Introduction

Plastics are classified as thermoplastic or thermosetting resins, depending on the effect of heat. Thermoplastic resins, when heated during processing, soften and flow as viscous liquids; when cooled, they solidify. The heating/cooling cycle can be repeated many times with little loss in properties. Thermosetting resins liquefy when heated and solidify with continued heating; the polymer undergoes permanent cross-linking and retains its shape during subsequent cooling/heating cycles (see THERMOSETS). Thus, a thermoset cannot be reheated and molded again. However, thermoplastics can be melt-reprocessed, and hence readily recycled (see RECYCLING, PLASTICS).

Thermoplastic Resins. Almost 85% of the resins produced are thermoplastics (1,2). Although a number of chemically different types of thermoplastics are available in the market, they can be divided into two broad classes: amorphous and crystalline. Amorphous thermoplastics shown in Table 1 (3) are characterized by their glass-transition temperature T_g a temperature above which the modulus decreases rapidly and the polymer exhibits liquid-like properties; amorphous thermoplastics are normally processed at temperatures well above their T_g (see AMORPHOUS POLYMERS). Semicrystalline resins shown in Table 2 (3) can have different degrees of crystallinity ranging from 50 to 95%; they are normally processed above the melting point T_m of the crystalline phase (see SEMICRYSTALLINE POLYMERS). Upon cooling, crystallization must occur quickly, ie, in a few seconds. Addition of nucleating agents increases the crystallization rate (see CRYSTALLIZATION KINETICS). Additional crystallization often takes place after cooling and during the first few hours following melt processing.

Over 70% of the total volume of thermoplastics is accounted for by the commodity resins: polyethylene, polypropylene, polystyrene, and poly(vinyl

Polymer	$T_{ m g},^{\circ}{ m C}$
Polyamideimide (PAI)	295
Polyethersulfone (PES)	230
Polyarylsulfone (PAS)	220
Polyethermide (PEI)	218
Polyarylate (PAR)	198
Polysulfone (PSU)	190
Polyamide, amorphous (PA)	155
Polycarbonate (PC)	145
Styrene-maleic anhydride (SMA)	122
Chlorinated PVC (CPVC)	107
Poly(methyl methacrylate) (PMMA)	105
Styrene-acrylonitrile (SAN)	104
Polystyrene (PS)	100
Acrylonitrile-butadiene-styrene (ABS)	100
Poly(ethylene terephthalate) (PET)	67
Poly(vinyl chloride) (PVC)	65

 Table 1. Glass-Transition Temperature of Amorphous

 Thermoplastics^a

^aRef. 3.

chloride) (PVC) (1) (see ETHYLENE POLYMERS, HDPE; ETHYLENE POLYMERS, LDPE; ETHYLENE POLYMERS, LLDPE; PROPYLENE POLYMERS (PP); STYRENE POLYMERS; VINYL CHLORIDE POLYMERS). They are made in a variety of grades and because of their low cost are the first choice for a variety of applications. Next in performance and in cost are acrylics, cellulosics, and acrylonitrile-butadiene-styrene (ABS)

Incimopiastics		
Polymer	$T_{ m m},^{\circ}{ m C}$	
Polyetherketone (PEK)	365	
Polyetheretherketone (PEEK)	334	
Polytetrafluoroethylene (PTFE)	327	
Poly(phenylene sulfide) (PPS)	285	
Liquid crystal polymer (LCP)	280	
Nylon-6,6 ^b	265	
Poly(ethylene terephthalate) (PET)	260	
Nylon-6 ^b	220	
Nylon-6,12 b	212	
Nylon-11 ^b	185	
Nylon- 12^b	178	
Acetal resin ^{c}	175	
Polypropylene (PP)	170	
High density polyethylene (HDPE)	135	
Low density polyethylene (LDPE)	112	

Table 2. Melting Temperature of Semicrystalline Thermoplastics^a

^aRef. 3.

^bNylons are polyamides (qv).

^cAcetal resin in polyoxymethylene (POM).

terpolymers (see ACRYLIC ESTER POLYMERS; ACRYLONITRILE AND ACRYLONITRILE POLYMERS; CELLULOSE ESTERS, INORGANIC). Engineering thermoplastics (qv) such as acetal resins, polyamides (qv), polycarbonates (qv), thermoplastic polyesters (qv), and poly(phenylene sulfide), and advanced materials such as liquid crystal polymers, polysulfones (qv), and polyetheretheretheretores are used in high performance applications; they are processed at higher temperatures than their commodity counterparts.

With few exceptions, thermoplastics are marketed in the form of pellets. They are shipped in containers of various sizes, from 25-kg bags to railroad hopper cars. Resins are conveyed to silos for storage and from there to the processing equipment. Colored resins are available, but frequently it is more convenient and economical to buy uncolored resins and blend them with color concentrates. Using concentrates avoids handling dusty pigments and ensures uniform color distribution.

The packaging requirements for shipping and storage of thermoplastic resins depend on the moisture that can be absorbed by the resin and its effect when the material is heated to processing temperatures. Excess moisture may result in undesirable degradation during melt processing and inferior properties. Condensation polymers such as nylons and polyesters need to be specially predried to very low moisture levels (4,5), ie, less than 0.2% for nylon-6,6 and as low as 0.005% for poly(ethylene terephthalate) (PET), which hydrolyzes faster.

Thermoplastic Processing. A variety of processing equipment and shaping methods are available to fabricate the desired thermoplastic product (6-10). Extrusion (qv) is the most popular. Approximately 50% of all commodity thermoplastics are used in extrusion process equipment to produce profiles, pipe and tubing, film, sheet, wire, and cable (1). Injection molding (qv) follows as a preferred processing method, accounting for about 15% of all commodity thermoplastics. Other common methods include blow molding (qv), rotational molding (qv), thermoforming (qv), calendering, and, to some extent, compression molding. Details on the amounts of resins converted annually in the United States in terms of processes and products can be found in the following year's January issue of *Modern Plastics*. Computer-aided design software for molds and extruder screws is commercially available. These programs assist in the selection and fabrication of processing equipment, thereby saving research and development time. Modeling and simulation of polymer processing is described in specialized textbooks (11–17).

The range of processes that may be used for fabricating a plastics product is determined by the scale of production, the cost of the machine and the mold, and the capabilities and limitations of the individual processes. For example, complex and precise shapes can be achieved by injection molding, hollow objects via blow molding and rotational molding, and continuous lengths by extrusion.

