading, and contact areas. The abrasive wear of a lubricated wear is generally lower than that from an unlubricated specimen, probably because of a decreased heat buildup from friction [69]. A comparison of abrasion resistance (abrasion weight losses) of TPU to several other polymers is given in Table 9.3.

9.5.6 Ultraviolet Stability

TPUs based on aromatic isocyanates exhibit loss of mechanical properties and discoloration (yellowing) on exposure to sunlight [83]. The discoloration is explained by the photo-oxidation of the aromatic diurethane bridges [75]. TPUs based on aliphatic

Table 9.3 Abrasion Resistance of Different Polymers^a

Material	Weight Loss, mg
TPU	0.4–3.2
Ionomer	12
Nylon 6/10	16
Nylon 6/6	58
Impact-resistant PVC	89
Nylon 6	104
Natural rubber tread formulation	146
SBR premium tread formulation	177
SBR tread formulation	181
High-impact polystyrene	545

^aASTM C501, CS-17 Wheel, 100 g load, 5000 revolutions. Ref. [65].

diisocyanates, such as HDI or H12-MDI, do not show this discoloration [69]. The UV stability can be improved by the addition of UV stabilizers [84,85]. Compositions containing carbon black also exhibit improved UV stability [86].

9.5.7 Electrical Properties

Because of the hydrophilic nature of TPUs, they are not used in applications where consistently high insulating resistance is required [87]. However, due to their flexibility and excellent abrasion resistance, they are being frequently used as protective coverings in cable applications. Typical electrical properties are shown in Table 9.4.

9.6 Processing of TPUs

The ease of processing is one of the major advantages of TPUs. They can be processed by the usual melt-processing methods, such as extrusion, injection molding, and calendering. Because some of the compositions can be dissolved in solvents, they can be processed by the solution fabrication. Not all

the grades can be used universally; each method requires specific grades with appropriate morphology and melt viscosity.

9.6.1 Rheology of TPUs

Under processing conditions, TPU melts have much higher viscosities than those of low-molecular-weight fluids. The melts exhibit non-Newtonian flow behavior, or pseudoplasticity; that is, the melt viscosities depend not only on temperature and pressure but also on the rate of deformation (see Fig. 9.9). The response of melt viscosity to temperature, which is important in processing, is shown for different grades of TPUs in Fig. 9.10. Increasing the melt temperature by 10 °C typically results in an increase of the melt:volume ratio (MVR) by a factor of 2–4 [79].

9.6.2 Drying

TPUs absorb moisture rapidly on exposure to atmospheric air. The moisture pickup and equilibrium level are humidity dependent (see Fig. 9.11). Because the optimal moisture content of the material to be processed is less than 0.05%, it has to be dried.

Table 9.4 Typical Electrical Properties of Thermoplastic Polyurethane Elastomers

Property	Test	Unit/Condition	Value
Volume resistivity	ASTM D257	$10^{12} \Omega\text{-cm}$	2–50
Surface resistivity	ASTM D257	$10^{12} \Omega$	3–120
Dielectric constant	ASTM D150	@ 60 Hz	5–7
		@ 10^3 Hz	5–7
		@ 10^6 Hz	4–5
Dissipation factor	ASTM D150	@ 60 Hz	0.015–0.050
		@ 10^3 Hz	0.020–0.050
		@ 10^6 Hz	0.050–0.100
Loss factor	ASTM D150	@ 60 Hz	0.12–0.22
		@ 10^3 Hz	0.12–0.16
		@ 10^6 Hz	0.22–0.33
Capacitance	ASTM D150	$\mu\mu\text{Farad @ 60 Hz}$	65–70
		$\mu\mu\text{Farad @ } 10^3 \text{ Hz}$	61–69
		$\mu\mu\text{Farad @ } 10^6 \text{ Hz}$	52–57
Arc resistance		s	0.122
Dielectric strength	ASTM D149	V/mil, short time	300–500

Ref. [76]; Texin and Desmophan, *Thermoplastic polyurethane elastomers: a guide to engineering properties*. Pittsburgh (PA): Bayer Material Science LLC; 2004. p. 233.

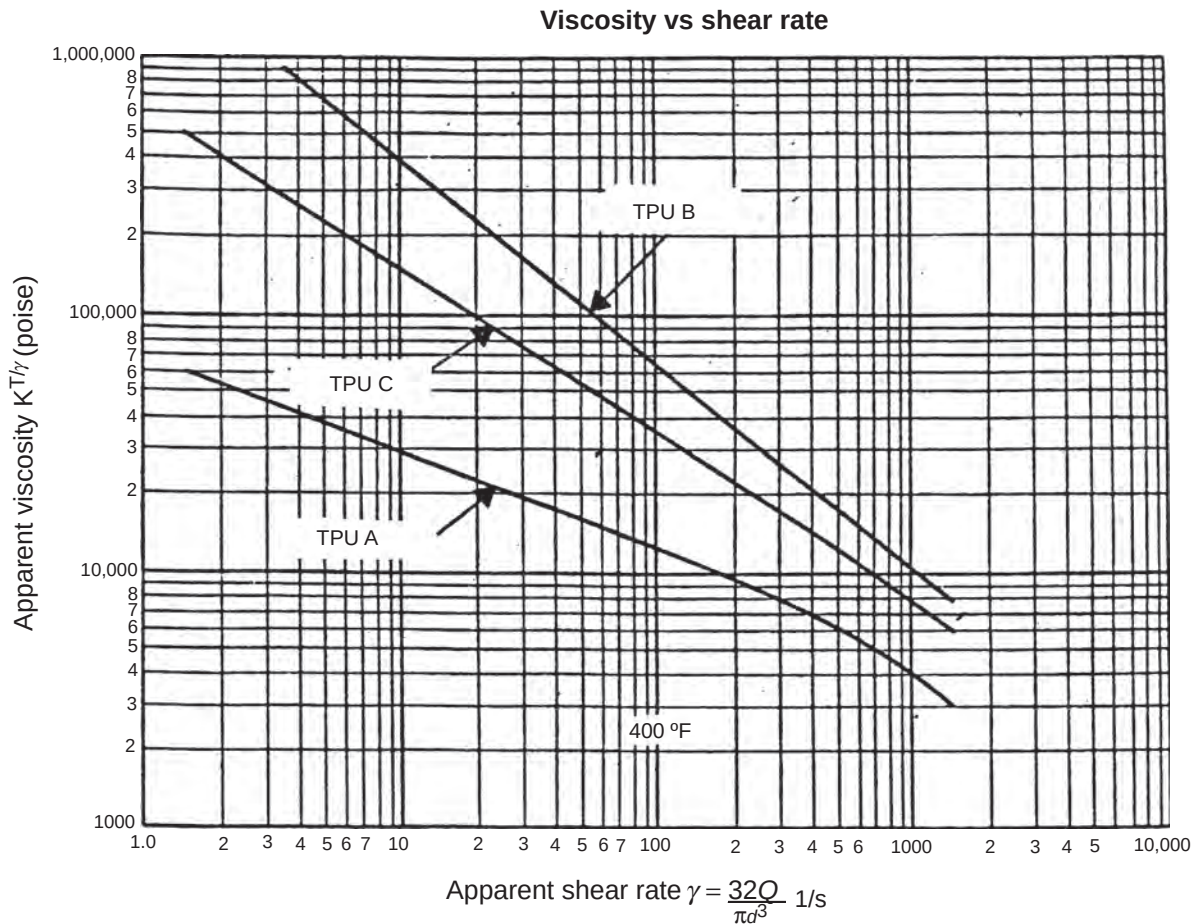


Figure 9.9 Melt viscosity vs shear rate of different grades of thermoplastic polyurethane elastomer (TPU). TPU B (55 Shore D), TPU C (91 Shore A), TPU A (85 Shore A).

Excessive moisture content in the material being processed results in molding and extrusion difficulties. In extrusion process bubbles, poor surfaces, wave forms, surging, and degradation are observed. In injection molding, defects due to excessive moisture are blisters, splay marks, bubbles, porous (foamy) melt, nozzle drool, and poor physical properties of the finished parts. One possible drying procedure is on trays in an oven by circulating air heated to 80–100 °C (176–212 °F) [79] for several hours. In such a case, pellets of the TPU should be spread 1 inch deep maximum. A better method is using desiccant hopper driers (Fig. 9.12) capable of providing hot air with a dew point of –18 °C (0 °F) maximum. In this drying equipment, softer grades of TPUs are dried typically at temperatures of 82 °C (180 °F) and harder grades at 104 °C (220 °F) with residence times of 1–3 h [65]. Prolonged drying should be avoided to prevent material discoloration [88].