Thermoplastics processing operations produce emissions into the air, wastewater, and solid waste resulting from both polymers and additives. Most important are volatile organic compounds emitted from heated cylinders and molds. The identification of such volatiles and the development of analytical techniques for measuring their concentration in the workplace are of paramount importance to establish or revise threshold limit values that would minimize exposure to hazardous chemical substances. Environmental issues in polymer processing are reviewed in References 18 and 19.

Extrusion

Extrusion is defined as continuously forcing a molten material through a shaping device. Because the viscosity of most plastic melts is high, extrusion requires the development of pressure in order to force the melt through a die. Manufacturers of plastic resins generally incorporate stabilizers and modifiers and sell the product in the form of cylindrical, spherical, or cubic pellets of about 2–3 mm in diameter. The end-product manufacturers remelt these pellets and extrude specific profiles, such as film, sheet, tubing, wire coating, or as a molten tube of resin (parison) for blow molding or into molds, as in injection molding.

To provide a homogeneous product, incorporation of any additives, such as antioxidants (qv), colorants (qv), and fillers (qv), requires mixing them into the plastic when it is in a molten state. This is done primarily in an extruder. The extruder, as shown in Figure 1, accepts dry solid feed (F, E, J) and melts the plastic by a combination of heat transfer through the barrel (B, C) and dissipation of work energy from the extruder drive motor (I). In the act of melting, and in subsequent sections along the barrel, the required amount of mixing is usually achieved. Venting may also be accomplished to remove undesirable volatile components, usually under vacuum through an additional deep-channel section and side vent port. The final portion of the extruder (L) is used to develop the pressure [\leq 50 MPa (7500 psi)] for pumping the homogenized melt through a filtering screen (optional) and then through a shaping die attached to the end of the extruder.

Extruders are defined by their screw diameter and length, with the length expressed in terms of the length-to-diameter ratio (L/D). Single-screw extruders

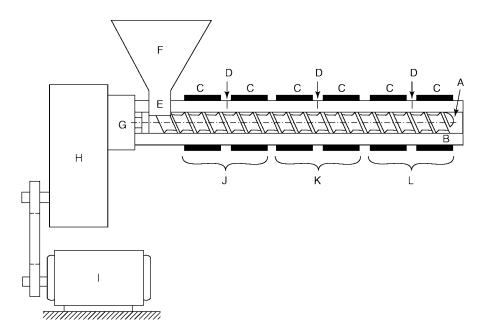


Fig. 1. Parts of an extruder: A, screw; B, barrel; C, heater; D, thermocouple; E, feed throat; F, hopper; G, thrust bearing; H, gear reducer; I, motor; J, deep-channel feed section; K, tapered channel transition section; and L, shallow channel metering section (20).

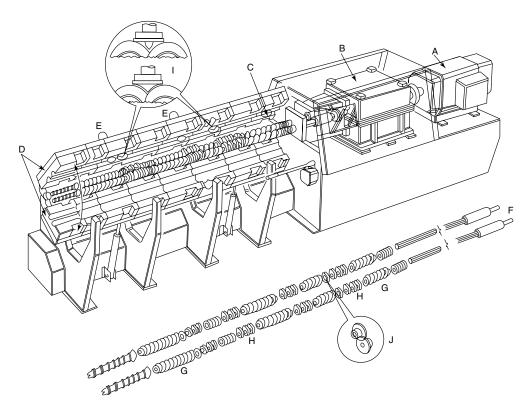


Fig. 2. Intermeshing corotating twin-screw extruder: A, motor; B, gear box; C, feed port; D, clam shell barrel; E, vent port; F, screw shafts; G, conveying screws; H, kneading paddles; I, barrel valve; and J, blister rings. Courtesy of APV Chemical Machinery Inc.

range from small laboratory size (6 mm diameter) to large commercial units (450 mm diameter) capable of processing up to 20 t/h. Melt-fed extruders run at a L/D of about 8; solids-fed extruders run at a L/D of about 20–40 depending on whether intermediate venting is provided.

Varieties of twin-screw extruders are also utilized, particularly when the ingredient mixing requirements are difficult to fulfill or require multiple staging, as in reactive extrusion. Twin-screw extruders are classified as being tangential or intermeshing, and the latter as being counter- or corotating. These extruders are generally supplied with slip-on conveying and kneading screw elements and segmented barrels. These elements, shown in Figure 2, give the processor improved mixing and pumping versatility. Single-screw extruders are usually flood-fed, with the feed rate determined by screw speed. Twin-screw extruders are generally starve-fed. Starve feeding permits greater flexibility in operation as screw speed now becomes a process control variable, independent of feed rate.

Reactive extrusion is the term used to describe the use of an extruder as a continuous reactor for polymerization or polymer modification by chemical reaction (21,22). Extruders are uniquely suitable for carrying out such reactions because of their ability to pump and mix highly viscous materials. Extruders readily permit multiple process steps in a single machine, including melting, metering, mixing, reacting, side-stream addition, and venting.

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Mechanism of Extruder Operation. An extruder employs drag flow to perform a conveying action that depends on the relative motion between the screw and the barrel. With higher friction on the barrel than on the screw, the solids are conveyed almost as solid plug in the deep-feed channel section. As the channel depth becomes shallower, the compressive action causes more frictional heat, which, combined with the conduction supplied by the barrel heaters, causes the plastic to melt. The molten plastic then enters a constant shallow depth section of the screw called the metering section, where the pumping pressure necessary for extrusion through the final shaping die is developed.

The drag flow or volumetric conveying capability Q_d for the plastic melt is dependent only on screw speed *N* and the geometry *A* of the screw:

$$Q_{\rm d} = AN$$

The drag flow is most easily visualized by unwrapping the screw and dragging a flattened barrel surface diagonally across the channel (Fig. 3).

At the discharge end of the metering section, enough pressure must be generated to overcome the resistance of the transfer piping and the shaping die. This same pressure in effect also causes the plastic melt to want to flow back down the channel and possibly also over the flight tips. This pressure flow Q_p , is dependent on the screw geometry B, pressure driving force ΔP , filled length of the screw L, and melt viscosity μ :

$$Q_{\rm p} = B \Delta P / \mu L$$

The pressure flow is independent of screw speed, except as the latter affects the viscosity of the melt.

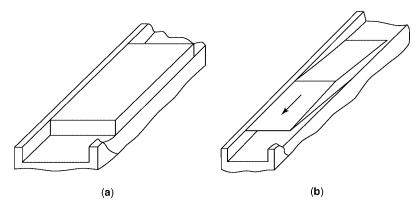


Fig. 3. (a) Channel with block of molten plastic; (b) channel with moved block of molten plastic; arrow indicates direction of material movement (20).

The net flow Q of an extruder is simply the difference between drag and pressure flows:

$$Q = Q_{\rm d} - Q_{\rm p}$$

The pressure and drag flow equations for twin-screw extruders are similar to those expressed above for single-screw extruders but with different geometric constants. The amount being forwarded per revolution (Q_d/N) for fully intermeshing co-rotating twin-screw extruders is one half of the process volume contained in one turn of the screw:

$$Q_{\rm d}/N = 1.54 hDz$$

Where h is the channel depth, D is the screw diameter, and z is the lead length of the screw (23).

Mixing in Extruders. In addition to the conveying and melting steps, extruders perform the vital task of homogenization of additives such as Fillers (qv), stabilizers, and pigments into the base resin (24,25). Incorporation of powdered filters is best accomplished by downstream addition into the barrel after the polymer resin is fully melted. Otherwise, the forces that are generated during melting can cause severe abrasive wear of screws and barrels, and frequently can lead to difficult-to-disperse agglomerates formed by compaction.

If the cross-channel mixing provided by the drag and pressure flows in singlescrew extruders is insufficient, various mixing enhancers are available. These generally ensure dispersion by forced passage over a higher shear-restricting slot or an improved distribution by multiple reorientations of flow and sequences of extensional flow.

Mixing in twin-screw extruders benefits from the additional interaction of the two screws with each other as well as with the barrel. Various arrays of kneading paddles are generally used in the most common type, namely the co-rotating, intermeshing, twin-screw extruder. The kneading paddles improve mixing by causing extensive melt reorientation, backmixing, and elongational flow patterns (26).

Further information on extruder operation and plastic processing is available (17,20,27–36). Technology updates and equipment options for specific processing steps are provided annually in publications such as the *Plastics Compounding Redbook* and in *Modern Plastics Encyclopedia*.

Pipe and Tubing. A typical die for extruding tubular products is shown in Figure 4. It is an in-line design, ie, the center of the extruded pipe is concentric with the extruder barrel. The extrudate is formed into a tube by the male and female die parts. The male die part is supported in the center by a spider mandrel. Melt flows around legs of the mandrel and meets on the downstream side. The position of the female die part can be adjusted with bolts; adjustment is required to obtain a tube with a uniform wall thickness.

A vacuum calibrator usually is used for controlled cooling of the tube, as shown in Figure 5. It is a long, closed tank that contains cooling water and uses a vacuum to maintain a constant tube diameter and thickness.

The molten tube enters the tank through a series of cooling rings, and atmospheric pressure inside the tube forces the melt against the rings. The rings

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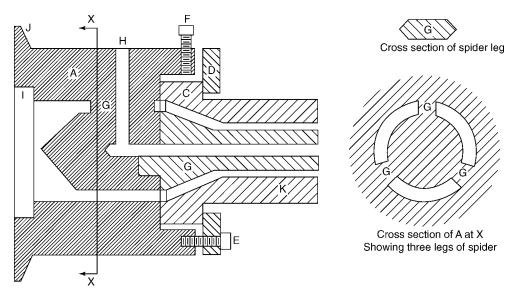


Fig. 4. Pipe or tubing die for in-line extrusion: A, die body; B, mandrel, pin, and male die part; C, die, die bushing, and female part; D, die-retaining ring; E, die-retaining bolt; F, die-centered bolt; G, spider leg; H, air hole; I, seat for breaker plate; J, ring for attachment to extruder; and K, die land (20).

control the expansion of the tube and establish its outside diameters. Water cools the tube and adds strength to it, allowing it to withstand expansion forces. The tube exits the tank through a rubber gasket. A variable-speed takeoff controls the rate at which the tube is pulled through the tank.

Tubing extrusion usually involves drawdown of the resin from the die, ie, the diameter and wall thickness of the tubing are less than that of the die opening. The amount of drawdown is expressed as the ratio of the cross-sectional area of the die opening to the cross-sectional area of the tube wall. Drawdowns in tubing

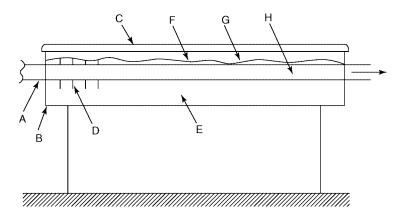


Fig. 5. Vacuum calibrator for pipe and tubing extrusion: A, molten tube from die; B, tank; C, hinged cover with gasket; D, sizing rings; E, circulated and temperature-controlled water; F, water level; G, vacuum; and H, inside of pipe open to atmospheric pressure (20).

extrusion usually range from 2:1 to 8:1. Drawdown in pipe extrusion is often less than 1.1:1. Pipe and tubing may be cut in straight lengths or may be coiled, depending on use and stiffness, eg, polyethylene pipe usually is cut to length, whereas laboratory tubing is coiled. ABS and PVC pipe are made in straight lengths, and soda straws are cut in short lengths.

Pipe extrusion is commonly used in the manufacture of thick-walled products. Die openings are large and resistance to flow is small. Cooling of the pipe is slow because plastics are poor conductors of heat. Long quench tanks and good circulation of cooling water are needed. Low melt temperatures relative to melting or softening points characterize pipe extrusion. Large die openings permit the use of viscous, high molecular weight resins, which yield tougher products.

Profile Extrusion. This method is similar to pipe and tubing extrusion, except that special profile dies are used to produce a variety of asymmetrical products. Typical products include housing siding, window sash molding, decorative trim, plastic lumber, gaskets, and channels. Dies for profile extrusion are designed to allow for shape changes that occur during quenching. Usually, a water trough is used for cooling, but air or cooled metal surfaces are also used. Profile extrusion typically relies on amorphous thermoplastics, such as PVC, ABS, polystyrene, thermoplastic elastomers, etc. The rapid shrinkage accompanying crystallization can result in severe distortion of the profile.