9.6.3 Injection Molding

The primary function of injection molding is to shape polymeric materials into desired articles. It is a discontinuous process, divided into plasticating, injection, and ejection stages. TPUs can be molded on both inline reciprocating screw-type or ram-type machines. The inline reciprocating screw machine is preferred because it provides a more homogeneous melt with more uniform temperature. Moreover, it permits processing at lower temperatures, which is generally an advantage.

A machine suitable for the injection molding of TPUs should have temperature control capabilities up to 475 °F (246 °C) and deliver an injection force up to 15,000 psi (105 MPa). The mold clamp force needed for most TPUs is 3–5 tons per in² or 0.5–0.8 metric ton per cm² of the projected area of the part. A nonreturn valve for TPU resins should be a free-flowing, sliding check-ring type made from

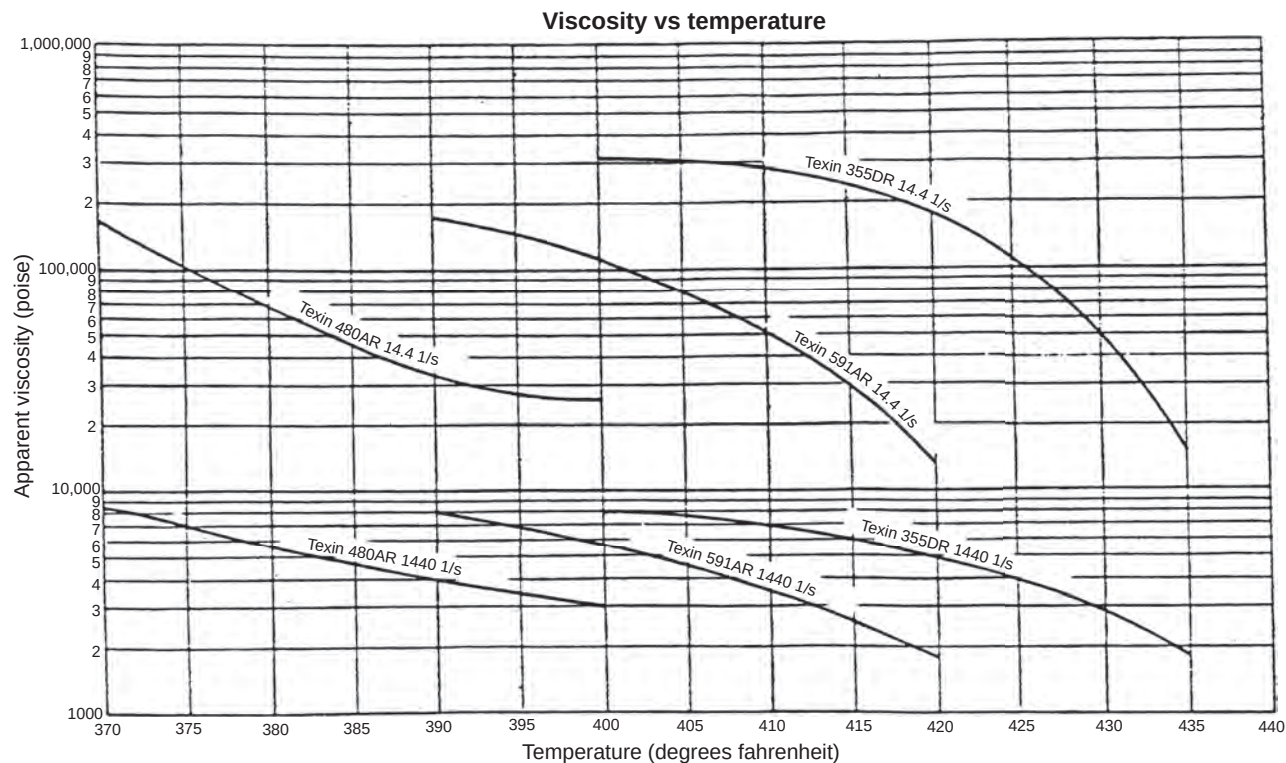


Figure 9.10 Melt viscosity vs temperature of different grades of thermoplastic polyurethane elastomer (TPU). Texin 355 DR (55 Shore D) (TPU B), Texin 591 AR (91 Shore A) (TPU C), Texin 480 AR (85 Shore A) (TPU A).

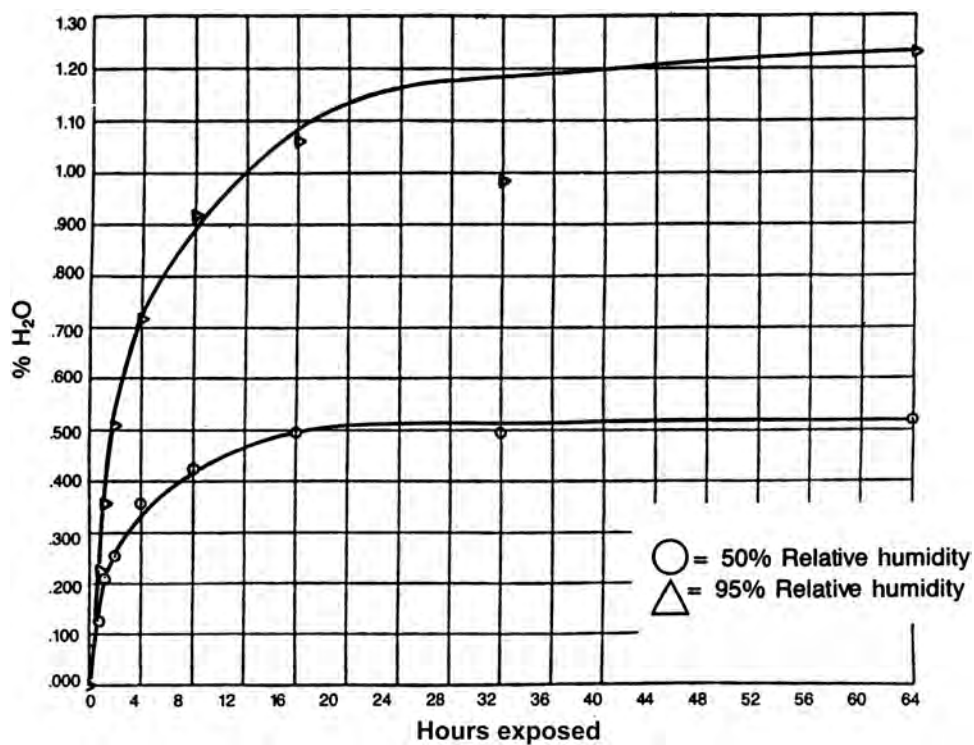


Figure 9.11 The moisture pickup rate in dependence on relative humidity for an 85 Shore A thermoplastic polyurethane elastomer TPU.