Foam Extrusion. Foamed thermoplastics provide excellent insulating properties because of their very low thermal conductivity, good shape retention, and good resistance to moisture pickup. As such, cylindrical shapes are extruded for pipe insulation, and sheets for building panel insulation. Chemical blowing agents are usually solid powders that can be incorporated into molten plastics without reacting to release their by-product gases until subsequently heated to a higher temperature. Physical blowing agents are dissolved and held in solution by the pressure developed in the extruder (37). As the molten thermoplastic exits the extruder die, the pressure release causes instantaneous foaming. The chlorinated fluorocarbons formerly used as blowing agents have been replaced with more environmentally friendly substitutes, such as hydrochlorofluro carbons (HCFCs) or low molecular weight hydrocarbons such as butane or isopentane. For some thermoplastics, carbon dioxide, nitrogen, or argon can be used (38,39). Critical to the success of most foaming extrusion operations is cooling of the melt just prior to entry to the die. Cooling is most effectively accomplished with a tandem arrangement of two extruders, as shown in Figure 6, wherein the first extruder ensures complete dissolution of the blowing agent, and the second extruder is operated at slow speed for optimum cooling. Additional information on extrusion of foams is contained in References 28,37, and 40 (see Cellular MATERIALS).

Film Forming Processes

Blown Film. The blown film process (Fig. 7) uses a tubular die from which the extrudate expands in diameter while traveling upward to a film tower. The top of the tower has a collapsing frame followed by guide and pull rolls to transport the collapsed film to subsequent slitting and windup rolls. The tubular bubble from the die is inflated to the desired diameter by air passing through the center of the

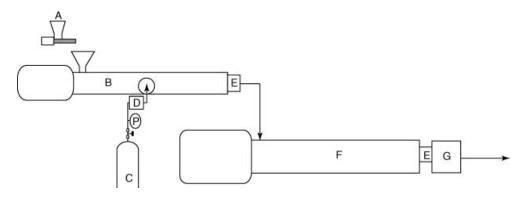


Fig. 6. Foam extrusion line: A, resin feed; B, extruder for melting and gas incorporation; C, gas supply; D, gas metering and compression; E, optical windows; F, cooling extruder; and G, die. P represents a pressure gauge. Courtesy of Polymer Processing Institute.

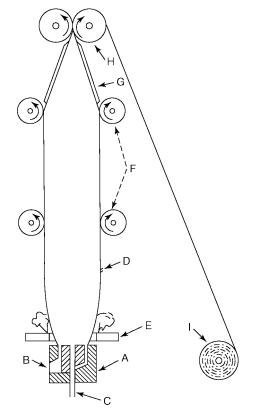


Fig. 7. Extrusion of blown film: A, blown-film die; B, die inlet; C, air hole and valve; D, plastic tube (bubble); E, air ring for cooling; F, guide rolls; G, collapsing frame; H, pull rolls; and I, windup roll (20).

die. Although primary cooling to solidify the melt is supplied by an external air ring, chilled air may also be used internally. Polyethylene is the primary plastic used in most films, especially for packaging and trash bags. Coaxial dies can be used for manufacture of coextruded multilayer films.

The tube is characterized by its blow-up ratio, ie, a larger diameter than the die opening, which is expressed as the ratio of bubble diameter to the die diameter. Typical blow-up ratios range from 2:1 to 4:1. The final film thickness is much thinner than the die gap. Die gaps are slits of ca 0.65 mm. Typical film thicknesses are 0.007–0.125 mm. The process requires a high melt viscosity resin so that the melt can be pulled from the die in an upward direction. Since only air is used for cooling, removal of heat tends to be slow and rate-limiting. Chilled air can also be used internally to improve the efficiency of the air cooling process. The film may be treated for subsequent printing, and it can be slit into various widths and wound onto separate cores.

Cast Film. The cast film process provides a film with gloss and sparkle and can be used with various resins. Figure 8 is an illustration of the essential features of the extrusion equipment. The die opening is a long straight slit with an adjustable gap ca 0.4 mm wide. The die is positioned carefully with respect to the casting roll. The casting or chill roll is highly polished and plated and imparts a smooth and virtually flawless surface to the film. The roll is cooled by rapid circulation of water. Temperature control is critical. A die somewhat longer than the width of the film is needed, because the molten web becomes narrow as it is drawn from the die; this is called neck-in. Edges of the film thicken and are mechanically removed before the film is wound on a roll. The edge trim can be reprocessed.

One of the requirements of this process is that the melt maintain good contact with the chill roll, ie, air must not pass between the film and the roll. Otherwise, air insulates the plastic and causes it to cool at a rate different from the rest of the plastic and this spoils the appearance of an otherwise satisfactory product. The melt should not emit volatiles, which condense on the chill roll, reduce heat

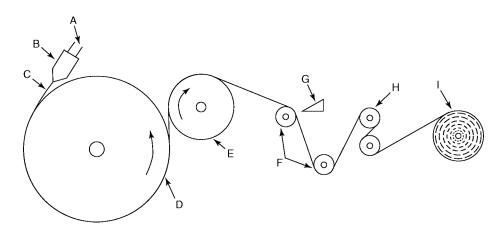


Fig. 8. Extrusion of roll-cast film: A, die inlet; B, cast-film die; C, air gap with molten web; D, casting roll; E, stripping roll; F, idler roll; G, edge-trim slitter; H, pull rolls; and I, windup roll (20).

transfer, and mar the film's appearance. The cast film process allows the use of a higher melt temperature than is characteristic of the blown film process. The higher temperature imparts better optical properties.

Film stretching is a process to impart biaxial orientation in the film by stretching it in two directions simultaneously, the transverse and machine directions, respectively. The process is carried out in a device that grips the edges of the film and extends them to larger widths as the film moves from the inlet to the exit roller. The objective is to increase the modulus and strength of the film uniformly along the entire film plane. Polypropylene and PET have been used successfully in this process (41).

Sheet. The process used to make an extruded plastic sheet is illustrated in Figure 9. Sheeting thicknesses are 0.25–5 mm and widths are as great as 3 m. Heavier gauge sheets are usually cut to a specified length and are stacked. Cooling is controlled by a three-roll stack. The rolls are 25–50 cm in diameter, highly polished, and chrome-plated. They are cored for cooling with circulating water, and the temperature of each roll is controlled by a circulator and temperature control unit. Often the rolls are operated at high temperature to maximize the gloss of the sheeting surface.

A web of molten plastic is pulled from the die into the nip between the top and middle rolls. At the nip, there is a very small rolling bank of melt. Pressure between the rolls is adjusted to produce sheet of the proper thickness and surface appearance. The necessary amount of pressure depends on the viscosity. For a given width, thickness depends on the balance between extruder output rate and the takeoff rate of the pull rolls. A change in either the extruder screw speed or the pullroll speed affects thickness. A constant thickness across the sheet requires a constant thickness of melt from the die. The die is equipped with bolts for adjusting the die-gap opening and with an adjustable choker bar or dam located inside the die a few centimeters behind the die opening. The choker bar restricts flow in the center of the die, helping to maintain a uniform flow rate across the entire die width.

Drawdown from the die to nip is typically ca 10%. Sheet extrusion requires that the resin be of high melt viscosity to prevent excessive sag of the melt between

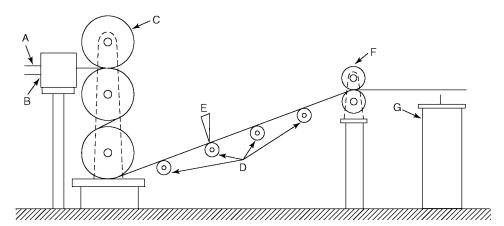


Fig. 9. Sheet extrusion: A, die inlet; B, die; C, three-roll finisher; D, support rollers; E, edge-trim cutter; F, pull rolls; and G, saw or shear (20).

the die and the nip. The melt should reach the nip before touching any other part of the middle roll to prevent uncontrolled cooling of the resin. The appearance of the lower surface of the sheet is determined by the middle roll, ie, its polish, surface temperature, and freedom from condensed materials. The upper surface is cooled by air and has a more glossy appearance. Neither the top roll nor the bottom roll greatly affects the appearance of the top surface of the sheet. Edges of the sheet are trimmed.

Multilayer structures can be formed by simultaneous coextrusion of different layers through a feed block die. The individual layers can be selected for their specific attributes, such as strength, barrier properties, etc, or for incorporation of recycled material. When the basic layers are incompatible, tie layers can also be included to form a cohesive composite structure.

There usually is no need for a high melt temperature to obtain flow through a sheeting die, because die openings are large. Cooling of the sheet is slow because sheeting is thick. Most sheeting is used for thermoforming.

Extrusion Coating. A coating of an appropriate thermoplastic, such as polyethylene, may be applied to a substrate of paper, thin cardboard, or foil to provide a surface property which enables heat sealing or better barrier performance (see BARRIER POLYMERS). Figure 10 is a sketch of the extrusion-coating process. A molten web of resin is extruded downward, and the web and substrate make contact at the nip between a pressure roll and a chill roll. Typical coating thicknesses are 0.005–0.25 mm; the die opening is ca 0.5 mm. The melt web is narrower than the die, which is characteristic of a neck-in, and the edge tends to bead or thicken. Coated substrate is trimmed to the desired width. The highly polished and water-cooled chill roll determines the nature of the surface and removes the heat from the resin. The pressure roll pushes the substrate and the molten resin against the chill roll. Pressure and high melt temperatures are needed for adhesion of resin and substrate.

In contrast to most extrusion processes, extrusion coating involves a hot melt, ca 340°C. The thin web cools rapidly between the die and nip even at high linear rates. Both mechanical and chemical bonding to substrates are involved. Mechanical locking of resin around fibers contributes to the resin's adhesion to paper. Some oxidation of the melt takes place in the air gap, thereby providing

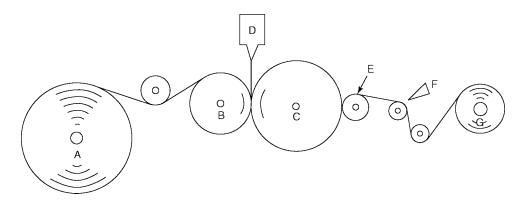


Fig. 10. Extrusion coating: A, unwinding of substrate; B, pressure roll; C, chill roll; D, die; E, stripper roll; F, edge trimmer; and G, windup of coated substrate (20).

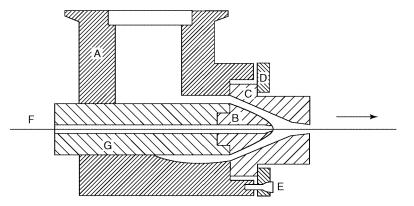


Fig. 11. Wire-coating pressure die: A, die body, crosshead; B, guider tip; C, die; D, die-retaining ring; E, die-retaining bolt; F, wire; and G, core tube (20).

sites for chemical bonding to aluminum foil. Excessive oxidation causes poor heatsealing characteristics.

Wire and Cable Coating. Protective and insulating coatings can be applied continuously to wire as it is drawn through a cross-head die, as shown in Figure 11. A typical wire coating line consists of a wire payoff, wire preheater, extruder, die, cooling trough, capstan, and wire takeup (Fig. 12).

The melt flows from the extruder into the die where it flows around the bend and around the core tube. On the far side of the core tube, it forms a weld. Melt sticks to and is pulled by the moving wire. Details of the sizes and shapes of the die parts in contact with the melt are important in obtaining a smooth coating at high rates. The die exit usually is the same diameter as that of the coated wire and there is little drawdown. Die openings are small and pressures inside the die are high at ca 35 MPa (5000 psi). Wire take-up systems operate as high as 2000 m/min.

Injection Molding

In injection molding a molten thermoplastic is injected under high pressure into a steel mold. After the plastic solidifies, the mold is opened and a part in the shape

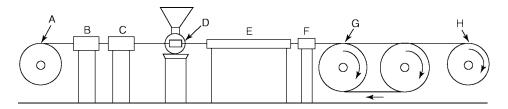


Fig. 12. Wire-coating line: A, unwinding of wire (payoff); B, straightener; C, preheater; D, extruder; E, water trough; F, tester; G, capstan (puller); and H, windup of coated wire (20).

of the mold cavity is removed. General descriptions of the process and related equipment are given in References 2 and 42–45.

Equipment. The machine consists of an injection unit and a clamp unit. The injection unit is usually a reciprocating single-screw extruder that melts the plastic and injects it into the mold or tool. The clamp unit opens, closes, and holds the mold closed against the pressure of injection. The size of an injection molding machine is described by the capacity of its clamping unit, ranging from 50 to 1000 tons. A machine with a given clamp unit can be supplied with a variety of injection units. Injection unit capacity is described by the shot size, which is the maximum volume of melt that can be injected in a single cycle. Shot size is determined by the diameter of the screw and the distance over which it is designed to reciprocate. Shot size is usually expressed as weight or as volume.

An injection molding machine is operated by hydraulic power and equipped with an electric motor and hydraulic pump. The maximum hydraulic oil pressure is ca 14 MPa (2000 psi). A hydraulic cylinder opens and closes the mold and holds the mold closed during injection; another cylinder forces the screw forward, thereby injecting the melt into the mold. A separate hydraulic motor turns the screw to plasticate, homogenize, and pressurize the melt. Control of these movements is a combined function of the hydraulic and electrical systems.