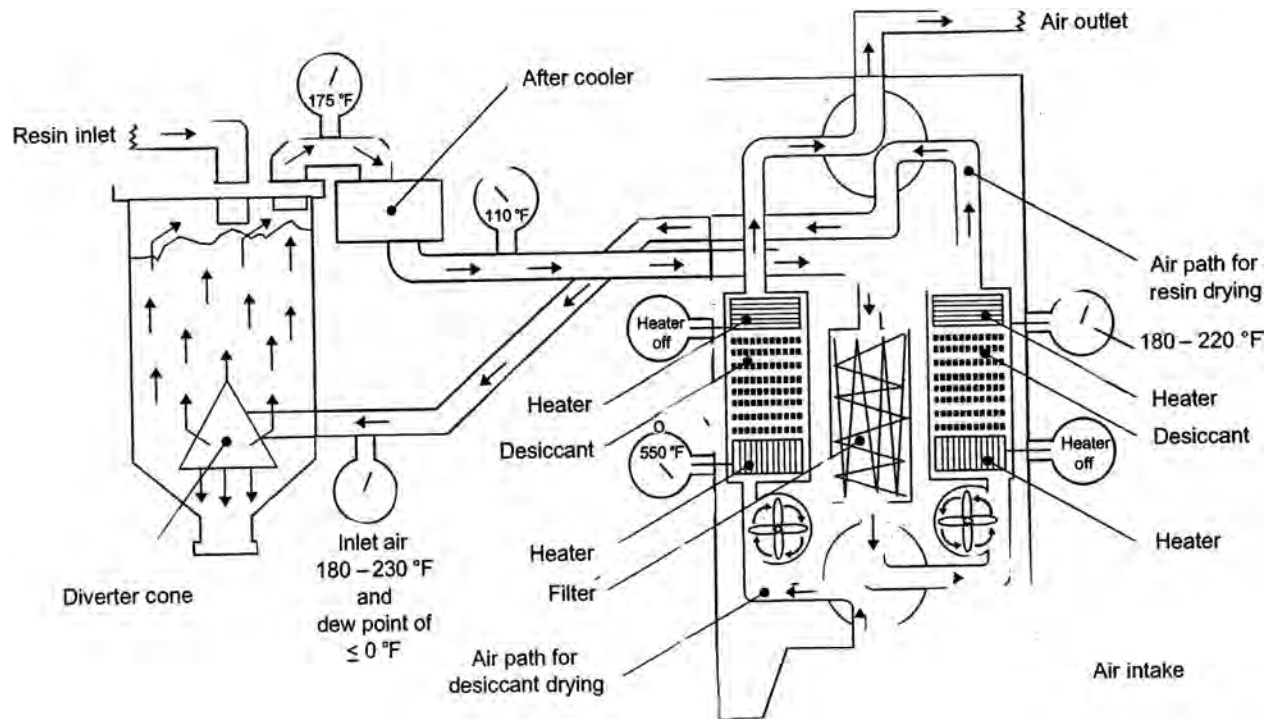


Figure 9.12 Schematic of a desiccant dehumidifying hopper dryer system.

hardened steel, preferably nitrided to retard wear, and installed near the screw tip area to prevent backflow and maintain maximum pressure.

A general-purpose screw with a length-to-diameter ratio L/D of at least 20:1 with a compression ratio 2.0:1 to 3.0:1 is preferred, although a 2.5:1 compression ratio is satisfactory for most applications (see Fig. 9.13). Nylon-type (rapid-transition) screws are not recommended because they cause excessive buildup of melt temperature and very likely

will cause its degradation. A chrome-plated screw is advantageous for an easy cleaning. The barrel liner should be made from bimetallic abrasion-resistant alloy, such as XaloyTM [89].

A general-purpose, free-flowing nozzle with a reverse taper at the nozzle exit has been found to be suitable for the processing of TPUs. The nozzle should be as short as possible. It is essential that the nozzle and sprue bushing mate properly and that its orifice is slightly smaller (about 20%) than the sprue

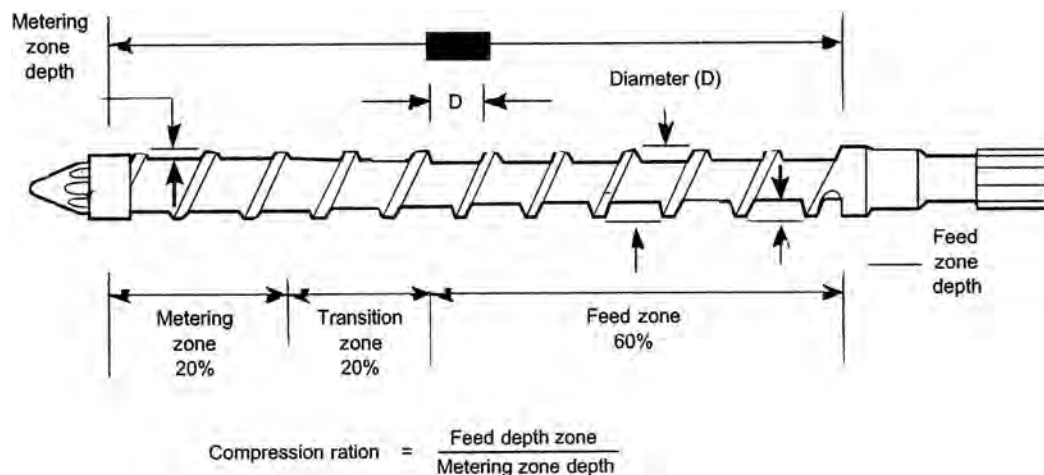


Figure 9.13 Injection molding screw for thermoplastic polyurethane elastomer TPU.

bushing orifice. A separate temperature control for the nozzle is preferred.

Uniform molding cycles are essential to maintaining optimum processing conditions and producing the highest quality parts. This can be accomplished by the installation of state-of-the-art closed-loop systems that can ensure both the precise injection stroke and switchover point that are critical for molding quality parts. This control equipment can adjust hold pressure in increments to minimize sinks and voids. In addition, it can maintain melt pressure in the mold cavity uniformly from shot to shot despite variations in the operating conditions of the machine.

When using screw-type machines, use of 40–80% of the barrel capacity is desirable. If the shot weights are smaller than 40%, there is a chance that the material can degrade due to its small weight and excessive heat buildup in the melt.

9.6.3.1 Operating Conditions

Operating parameters of temperature, time, and pressure affect the properties of the finished part to a high degree. A homogeneous and off-white to beige color melt should be obtained with the proper processing conditions.

Barrel temperatures vary with different grades of TPUs (different hardness), with part design, ratio of shot volume to barrel volume, and cycle time. Typical temperature profile ranges from 350 to 450 °F (177–232 °C).

Injection pressure in the range 6000–15,000 psi (41–103 MPa) is adequate for most parts made from TPUs. Low injection molding pressures may not fill the mold completely with the material. Too much pressure may cause the material to overfill the mold and create flash.

Hold pressure: Typically, hold pressure is about 60–80% of the injection pressure.

Injection cushion (resin feed): Best results are obtained when the cushion does not exceed 0.125 in (3.175 mm). Too much cushion can lead to overpacking of the part [89].

Screw back-pressure below 200 psi (1.4 MPa) is needed for sufficient homogenization.

Screw speed: Because low shear is generally required for processing TPUs, screw speeds of 20–80 rpm are typical, with 20–40 rpm being preferred [90].

Injection speed: It is of advantage to fill the mold as fast as possible to minimize the appearance of weld lines, improve weld-line strength, improve surface appearance, and lower the injection pressure. Thicker section parts require a slower injection speed; thinner ones require a faster injection rate. Overall injection time depends on the machine and the part geometry.

Mold temperature: The optimum mold temperature varies with the thickness of the part and hardness of the TPU being processed. Thicker parts require a lower temperature to effectively cool the resin within a reasonable cycle time. Softer resins require lower mold temperature than harder ones. The range is typically 50–150 °F (10–66 °C). Proper mold temperature ensures a proper release of parts.

Cycle time: The optimum cycle to produce quality parts includes a fast fill, a hold time just long enough for the gates to freeze, and cooling time long enough so that the part ejectors do not penetrate the part. Cooling time is the major part of the total molding cycle.

9.6.3.2 Insert Molding

TPUs can be combined with a variety of materials that are molded inside the resin as an insert. The design of the insert can be straight with a smooth wall but can also have knurls, splines, reverse tapers, or undercuts.

9.6.3.2.1 Metal Inserts

Inserts of steel, aluminum, brass, zinc, and other metals can be molded into TPUs. In a majority of cases, sufficient bond strength can be obtained by simply degreasing the insert, applying an adhesive to their surfaces, and heating them to 220–250 °F (104–121 °C) before placing them into the mold. Very often, polyurethane-based adhesives work well [89].

9.6.3.2.2 Nonmetallic Inserts/Overmolding

TPUs can be also joined to many nonmetallic parts, including other thermoplastics in the mold, thus obtaining molded parts with both flexible and rigid components. Usually, the rigid substrate (molded part) is molded first and placed after a short time (usually less than 3 h to ensure a proper bonding) to an injection mold, and the flexible

component is injected onto it [89]. The factors for a good bond are:

- Chemical affinity (adhesion)
- Mechanical anchoring potential of the substrate material
- Processing order

Bonding of TPUs to different materials is illustrated in Table 9.5.

9.6.3.3 The Use of Regrind

Sprues, runners, and scrapped parts from TPUs can be ground and reused. Although up to 100% regrind has been used successfully [91], the maximum amount of 20% may be used with virgin material, depending on the end-use requirements of the molded parts. The regrind must be clean, dried at 180–230 °F (82–110 °C) for 1–3 h [89], and thoroughly blended with virgin resin prior to drying and processing. The use of regrind should be avoided

where material properties equivalent to virgin resin are required, including color, impact strength, and load-bearing performance.

9.6.4 Extrusion

9.6.4.1 Screw Design

TPUs can be extruded on all modern conventional, single-screw extruders. The screws for the extrusion of TPU should have an L/D ratio of at least 24:1 with a compression ratio of least 3:1. The transition zone should be long and gradual, with the metering zone long (up to 50% of the entire screw length). The metering zone should be rather shallow to sufficiently homogenize the melt temperature. The material recommended for screws is SAE 4140 steel or a similar material with flights either flame hardened or made from Stellite™ (Cabot Corporation) alloy. The screw surface should be chrome-plated for optimum resin flow. A removable tip is desirable to allow the later addition of a mixing segment for improved processing of custom materials.

Table 9.5 Bonding of Different Injection Molded Materials

Substrate	Material Injection Molded to Substrate	Adhesion
ABS	TPU	Good adhesion
PC	TPU	Good adhesion
PC/abs blend	TPU	Good adhesion
Rigid PVC	TPU	Good adhesion
Rigid TPU	TPU	Good adhesion
PBT	TPU	Inadequate adhesion
PA	TPU	Inadequate adhesion
TPU	ABS	Good adhesion
TPU	PC	Good adhesion
TPU	PC/abs blend	Good adhesion
Flexible TPU	Rigid TPU	Good adhesion
TPU	PBT	Better adhesion, depending on type
TPU	PA	Better adhesion, depending on type
PE	TPU	No adhesion
PP	TPU	No adhesion
TPU	PE	No adhesion
TPU	PP	No adhesion

Texin and Desmopan, Thermoplastic polyurethanes, a processing guide for injection molding, Bayer Corporation; 1995.

9.6.4.2 Die Design

Because of their relatively high elastic recovery, TPU resins exhibit a significant die swell. The extrudate should be cooled as soon as it exits the die, either by immersion in water or by refrigerated cooling air, to preserve the extrudate shape [92].

9.6.4.3 Extrusion Temperature Profiles

The temperature during extrusion depends on the size of the extruder, the throughput, and the grade of the material processed and may vary between 350 and 450 °F (175–230 °C). The temperature profile used for TPU usually increases from the feed zone to the compression zone and then gradually drops off at the metering zone.

It is recommended that a water-cooled throat section be used to minimize any tendency of the material to bridge in the hopper feeder [89,92].

9.6.4.4 Extrusion Methods Used

TPUs are versatile materials and can be used for the following extrusion methods:

- Extruded sheet and film
- Cast film
- Blown film
- Tubing
- Profiles
- Crosshead extrusion (wires or other substrates)

9.6.4.5 Postextrusion Conditioning

Most extruded products from TPUs are used in service without any particular treatment, because they attain their ultimate properties shortly after normal fabrication [89]. However, if lower compression set, lower creep, and tensile decay are required, a postextrusion conditioning will enhance these properties. Usually, the property improvement is attained after 2–3 weeks' storage at ambient air. To achieve ultimate mechanical properties immediately after fabrication, the products are annealed at 230 °F (110 °C) for 4–16 h in a circulating air oven.

9.6.5 Calendering

Continuous sheet, film, and coating of varied flat substrates can be readily done on a multiroll calender. Special lubricated TPU grades with processing temperatures ranging between 280 and 330 °F (140–165 °C) are required for this process. The molten material can be delivered to the calender from an extruder or from a heated roll-mill [93].

9.6.6 Blow molding

At this writing, there were only two reports on blow molding of TPUs: a process of blow molding TPU over and through holes in aluminum or steel inserts [94] and a process of making bellows from TPU [95].

9.6.7 Thermoforming

TPUs alone are not processed by thermoforming, but sheets prepared by coextrusion with other polymers or lamination (e.g., onto ABS) are processed. TPUs provide abrasion resistance, soft feel, and improved weather resistance [96].

9.7 Blends of TPUs with Other Polymers

TPUs are miscible with certain other polymers [97–99], but they are not compatible with polyolefins. When preparing blends with compatible polymers, temperatures above 280 °C (536 °F) should be avoided. TPUs can be used as a modifier if used as a minor component, such as to improve the impact resistance of high modulus plastics [100]. Another use is as nonmigrating, nonvolatile plasticizer of PVC [101] and for improvement of adhesion of less-polar TPEs to ABS [102].

Other examples of blends of TPUs with other polymers include:

- TPU/polycarbonate: good processing properties and an interesting profile of mechanical data in the modulus range around 1000 MPa [103].
- T/ABS: These two materials show miscibility over the complete range. Increasing the ABS content results in a higher modulus and reduced abrasion resistance and tear strength. Due to the low cost of styrenics, such blends may offer economic advantage [104–106].

- Many other blends with different styrene copolymers are reported [107–109].
- Small amounts of ABS (less than 20%) are used as low-temperature impact modifiers for high-modulus TPUs or as a phase compatibilizer for hard polyester-based grades [110–112], in applications such as ski boots. Other polymers, such as acrylics, copolyamides, and ionomers, can be used as processing aids [113–115].

Mixing of different grades of TPUs is a common practice. Blends of grades of different hardness provide materials with intermediate properties or with improved processing. Blends of materials with different melt viscosities are reported to give better demolding properties in blow molding operations [116].

9.8 Bonding and Welding

9.8.1 Heat Welding and Sealing

Because of their thermoplastic nature, TPUs can be readily joined by welding. There are several methods to do so. The simplest one is *heat* or *hot plate welding*. In this method, a heated platen usually coated with polytetrafluoroethylene (PTFE) makes contact with two plastic parts until the joint area melts. The parts are then pressed together under slight pressure until the bond is set.

Bar sealing involves holding films between a double-heater element for a short period time at a given temperature and pressure, depending on the polymer used and film thickness.

Other welding methods are [117,118]:

- *Hot air or nitrogen welding* (the gas stream should be heated to 290–330 °C (554–626 °F); a round cord of TPU can be used as a weld filling material).
- *Heated mirror welding* (suitable for welding of profiles at the front). The mirrors are heated to temperatures 270–320 °C (518–608 °F).
- *Heating tool and thermal impulse welding* is used mainly for thin wall articles, such as films.
- *High-frequency welding* is suitable for flat parts with wall thickness up to 2 mm (0.08 in).
- *Friction welding* can be done on parts that are rotationally symmetrical. They have to have

sufficient torsional stiffness and resistance to pressure.

- *Ultrasonic welding* is a method using high-frequency vibration (typically 20–40 kHz) to melt mating surfaces.

9.8.2 Solvent and Adhesive Bonding

A TPU can be bonded to itself using solvents such as *N*-vinyl pyrrolidone or dimethylformamide as long as the surface is small. Two-component reactive polyurethane adhesives are suitable to bond TPUs to themselves and other polar plastic materials, metals, woods and leather, and other substrates [119]. Epoxy resins can also be used in most cases.

9.9 Use of Bio-Based Raw Materials in TPUs

Recently, there has been a significant amount of work done with the use of polydiols from plant sources. It has been established that such raw materials produce TPUs with equal properties, and several manufacturers have been producing and marketing “eco” products, some of them since 2007 [120]. These are used in industrial products [121], athletes’ shoes [122], and other applications.

9.10 New Commercial Development

Bayer Material Science has expanded its Desmopan 600 series based on C3 ether modules by three new grades, namely *Desmopan DP 6064A*, *DP 6072A*, and *DP 6080A*, to give consumers greater choice in selecting ether TPUs. These materials were optimized in their mechanical properties and processing behavior. Their hardness values range from about 60 Shore A to just over 80 Shore A. The objective in the development work was to provide alternatives to SBC and TPV of similar hardness. In comparison to those materials, they are superior in terms of their tensile strength and abrasion resistance. Another advantage of the new TPU grades is their high dimensional stability; they display hardly any tendency to creep. Their good low-temperature flexibility (T_g in the region of –40 °C) is a major advantage in low-temperature applications. In

processing behavior, the three new materials exhibit a very good flow and fast melt hardening. In addition, they display a good adhesion to various substrates when used in overmolding; they are compatible with PA, PC, PC/ABS, and PBT and their glass fiber-reinforced versions. The parts that can be made from them have antislip, soft-touch surfaces; examples are grips, knobs on hand tools, electric tools, or household appliances. Another potential also exists for usual injection moldings, such as mats and cable bushings, as well as for use in athletes' and children's footwear [123].