In the injection molding machine shown in Figure 13, the clamp unit is on the left and the injection unit on the right. A mold is shown in position between the platens of the clamp unit with one half of the mold fastened to the fixed platen and the other to the movable platen. When the mold is opened, the movable platen moves away from the fixed platen and the molded part can be removed. After part ejection, the mold is closed in preparation for the next injection cycle. In contrast to extrusion, the screw in the injection unit rotates only during part of molding cycle. When the screw turns, it pumps melt forward. The rearward movement of the screw is controlled by the placement of a limit switch, which stops the hydraulic motor. The maximum length of reciprocation is approximately three screw diameters. The shot size is directly proportional to the amount of screw

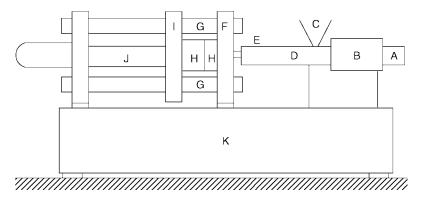


Fig. 13. Injection molding machine: A, hydraulic motor for turning the screw; B, hydraulic cylinder and piston allowing the screw to reciprocate about three diameters; C, hopper; D, injection cylinder (a single-screw extruder); E, nozzle; F, fixed platen; G, tie rods; H, mold; I, movable platen; J, hydraulic cylinder and piston used to move the movable platen and supply the force needed to keep the mold closed; and K, machine base.

reciprocation. The front of the screw is usually equipped with a check valve. While the screw rotates, the melt can move freely forward through the valve. However, the valve closes to prevent any reverse flow. The position of the screw is adjusted in such a way that there is always some melt in front of the screw when the mold is full. This pad or cushion of melt transfers pressure from the screw to the plastic in the mold. After initial filling, some additional melt flows into the mold; this is called packing. The cross section of the hydraulic cylinder, which pushes the screw, is approximately 10 times the cross section of the melt in front of the screw. Thus, 14 MPa (2000 psi) oil pressure corresponds to ca 140 MPa (20,000 psi) melt pressure.

Molding Cycle. The molding cycle begins when the empty mold is closed and full clamp force develops. The screw is then pushed forward in order to inject melt into the mold. The screw holds melt under pressure in the mold for a certain time, often called the injection time, until the gate freezes. When the injection is finished (46,47), the pressure holding the screw forward is reduced to a minimum, the screw starts to rotate, and a mold-closed timer is activated. Before the time expires and the mold opens, the screw stops turning and the next shot is ready for injection. The speed of screw rotation is chosen in such a way that the screw rotation time is less than the mold-closed time. The mold remains open only long enough for the part(s) to be ejected. The length of the molding cycle depends on cooling the part sufficiently so that it may be removed from the mold without distortion. Mold cooling systems are used for cycle reduction. The length of the cycle may also be determined by the appearance of the part; a hotter mold usually imparts a more attractive finish than a cooler mold. Cycle time and quality of moldings are optimized through microprocessor-based controllers that receive inputs from temperature, pressure, and ram position sensors.

Molds and Mold Design. The molds are custom-machined from steel. Cavities must be polished to a very high gloss, since the plastic reproduces the surface in every detail. The cavities are hardened and frequently chrome-plated. Details on mold design are given in References 48–50. A typical shot from a mold, shown in Figure 14, consists of a sprue, runners (43), gates, and two parts. Gate

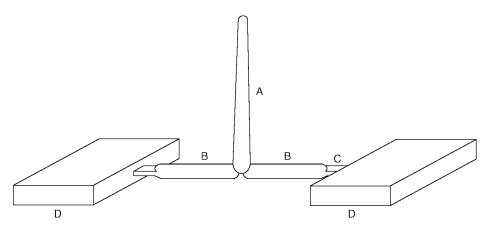


Fig. 14. A full shot: A, sprue; B, runner; C, gate; and D, part.

design is influenced by part geometry, resin type, and processing conditions. Sprue and runners channel the melt into the cavities. After ejection they are separated from the parts, ground, and fed back into the injection unit for reprocessing. Modern mold design tends to reduce or eliminate sprue and runner scrap through a variety of techniques such as hot runners, insulated runners, or by designs that place the nozzle directly against the mold cavity (45,51).

When the mold is opened, the part should be easily removable. Cavities are made with a slight taper to reduce frictional drag of the part on the mold. The half of the mold attached to the movable platen is equipped with ejector pins, which push the part out of the cavity while the mold is being opened. When the mold is closed, the pins are flush with the cavity surface. Release agents or lubricants facilitate ejection and shorten the molding cycle. Some complex parts require that the mold open in several directions in addition to the direction of the platen movement. For a threaded part, eg, a bottle cap, part of the mold must be rotated to remove the article from the mold.

Mold designs must take into account that cooled moldings are always smaller than the cavity, owing to shrinkage. Amorphous plastics shrink less than crystalline plastics (52). In practice, mold shrinkage is expressed as linear shrinkage, rather than volumetric shrinkage. Parts are measured the day after molding and are compared with the size of the mold at room temperature. In actual molding, pressure is maintained to continue packing during cooling to minimize voids and excessive sink marks.

Developments. A variety of process modifications aimed at improving surface finish or weld line integrity, process efficiency, and product costs have been described. They include gas-assisted injection molding developed for the production of hollow plastic parts with separate internal channels, microcellular foam molding that uses supercritical fluids to create microscopic cells throughout the polymer, coinjection, fusible core, multiple live feed, push–pull injection molding, and increasing use of robotic automation for enhanced productivity and part quality (53,57). An important development includes computer-aided design methods, wherein a proposed mold design is simulated by a variety of software packages and the melt flow through it is analyzed (58).

Structural Foam Molding. Structural foam is a modified injection molding process for large articles having a cellular core and an integral solid skin with an overall 20–50% reduction in density, compared to their solid counterparts (40,59,60). It is most frequently used with polyethylene, high impact polystyrene, polypropylene, and several engineering resins. Some modifications to the resin, machine, and mold are required, and a blowing agent must be added to the resin. A chemical blowing agent, which releases gas when heated, is commonly used. The choice of blowing agents depends on the processing temperature required. The most common blowing agent is azodicarbonamide (1,1'-azobisformamide) used at 200–260°C. Upon decomposition, it releases nitrogen, carbon monoxide, and carbon dioxide (qv). Approximately 0.5 wt% of a blowing agent is normally added to the resin pellet as a surface coating or as a pelletized concentrate. Instead of a chemical blowing agent, nitrogen may be mixed with the melt while it is under pressure in an extruder and the mixture maintained under pressure until it is injected into the mold.