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Abbreviations and Acronyms

ABS: Acrylonitrile/Butadiene/Styrene resin	MFI: Melt flow index
Ac: Alternating current	MFR: Melt flow rate
ACM: Acrylic rubber	MPa: Megapascal (stress or pressure unit)
ACS: American Chemical Society	MPR: Melt processable rubber
ANTEC: Annual Technical Conference of SPE	MWD: Molecular weight distribution
ASTM: American Society for Testing and Materials	NBR: Nitrile-butadiene rubber
BR: Polybutadiene rubber	NR: Natural rubber
CED: Cohesive energy density	OBC: Olefin block copolymer
COPA: Polyamide thermoplastic elastomer	ODP: Ozone depletion potential
COPE: Copolyester thermoplastic elastomer	P: Poise (unit of viscosity)
CPE: Chlorinated polyethylene	Pa: Pascal (unit of pressure or stress)
CTE: Coefficient of thermal expansion	PA: Polyamide
dc: Direct current	PAE: Polyarylether
DKG: Deutsche Kautschuk Gesellschaft (German Rubber Society)	PAEK: Polyaryletherketone
DKT: Deutsche Kautschuk Tagung (German Rubber Conference)	PAI: Polyamide-imide
DOE: Design of Experiments	PAN: Polyacrylonitrile
DOP: Dioctyl phthalate	PC: Polycarbonate
DSC: Differential scanning calorimetry	PEBA: Polyether block amide
DTA: Differential thermal analysis	PEEK: Polyetheretherketone
E: Elastic modulus	PEI: Polyetherimide
EB: Electron beam	PEM: Polymer electrolyte membrane
ECTFE: Copolymer of ethylene and chlorotrifluoroethylene	PSA: Pressure sensitive adhesive
EOL: End-of-life	PV: Photovoltaic
EPDM: Ethylene–propylene–diene monomer rubber	PBT: Polybutylene terephthalate
EPR: Ethylene–propylene rubber	PCTFE: Polychlorotrifluoroethylene
ETFE: Copolymer of ethylene and tetrafluoroethylene	PE: Polyethylene
EVA: Copolymer of ethylene and vinyl acetate	PET: Polyethylene terephthalate
FCM: Farrel Continuous Mixer	PFOA: Perfluorooctanoic acid
FEA: Finite element analysis	PI: Polyimide
FEP: Copolymer of tetrafluoroethylene (TFE) and hexafluoroethylene (HFP), also known as <i>fluorinated ethylene–propylene</i>	PLED: Polymeric light emitting diode
FTIR: Fourier transform infrared (spectroscopy)	PMMA: Polymethyl methacrylate
G: Gibbs free energy	POE: Polyolefin elastomer
GFPA: Glass fiber reinforced polyamide	PP: Polypropylene
GFPP: Glass fiber reinforced polypropylene	PPS: Polyphenylene sulfide
Gy: Gray (unit of radiation dose)	PS: Polystyrene
H: Enthalpy	PSA: Pressure sensitive adhesive
HDPE: High-density polyethylene	PTFE: Polytetrafluoroethylene
HFP: Hexafluoropropylene	PVC: Polyvinyl chloride
HIPS: High-impact polystyrene	PVDC: Polyvinylidene chloride
IEEE: Institute of Electrical and Electronic Engineers	PVDF: Polyvinylidene fluoride
IR: 1. Infrared (radiation)	PVF: Polyvinyl fluoride
IR: 2. Polyisoprene rubber	RF: Radio frequency
ISO: International Standard Association	RIM: Reaction injection molding
JIS: Japanese Industrial Standards	RoHS: Restriction of hazardous substances
LCP: Liquid crystal polymer	RRIM: Reinforced reaction injection molding
LDPE: Low-density polyethylene	rTPO: Reactor thermoplastic elastomer
LED: Light emitting diode	S: Entropy
LLDPE: Linear low-density polyethylene	SAN: Styrene–acrylonitrile (resin)
M: Molar weight of a polymer	SBC: Styrenic block copolymer
MA: Maleic anhydride	SBS: Styrene–butadiene–styrene block copolymer
MDO: Machine direction orientation	SEBS: Styrene–(ethylene–butylene)–styrene block copolymer
MEK: Methyl ethyl ketone	SEPS: Styrene–(ethylene–propylene)–styrene block copolymer
	SI units: International system of units
	SiBS: Styrene–isobutylene–styrene block copolymer

SIBS: Styrene—(isoprene/butadiene) block copolymer	TPO: Polyolefin blend thermoplastic elastomer
SIS: Styrene—(isoprene/butadiene) block copolymer	TPS: Styrenic thermoplastic elastomer (ISO nomenclature)
SME: Specific mechanical energy (in mixing of polymers)	TPZ: Unclassified thermoplastic elastomer (ISO nomenclature)
SPE: Society of Plastics Engineers (USA)	TPU: Thermoplastic polyurethane (elastomer)
T_g: Glass transition temperature	TPV: Thermoplastic vulcanizate
T_m: Crystalline melting temperature	UHF: Ultra-high frequency
TAC: Triallylcyanurate	UHMWPE: Ultra-high molecular weight polyethylene
TAI: Triallylisocyanurate	UL: Underwriters Laboratories, Inc.
TDO: Transverse direction orientation	UV: Ultraviolet
TFE: Tetrafluoroethylene	VDI: Verein Deutscher Ingenieure (The Association of German Engineers)
TPA: Polyamide thermoplastic elastomer (ISO nomenclature)	VOC: Volatile organic compounds
TPC: Copolyester thermoplastic elastomer (ISO nomenclature)	XLPE: Cross-linked polyethylene
TPE: Thermoplastic elastomer	

A

Abrasion resistance - Wear rate or abrasion rate is an important property of materials during motion in contact with other materials. Abrasion or wear resistance is measured by a number of methods such as ASTM D3389, also known as the *Taber Abrasion Test*.

ACM - Acrylate rubber consists of the basic monomer (rubber base) containing different acrylate esters, which influence the physical properties of the compound and of a curing monomer needed for cross-linking. Current commercial products include *ethyl acrylate rubber* that has a good resistance to heat and mineral oils, and *butyl acrylate rubber* that has a better low-temperature flexibility.

Adhesive - A material, usually polymeric, capable of forming permanent or temporary surface bonds with another material as is or after processing such as curing. The main classes of adhesives include hot melt, pressure sensitive contact, UV cured, EB cured, emulsion, etc.

Adherend - A part to be covered by an adhesive and then joined into an adhesive joint.

Adhesive bonding - A method of joining two plastic or other materials in which adhesive is applied to the surfaces of the parts to be joined. Bonding occurs through mechanical or chemical interfacial forces between the adhesive and adherend and/or by molecular interlocking. Surface preparation of the adherends and curing of the adhesive may be required.

Adhesive bond strength - The strength of a bond formed by joining of two materials using an adhesive. Bond strength may be measured by

peeling or shearing the two adherends using extensimetry.

Adhesive failure - Failure of an adhesive bond at the adhesive—adherend interface. An example is a failure that leaves adhesive all on one adherend, with none of the other adherend. Adhesive failure is less desirable than cohesive failure because it is indicative of joints with lower adhesive strength. See also *Cohesive Failure*.

Amorphous phase - See *Amorphous Polymer* and *Semicrystalline Polymer*.

Amorphous polymer - A polymer having a non-crystalline or amorphous supramolecular structure or morphology. Amorphous polymers may have some molecular order but usually are substantially less ordered than crystalline polymers and subsequently have inferior mechanical properties.

Annealing - A process in which a material, such as plastic, metal, or glass is heated and then cooled slowly. In plastics and metals, it is used to reduce stresses formed during fabrication.

ASTM International - is an international voluntary standards organization that develops and produces technical standards for materials, products, systems, and services; developed from the original ASTM (acronym for American Society for Testing and Materials).

ASTM D471 - Standard Test Method for Property—Effect of Liquids; commonly used test for swelling of elastomeric materials in oils, fuels, etc.

ASTM Oil No. 2 - See *IRM 902*.

ASTM Oil No. 3 - See *IRM 903*.

Attractive intermolecular forces - See *van der Waals Forces*.

B

Bar - A metric (SI) unit of pressure, equal to $1.0 \times 10^6 \text{ dyn/cm}^2$ or 1.0×10^5 pascals (Pa). It has a dimension of unit of force per unit of area and is used to denote the pressure of gases, vapors, and liquids.

Biaxial orientation - Orientation in which the material is drawn in two directions, usually perpendicular to one another. Commonly used in films and sheets.

C

Calender - This is equipment used to form a thermoplastic material into a film or sheet. The equipment consists of two or more steel (often heated) rolls with adjustable gap between them.

Carbon black - A black colloidal carbon particle produced by partial combustion and/or thermal cracking of natural gas, oil, or another hydrocarbon. Depending on the starting material and the method of manufacture, carbon black can be called acetylene black, channel black, furnace black, etc. The properties and uses of each carbon black type can also vary. Carbon black is used mainly as reinforcing agent of elastomers, as a black pigment in rubber and plastics and also as an additive increasing UV resistance of polyolefins and other polymers. Special conductive carbon blacks are used to introduce electrical conductivity to polymeric compositions.