The injection molding machine must be equipped with a shutoff nozzle that maintains the melt under pressure while the mold is opened. The screw is retracted only part of the way needed for a full shot, and a short shot is injected into the mold. Without a blowing agent, only a section of a part, ie, a short shot, would be made; the empty space allows the blowing agent to expand the melt, forming the foam structure. Structural foam molding is limited to parts with wall thicknesses of at least 6 mm; below that thickness, reduction in part weight is usually insignificant. Parts, typically, have a dense skin and a foamed interior with various pore sizes. Compared to injection-molded surfaces, the surfaces of structural foam moldings are poor, and are characterized by a rough, swirly finish. Maximum pressure in the mold during foaming is much lower than in injection molding; also, no packing pressure needs to be maintained since the gas keeps the melt front moving. Surface appearance is improved by special techniques.

Because of low injection pressure, some cost savings are possible in mold and press construction. Molding cycles are somewhat longer than for injection molding. The part must be cooled in the mold long enough to be able to resist swelling from internal gas pressure. In structural foam parts there is almost a total absence of sink marks, even in the case of unequal section thickness. Structural foam has replaced wood, concrete, solid plastics, and metals in a variety of applications.

Blow Molding

Blow Molding (qv) is the most common process for making hollow thermoplastic components (61–63). In extrusion blow molding a molten tube of resin called a parison is extruded from a die into an open mold (Fig. 15**a**). In Figure 15**b** the mold is closed around the parison, and the bottom of the parison is pinched together by the mold. Air under pressure is fed through the die into the parison, which expands to fill the mold. The part is cooled as it is held under internal air pressure. Figure 15**c** shows the open mold with the part falling free.

As the parison is extruded, the melt is free to swell and sag. The process requires a viscous resin with consistent swell and sag melt properties. For a large

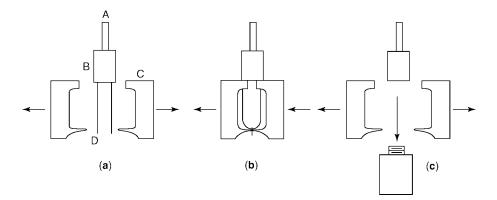


Fig. 15. Three stages of blow molding (**a**–**c**): A, air line; B, die; C, mold; and D, parison (see text).

container the machine is usually equipped with a cylinder and a piston called an accumulator. The accumulator is filled with melt from the extruder and emptied at a much faster rate to form a large parison; this minimizes the sag of the molten tube.

With a simple parison, the large-diameter sections of the bottle have a thin wall and the small-diameter sections have a thick wall. Certain modifications of the die can control the thickness of the parison wall along its length, which results in a bottle with improved wall thickness distribution and better strength. High density polyethylene (HDPE) is the most common blow-molding resin used to produce containers ranging in size from 30 cm³ to 200 L.

In injection blow molding, a parison is injection-molded onto a core pin; the parison is then rapidly transferred via the core pin to a blow mold, where it is blown by air into an article. This process is applied to small and intricate bottles.

Soft-drink bottles made from PET are usually made by stretch-blow molding in a two-step process. First, a test-tube-shaped preform is molded, which is then reheated to just above its glass-transition temperature, stretched, and blown. Stretching the PET produces biaxial orientation, which improves transparency, strength, and toughness of the bottle. A one-step process is used for many custom containers that are injection stretch-blow molded.

Development/trends in blow molding focus on the optimization of the viscoelastic properties and improvement in thermal stability of polymers other than HDPE to develop new extrusion/injection blow molding grades; fabrication of small containers by multilayer blow molding for improved barrier properties to water, oxygen, or hydrocarbons; prediction through software packages of wall thickness for parisons and final parts to minimize materials usage.

Other Molding Methods

Rotational Molding. Hollow articles and large, complex shapes are made by rotational molding (qv), usually from polyethylene powder of relatively low viscosity (64–66). The resin is in the form of a fine powder. A measured quantity is placed inside an aluminum mold and the mold is heated in an oven and rotated at low speed. The resin sinters and fuses, coating the inside of the mold. The mold is then cooled by water spray and the part solidifies, duplicating the inside of the mold.

A rotomolding machine has three long arms extending from a central driving mechanism; each arm rotates several molds in two planes. The arms are moved from one process station to the next, ie, from unloading and loading to heating and cooling. Tooling costs are low. The molds are usually made of cast aluminum, but sheet metal is also used. The melt is forced without pressure against the mold surface during heating or cooling, resulting in uniform wall thickness, zero orientation, and high physical properties. Cycle times are long because of the heating and cooling required; they depend on wall thickness and can be as high as 15 min for a 4-mm wall thickness. Common rotomolded products include large tanks and boxes, drums, furniture, and toys. PVC plastisol, a mixture of fine PVC particles and a plasticizer, may also be processed by rotomolding. Plastisols

are liquid at room temperature and are converted to soft solids when heated to ca 180°C. Playballs and toys are made from plastisols.

Among recent trends and developments in rotomolding are the use of microprocessors and temperature sensors for quality assurance, the refinement of methods to produce multiwalled solid or foamed structures all coupled with the continuing availability of new resin grades with suitable viscosities and high thermooxidative stability over the prolonged periods of time in the oven.

Expandable Polystyrene Molding. Molding expandable polystyrene gives foamed products such as insulation board shapes for packaging and disposable food and cup containers. Such processes are also called bead or steam molding (67,68). Expandable polystyrene moldings are manufactured from polystyrene beads 0.25-1.5 mm in diameter containing a blowing agent, such as pentane. These beads, when exposed to heat, expand from 2 to 50 times their original size. The beads are preexpanded by heating with steam or hot air to about the density of the final molded part. After preexpansion, they are stored from 3 to 12 h to let the air diffuse into the cells of the foam. Shaping of the beads is done in special presses and molds, into which the preexpanded beads are transferred by air-conveying systems. Steam causes further expansion and forces the surface fused particles to conform to the shape of the mold. In the manufacture of insulation boards, blocks are molded into cavities up to $5.5 \times 1.2 \times 0.65$ m by injecting steam. After storage and conditioning, the blocks are cut into sheets. Expandable bead molding has been extended to other thermoplastics such as polypropylene.