Cast film - Film produced by pouring or spreading resin dispersion, resin solution, or melt over a suitable temporary substrate (carrier), followed by curing via solvent or water evaporation or melt cooling, and removing of the film from the substrate.

Coalescence - Refers to a mechanism of consolidation of polymer particles in solvents and aqueous dispersions into a coherent system. After the polymer melts, adjacent particles begin to combine (i.e., coalesce) to form a film.

Coefficient of thermal expansion - The change in unit of length or volume that occurs due to a unit change in temperature. The expansion and

contraction of a material with temperature depends on its coefficient of linear thermal expansion (CLTE).

Cohesive failure - Failure of an adhesive bond that occurs within the adhesive layer, leaving adhesive attached on both adherends. Optimum failure is 100% cohesive failure when both shear areas are completely covered. See also *Adhesive Failure*.

Cold flow - See *Creep*.

Conduction - In heat transfer, migration of energy due to a temperature gradient is termed conduction. Heat is transferred by the movement of molecules at hotter or colder temperatures, with different degrees of thermal motion, into colder or hotter regions respectively.

Contact adhesive - An adhesive that will adhere to itself on contact. When applied to both adherends, it forms a bond without sustained pressure on the adherends. See also *Pressure Sensitive Adhesive*.

Contact angle - The angle a droplet or edge of a liquid forms with the solid plane of a substrate. A contact angle of zero degree indicates complete wetting, larger contact angle values represent limited wetting.

Convection - The mass movement of particles arising from the movement of a streaming fluid due to difference in a physical property such as density, temperature, etc. Mass movement due to a temperature difference results in heat transfer, as in the upward movement of a warm air current.

COPA - Polyamide thermoplastic elastomers with polyamide hard segments and soft segments based on aliphatic polyesters, aliphatic polyesters or aliphatic polycarbonates.

COPE - Copolyether—ester block thermoplastic elastomers with ester hard segments and ether soft segments.

Copolymer - See *Copolymerization*.

Copolymerization - A polymerization where more than one monomer takes part in the reaction and forms the polymer chain. The result is a *copolymer*.

Corona treatment - A process commonly used in nonpolar polymers (e.g., polyethylene) to increase wettability and surface reactivity. The result is an increased affinity to inks, adhesives, and coatings. Plastic films and sheets are passed over a grounded metal cylinder with a pointed high-voltage electrode above it to produce an electrostatic discharge. The discharge oxidizes the surface of the film, making it more receptive to finishing.

Covalent bond - A bond formed by the sharing of two or more electrons between two atoms. Covalent bonds can be single (two electrons shared), double (four shared electrons), or triple (six shared electrons).

Creep - Nonrecoverable deformation in a part subjected to a continuous load. Creep is dependent on temperature, and on the duration and the amount of the load.

Critical shear rate - Thermoplastic materials must be processed below the velocity at which the *melt fracture* occurs. The shear rate at that velocity is referred to as the *critical shear rate*.

Cross-linking - Reaction resulting in the formation of covalent bonds between chain-like polymer molecules. As a result of cross-linking, polymers such as thermosetting resins become hard and infusible. Thermosetting (conventional) elastomers become stronger and more elastic and cannot be dissolved. When immersed into solvents, they only swell. Reaction resulting in the formation of covalent bonds between chain-like polymer molecules. As a result of cross-linking, polymers such as thermosetting resins become hard and infusible. Thermosetting (conventional) elastomers become stronger and more elastic and cannot be dissolved. When immersed into solvents, they only swell. Besides this so-called chemical cross-linking, physical cross-linking results from glassy or crystalline domains attached to elastomeric domains as it is the case with most thermoplastic elastomers. Unlike chemical cross-links, physical cross-links are reversible, i.e., can be removed by heating above corresponding melting temperature and restored by cooling below it.

Crystalline melting point - The temperature of melting of the crystalline phase of a semi-crystalline polymer. It is higher than the melting of the surrounding amorphous phase.

Crystalline phase - It is an organized structural arrangement of polymeric molecules. In this arrangement, polymer chains are aligned into a closely packed ordered state called *crystalline phase*.

Crystallization temperature - Temperature, or temperature range at which a polymer crystallizes. The polymer chains, which were randomly distributed in the melt, become aligned into a closely packed ordered arrangement during the crystallization process.

Crystallinity - Crystalline content of the polymer expressed in weight percent. See also *Crystalline Phase*.

D

Deflection temperature under load - See *Heat Deflection Temperature*.

Deformation under load - See *Creep*.

Degradation - Loss of or undesirable change in polymer properties as a result of aging, chemical reactions, wear, use, exposure, etc. The properties include color, size, strength, etc.

Density - The mass of any substance (gas, liquid, or solid) per unit volume at specified temperature and pressure.

Die land - The part of the extrusion die (orifice) that is downstream from the convergent section where both cross-sectional area and shape are constant.

Dielectric breakdown strength or voltage - The voltage (minimum) required to break down through the thickness of a dielectric (insulation material, i.e., create a puncture). ASTM D149 is used to measure dielectric breakdown strength of plastic insulation material.

Dielectric constant - The dielectric constant of an insulation material is the ratio of the capacitance

of a capacitor insulated with that material to the capacitance of the same capacitor insulated with a vacuum.

Dielectric dissipation factor - The ratio of the power dissipated in a dielectric to the product of the effective voltage and the current; or the tangent of the dielectric loss angle; or the cotangent of the dielectric phase angle. Also called *tan delta* or *dissipation factor*.

Differential scanning calorimetry - Differential scanning calorimetry (DSC) is a technique in which the energy absorbed or produced is measured by monitoring the difference in energy output into the substance and a reference material as a function of temperature. Absorption of energy produces an endotherm; production of energy produces an exotherm. The method is used for processes involving energy change, such as melting, crystallization, resin curing, and loss of solvents, or for processes involving a change in heat capacity, such as the glass transition.

DSC - See *Differential Scanning Calorimetry*.

Durometer hardness - Indentation hardness of a material as determined by either the depth of an indentation made by an indenter under specified load or the indenter load required to produce a specified indentation depth. The tool used to measure indentation hardness of polymeric materials is called a *durometer* (e.g., *Shore durometer*).

E

Elasticity - Property whereby a solid material changes its shape and size under action of opposing forces but recovers its original configuration when the forces are removed.

Electron beam radiation - Ionizing radiation propagated by electrons accelerated by very high voltage (typically kilovolts to megavolts). This radiation is used frequently for cross-linking, modification, or degradation of polymeric materials.

Elongation at break - The increase in distance between two gauge marks, resulting from stressing the specimen in tension, at the exact

point of break. Measurement taken at the exact point of break according to ASTM D638.

F

Fatigue - Process of progressive localized permanent structural change occurring in a material subjected to conditions that produce fluctuating stresses and strains at some point or points and that may culminate in cracks or complete fracture after a sufficient number of fluctuations, according to ASTM E1150.

Fatigue life - Number of loading–unloading cycles of a specified type of material that can endure before failing in a fatigue test.

Fatigue strength - The limiting value of the median fatigue strength as the number of loading cycles sustained before failure becomes very large. Fatigue strength, here is the maximum stress that can be sustained without failure at this number of loading cycles.

Filament - A filament is a small individual strand that is melt extruded during fiber spinning. Bundles of filaments are called fiber or yarn.

Film - A product, e.g., plastic that is extremely thin compared to its width and length. There are supported and unsupported films such as coatings and packagings, respectively.

Flexural modulus of elasticity - The ratio within the elastic limit of the applied stress on a test specimen in flexure to the corresponding strain of the outermost fibers of the specimen.

Free radical - An atom or group of atoms with an odd or unpaired electron. Free radicals are highly reactive and participate in free radical chain reactions such as free radical polymerization, combustion, and polymer oxidation. Scission of a covalent bond by thermal degradation or radiation can produce a free radical.

G

Gamma radiation - Ionizing radiation propagated by high-energy protons, i.e., emitted by nucleus in transition between two energy levels.

Gamma ray irradiation - A technique for cross-linking or reduction of molecular weight of polymers by exposing them to a source of gamma rays such as ^{60}Co .

Graft copolymer - A chain of one type of polymer to which side chains are attached or grafted. Such copolymers are generally formed by generating active sites on one polymer A in the presence of a monomer B. The monomer B is then polymerized to form side chains (see *Grafting*).

Grafting - A process to attach side chains to the chain of a polymer or copolymer. First, active sites are generated chemically or by ionizing radiation. During the grafting process a monomer can react with the active site and form side chains by polymerization. Other methods, such as transfer or activation grafting are often accomplished by the use of ionizing radiation.

Graphite - A crystalline form of carbon. It occurs in nature but can also be produced by heating petroleum coke, carbon black, and organic materials. Used mainly as lubricating filler or as additive introducing electrical conductivity.

Gravure coating - A coating technique using engraved rolls capable of picking up a precise amount of coating (dispersion or ink) from a trough and transferring it to a web that is in contact with the roll. The engravings on the surface act as small reservoirs for the coating.

H

Heat deflection temperature - The temperature at which a material specimen (standard bar) is deflected by a certain degree under specified load. Also called *Heat Distortion Temperature (HDT)*.

Hot melt adhesive - An adhesive that is applied in a molten state, which forms a bond after cooling to a solid state unlike other adhesives that achieve bond strength through evaporation of solvent or through a chemical reaction.

Hysteresis - Incomplete recovery of strain during unloading cycle due to energy consumption. This

energy is converted from mechanical to frictional energy (heat).

Hysteresis loop - In dynamic mechanical measurement, the closed curve representing successive stress-strain status of the material during cyclic deformation; it is the cyclic noncoincidence of the elastic curves. The area of the resulting loop is equal to the heat that is generated in the system.

I

Impact strength - The energy required to break a specimen, equal to the difference between the energy in the striking member of the impact apparatus at the instant of impact with the specimen and the energy remaining after complete fracture of the specimen.

Injection molding - A molding procedure in which heat-softened plastic material (melt) is forced from a cylinder into a cavity, which gives the article the desired shape. It is used for thermoplastics and for some thermosets.

Ionomeric elastomers - Ionomeric elastomers have essentially acidic groups polymerized into the backbone chain and these are neutralized by metallic counterions (e.g., by sodium or zinc). The counterions associate together to form *ionic clusters* that can behave like the hard domains in block copolymers thus forming a physically cross-linked network. Examples of the backbone chains are ethylene-methacrylic acid copolymer and ethylene-acrylic acid copolymer.

Ionizing radiation - Any electromagnetic or particulate radiation, which in its passage through matter is capable of producing ions directly or indirectly. Examples are electron beam and gamma radiation.

IRM 902 - Industry Reference Material—replacement for ASTM Oil No. 2, but not exact equivalent, used for immersion tests (according to ASTM D471).

IRM 903 - Industry Reference Material—replacement for ASTM Oil No. 3, but not exact equivalent, used for immersion tests (according to ASTM D471).

L

Lap joint - A joint, in which one adherend is placed partly over the other adherend; overlapped areas are bonded together.

Laser - A device used to produce an intense light beam with a narrow bandwidth. Laser is an acronym for *light amplification by stimulated emission of radiation*.

Lewis base - A substance that donates a pair of electrons in a chemical reaction to form a bond with another substance.

Limiting oxygen index (LOI) - LOI is defined as the required minimum percentage of oxygen in a mixture with nitrogen, which allows a flame to be sustained by an organic material such as a plastic.

M

Matched die forming - A type of thermoforming process consisting of preheating the plastic sheet prior to forming and then subjecting it to simultaneous motion of two mold halves.

Melting point - The temperature at which the solid crystalline and liquid phases of a substance are in thermodynamic equilibrium. The melting point is usually referred to normal pressure of 1 atm.

Melt processible polymer - A polymer that melts when heated to its melting point and forms a molten material with definite viscosity value at or somewhat above its melting temperature. Such a melt can be pumped and should flow when subjected to shear rate using commercial processing equipment such as extruders and molding machines.

Micron - A unit of length equal to 1×10^{-6} m. Its symbol is Greek small letter mu (μ).

MPR - Melt-processable rubber (MPR), described as alloys of proprietary ethylene interpolymers and chlorinated polyolefins in which the ethylene polymer component has been partially cross-linked in situ. These are comprised of blends of molecularly miscible polymers having a single glass transition temperature (T_g).

N

Nanometer - A unit of length equal to 1×10^{-9} m. Often used to denote the wavelength of radiation especially UV and visible spectral region. Its symbol is nm.

Newtonian fluid - A term to describe an ideal fluid in which shear stress is proportional to shear rate. The proportionality coefficient is called viscosity, which is independent of shear rate, in contrast to nonideal fluids where viscosity is a function of shear rate. Paints and polymer melts are non-Newtonian fluids.

O

Offset printing - A printing process in which the image to be printed is first applied to an intermediate carrier such as roll or plate, then is transferred to the surface of a substrate such as paper or plastic.

Olefins - The group of unsaturated hydrocarbons of the general formula C_nH_{2n} , and named after the corresponding paraffins by the addition of “ene” “ylene” to the stem. Examples are ethylene, propylene, or butenes. Polymers of olefins are polyolefins.

Orientation - A process of drawing or stretching of thermoplastic films or as spun synthetic fibers to orient polymer molecules in the direction of stretching. The fibers are drawn uniaxially, whereas films may be drawn in one direction (uniaxially, either longitudinally or transversely) or two directions (biaxially). Oriented films and fibers have enhanced properties in the direction of stretching. The film will shrink in the direction of stretching, when reheated in the direction of stretching.

Ozone - A molecule consisting of three atoms of oxygen, i.e., O_3 .

P

Paraffins - Linear saturated hydrocarbons with the general formula C_nH_{2n+2} .

Parison - Parison is a tube used for blow molding, which in principle at least has a constant wall

thickness at all points around its circumference and along its length. Thickness along the parison may vary due to tensile thinning caused by its own weight.

Pascal - An SI unit of measurement of pressure equal to the pressure resulting from a force of 1 N over an area of one square meter. Used to denote the pressure of gases, vapors, or liquids and the strength of solids. The symbol is Pa.

Peel strength - The strength of an adhesive bond between two flexible substrates or between one flexible and one rigid substrate measured by peeling. The resistance of the bond to separation by peeling is measured using an extensometer.

Pendant methyl group - A methyl group (CH_3) attached to the main chain of a polymer molecule.

PEO - Abbreviation for *polyethylene oxide*. Low molecular weight polymers of ethylene oxide are viscous liquids or waxes. Those of high molecular weight are tough, crystalline ductile thermoplastics. All PEO resins are soluble in water.

Permeability - The capacity of a material to allow another substance to pass through it; or the quantity of a specific gas or other substance, which passes through under specific conditions.

Poisson's ratio - This ratio is defined as the ratio of the change in the width of a material to the change in its length per unit length, as a result of strain in the length direction. It is designated by the Greek letter ν . Poisson's ratio values always fall within the range 0–0.5. The value for rubber is 0.5.

Polar molecule - A molecule, in which the positive and negative electrical charges are permanently separated. Polar molecules ionize in solution and impart electrical conductivity to the solution. Water, alcohol, and sulfuric acid are examples of polar molecules; hydroxyl and carboxyl are polar functional groups.

Polyethylene (PE) - A family of polyolefins consisting of linear and branched polyethylenes. Polyethylenes are thermoplastic but can be readily cross-linked by irradiation or chemically.

Polyolefins - Polyolefins are a large class of carbon-chain elastomeric and thermoplastic polymers usually prepared by addition of polymerization or copolymerization of olefins or alkenes such as ethylene. The most important representatives of this group are polyethylene and polypropylene.

Polypropylene (PP) - Polypropylene is a carbon-chain thermoplastic comprised of polypropylene homopolymer prepared either by stereospecific polymerization using Ziegler–Natta catalysts or by the polymerization using metallocene catalysts.

Polytetrafluoroethylene (PTFE) - Thermoplastic prepared by free-radical polymerization of tetrafluoroethylene. It has a superior chemical resistance, very high thermal stability, very high weather resistance, low friction coefficient, low flammability, very good release properties, and a low dielectric constant. On the other hand, it has a low creep resistance, relatively low strength and high permeability. Because of its high melt viscosity, PTFE can be processed either by sinter molding, powder coating, and coating from aqueous dispersions.

Polyvinyl chloride (PVC) - PVC is a thermoplastic prepared by free-radical polymerization of vinyl chloride in dispersion (emulsion), bulk or suspension process. Unmodified PVC is very rigid and requires plasticizers to make it more flexible. The main end forms are rigid PVC and flexible PVC. The flexible form is often made from plastisols, suspensions of PVC in plasticizers. Flexible form is also obtained when PVC is blended with nitrile rubber (NBR).

Polyvinylidene fluoride (PVDF) - Thermoplastic prepared by free-radical polymerization of vinylidene fluoride. It has a very high tensile strength, wear resistance and creep resistance, high dielectric constant and dielectric loss factor. PVDF is nonflammable, resists most solvents, and has excellent weather resistance. It exhibits piezoelectricity and pyroelectricity.

Pressure sensitive adhesive - An adhesive that requires applied pressure to the parts for the

bonding to occur. It is usually composed from an elastomer and modifying tackifiers. Pressure sensitive adhesives are applied as melts or solvent-based or water-based systems. In most cases curing of the adhesive does not usually occur.

Primer - In adhesive bonding a special reactive chemical dispersed in organic solvent or water is applied to the substrate prior to the application of an adhesive or a coating. A primer acts as a chemical bridge between the substrate and the adhesive or coating. Examples of primers are organosilanes and isocyanates.

R

Radiation dose - Amount of ionizing radiation energy absorbed by a material during irradiation. The unit of radiation is a grey (Gy) defined as 1 J per kilogram (J/kg). In practical application a larger unit, namely kGy (10^3 Gy), is used. Previously used unit, no longer official since 1986, is megarad (Mrad), equal to 10 kGy. See ***Ionizing Radiation***.

Reference fuel A - 100% isooctane; used frequently for immersion tests (according to ASTM D471).

Reference fuel B - 70% isooctane, 30% toluene (by volume) used frequently for immersion tests (according to ASTM D471).

Reference fuel C - 50% isooctane, 50% toluene (by volume) used frequently for immersion tests (according to ASTM D471).

Reference fuel D - 40% isooctane, 60% toluene (by volume) used frequently for immersion tests (according to ASTM D471).

Rheology - A science that studies and characterizes flow of polymers, resins, gums, and other materials.

S

SBC - Styrenic block copolymer, general.

S-B-S - Styrene-butadiene-styrene block copolymer, a triblock copolymer with polystyrene hard segments and polybutadiene soft mid-block.

S-EB-S - Styrene-(ethylene-butylene)-styrene block copolymer, a triblock copolymer with polystyrene hard segments and poly(ethylene-butylene) soft mid-block. S-EB-S is prepared by hydrogenation of S-B-S.

Semicrystalline polymer - A polymeric material characterized by localized regions of crystallinity. See also ***Amorphous Polymer***.

S-EPP-S - Styrenic block copolymer with ethylene/propylene-ethylene elastomeric mid-block.

S-EP-S - Styrene-(ethylene-propylene)-styrene block copolymer, a triblock copolymer with polystyrene hard segments and poly(ethylene-propylene) soft mid-block. S-EP-S is prepared by hydrogenation of S-I-S.

Shear - Displacement of a plane of solid body parallel to itself, relative to other parallel planes within the body; deformation resulting from this displacement.

Shelf life - Time during which a physical system such as material (solid compound, adhesive, coating, etc.) retains its properties during a long-term storage under specified conditions.

Shore hardness - Indentation hardness of a material as determined by the depth of an indenter of the Shore-type durometer. The scale reading on this durometer is from 0, corresponding to 0.1 in (2.5 mm) depth to 100 for zero depth. The Shore A indenter has a sharp point, which is spring-loaded to 822 gram-force (gf), and is used for softer plastics and rubber. The Shore D indenter has a blunt point, is spring-loaded to 10 pound-force (lbf) (4540 gf), and is used for harder plastics.

S-iB-S - Styrene-isobutylene-styrene block copolymer, a triblock copolymer with polystyrene hard segments and polyisobutylene soft mid-block. Prepared by carbocationic polymerization.

S-IB-S - Styrene-isoprene/butadiene-styrene block copolymer with polystyrene hard segments and a hybrid isoprene/butadiene soft mid-block with controlled distribution of monomeric units.

S—I—S - Styrene—isoprene—styrene block copolymer, a triblock copolymer with polystyrene hard segments and polyisoprene soft mid-block.

Softening point - Temperature at which a material changes from rigid to soft or exhibits a sudden and substantial decrease in hardness.

Solubility - The solubility of a substance is the maximum concentration of the material in a binary mixture at a given temperature forming a homogeneous solution.

Solubility parameter - Solubility parameter characterizes the capacity of a substance to be dissolved in another substance, e.g., of a polymer in a solvent. It represents the cohesive energy of molecules in a substance and determines the magnitude and the sign of the heat of mixing two substances in given concentrations. The magnitude and the sign of the heat of mixing determine the sign of the free energy of mixing. The solution occurs when the sign of the free energy of mixing is negative. The symbol used is δ .

Spherulite - In polymers, a rounded aggregate of radiating lamellar crystals with amorphous materials between the crystals. It has the appearance of a pom-pom. Spherulites exist in most semicrystalline polymers and usually impinge on one another to form polyhedrons. They range in size from a few tenths of a micron in diameter to several millimeters.

Star block (radial) copolymers - Block copolymers consisting of a core and three or more arms emanating from the core.

Strain - The per unit change, due to force, in the size or shape of a body referred to its original size or shape. Note: Strain is nondimensional but is often expressed in units of length or percent.

Stress relaxation - Time-dependent decrease in stress in a solid material as a result of changes in internal or external conditions.

Surface tension - The surface tension is the cohesive force at a liquid surface measured as a force per unit length along the surface or the work, which must be done to extend the area of a surface by

a unit area, e.g., by a square centimeter. Also referred to as *free surface energy*.

T

Taber Abrasion resistance - The weight loss of a plastic or other material specimen after it was subjected to abrasion in the Taber Abraser for a prescribed number of specimen disk rotations, usually 1000. A Taber Abraser consists of an idling abrasive wheel, designated depending on the type and grit of abrasive used as CS-10F, H 22, etc. and a rotary disk with the specimen mounted on it. The load is applied to the wheel. The produced motion simulates that of rolling with slip.

Tensile strength - The maximum tensile stress that a specimen can sustain in a test carried to failure. Measured according to ASTM D638.

Tensile strength at yield - The maximum load per original minimum cross-sectional area of the plastic specimen in tension within the gauge length, when the maximum load corresponds to the yield point. Measured according to ASTM D638.

Tensile stress - The force related to the smallest original cross-section of the specimen at any time of the test.

Thixotropic liquid - This liquid exhibits lower viscosity as shear rate increases. A practical example is house paint, which appears thinner when stirred.

TPE - Thermoplastic elastomer, consisting of a polymer or blend of polymers that has properties at its service temperature similar to those of vulcanized rubber but can be processed and reprocessed at elevated temperature like a thermoplastic.

TPO - Polyolefin-based thermoplastic elastomers, blends of isotactic polypropylene and ethylene—propylene copolymers.

TPU - Thermoplastic elastomers based on polyurethanes, prepared from long-chain diols, short-chain diols (chain extenders), and isocyanates. There are essentially random block copolymers

with crystalline hard segments and soft flexible polyester or polyether segments.

TPSiV - Thermoplastic elastomer based on dynamically vulcanized silicone elastomer and polyamide or other thermoplastic matrix polymer.

TPV - Thermoplastic elastomers based on dynamically vulcanized elastomer—plastic blends, such as ethylene propylene diene monomer (EPDM) elastomer and polypropylene or acrylic rubber and polyamide.

U

Ultraviolet (UV) radiation - Electromagnetic radiation in the 40–400 nm wavelength region. Sun is the main natural source of UV radiation on the Earth. Artificial sources are many, including special UV lamps of different designs. Ultraviolet radiation causes polymer degradation and other chemical reactions, including polymerization and cross-linking of monomeric and oligomeric systems.

V

van der Waals forces - Weak attractive forces between molecules, weaker than hydrogen bonds and much weaker than covalent bonds.

Viscosity - The internal resistance to flow exhibited by a fluid, the ratio of shear stress to shear rate. A viscosity of 1 (Poise) P is equal to a force of

1 dyne/square cm that causes two parallel liquid surfaces 1 sq cm in area and 1 cm apart to move past one another at a velocity of 1 cm/s. The SI unit of viscosity is Pas (Pascal second).

W

Wetting - The spreading out (and sometimes absorption) of a fluid onto (or into) a surface. In adhesive bonding, wetting occurs when the surface tension of the liquid adhesive is lower than the critical surface tension of the substrates being bonded. Good surface wetting is essential for high strength adhesive bonds; poor wetting is evident when the liquid beads up on the part surface. Wetting can be increased by preparation of the part surface prior to adhesive bonding.

Y

Yield deformation - The strain at which the elastic behavior begins, while the plastic is being strained. Deformation beyond the yield deformation is not reversible.

Young's modulus - In the elastic region, the relationship between stress and strain of a polymer, undergoing tensile or compressional strain, is linear (i.e., follows Hooke's law). In this relation the stress is proportional to strain. Young's modulus is the coefficient of proportionality in this stress—strain relationship.