Thermoforming

Thermoforming (qv) is a process for converting a preform, usually an extruded plastic sheet, into an article such as a thin-wall container or a tray for packaging meat (69–72). Under vacuum the process is called vacuum forming. The sheet is clamped in a frame and exposed to radiant heaters. The sheet softens to a formable condition, is moved over a mold, and sucked against the mold by vacuum. Excess plastic is trimmed and recycled. Timers control the length of the heating and cooling periods, which depend on composition and sheet thickness. Frequently, the process is improved by using mechanical aids (plug-assisted, air-cushioned plug-assisted, drape-assisted). The molds are made of wood, aluminum, steel, or epoxy (73). In some plants the vacuum forming line is run in-line with the sheeting extruder.

Amorphous resins such as styrenics, acrylics, PVC, and some crystalline resins such as polyolefins, PP, and PET are used for thermoforming. Foamed polystyrene sheet is also thermoformed. The polymers must be of fairly high molecular weight because the heated sheet must be form-stable. The significant property is melt elasticity. Sheets of these resins soften but do not sag when heated. Sagging causes thinning; a sagged sheet may have more surface area than the mold, resulting in folds and areas of uneven thickness. Thermoforming is employed for small items such as cups, plates, trays, and larger, deep-drawn moldings such as boats, bath tubs, and freezer liners. Skin packaging, which employs a flexible plastic skin drawn tightly over an article on a card backing, is made by thermoforming.

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The process also is used for blister packaging. Thermoforming can be continuous by using rolls of sheet or batch by using precut shapes.

Thermoforming is competing with injection blow molding and rotomolding to prepare hollow parts by refining the twin sheet process by simultaneous or sequential forming of both halves and then compressing at the periphery to effect closure. The growth of thermoforming is also related to the development of software for wall thickness prediction.

Calendering

Calendering is a process uniquely applied to rubbery polymers, mainly semirigid and flexible PVC, for making sheeting of uniform thickness from 0.75–0.05 mm after stretching (74–77). A calender has four heavy, large steel rolls, which are usually assembled in an inverted "L" configuration as shown in Figure 16. This design is preferred for thick sheeting because it gives a long dwell for full heating. The forces generated between the rolls are considerable and sufficient to bend the rolls, resulting in uneven sheet thickness. A common method of compensating for roll bending is by grinding an opposite contour on the roll. A two-roll mill, a Banbury mixer, or an extruder melts the resin, which is subsequently transferred to the calender. Sheet can be made 2.5 m wide and production rates can be as high as 100 m/min. Calendering is often followed by printing, laminating, and embossing. PVC calenders are run at temperatures approaching 200°C to produce highly oriented sheets for items such as shower curtains, rainwear, luggage, and wall paneling.

Casting

Casting refers to the formation of an object in a batch process by pouring a fluid monomer–polymer solution into a mold where it solidifies or by continuously

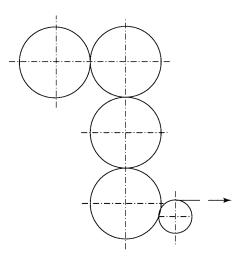


Fig. 16. A four-roll, inverted "L" calender.

pouring the liquid onto a moving belt. The casting process is most frequently used with acrylics. Since the 1950s, cast acrylic sheeting has been made by polymerization of methyl methacrylate in a cell assembled from two glass plates and a flexible gasket. Heating for a few hours until polymerization is complete gives sheets with excellent optical properties. Acrylic sheeting is also made by continuous casting, ie, a monomer-polymer-catalyst mixture is fed onto a stainless steel belt, on which the polymerization is completed. These products are used for glazing and thermoforming. Nylon-6 products with higher molecular weight and crystallinity than extruded or molded resins are also produced by casting in the mold by a process known as *in situ* anionic polymerization.

Thermosetting Resins Processing

Common thermosetting resins are unsaturated polyesters, phenolic resins (qv), amino resins (qv), polyurethanes (qv), epoxy resins (qv), and silicones (qv) (see POLYESTERS, UNSATURATED; URETHANE COATINGS). Less common thermosets (qv) employed in specialized applications are bismaleimides, polyimides (qv), and furan resins. Thermosetting resins are usually low viscosity liquids or low molecular weight solids that are formulated with suitable additives known as cross-linking agents to induce curing; curing involves permanent chemical changes resulting in infusible, insoluble products with excellent thermal and dimensional stability. Thermosetting resins are commonly used in combination with fillers or fibrous reinforcements; as a result, processing methods are often quite different from those employed for thermoplastics (78–80).

Compression, Injection, and Transfer Molding. Compression molding is the oldest process of the plastics industry. General information on the process, which is also applicable to a certain extent to thermoplastics, is found in References 81-85. It is still common, although many thermosetting materials are also injection-molded (86–88). The equipment consists of a vertical hydraulic press with platens for mold attachment. The mold comprises a matched pair of male and female dies. Mold cavities are hardened and highly polished, similar to those of an injection mold. A measured quantity of thermosetting resin compound in granular, sheet, or other form is placed in the hot mold. The mold is closed and the liquified resin through pressure fills the cavity. Continued heating cures the resin within a few minutes, and the part is removed from the mold. Compression molding is commonly employed for phenol-formaldehyde, urea-formaldehyde, melamineformaldehyde, and polyester molding compounds. To shorten the total cycle, some of these compounds are partially polymerized or preformed into various shapes that are preheated to intermediate temperature before being inserted into the mold. Laminates made of reinforcement layers impregnated with partially polymerized resins are also prepared by compression molding.

Sheet molding compound (SMC) is used in the manufacture of large reinforced compression moldings, which are employed extensively in automotive panels. SMC is prepared as a sandwich, rolled between two polyethylene films; it contains polyester resin, filler (usually calcium carbonate), and 20–30 wt% chopped glass fibers. Other components such as peroxides for cross-linking, thermoplastic additives for shrinkage control, and alkaline-earth oxides and hydroxides to assist maturation are present in smaller amounts. Maturation involves a thickening chemical reaction that produces within a few days after compounding a tack-free sheet with desirable flow characteristics during molding. The required amount of sheet is then cut to size for placement on the bottom of two matched mold halves to cover at least 70% of the mold area. It is molded at pressures up to 15 MPa (2100 psi) and temperatures in the range 140–180°C. Cure cycles depend on part size and complexity, pressure and heat applied, and formulation characteristics. Cure cycles of 60 s are common. The properties of cured SMC depend on the amount, length, and orientation of the glass fibers.

Bulk molding compound (BMC) is similar to SMC in formulation, but contains shorter glass fibers and higher filler levels (89). The premixed material has the consistency of dough and is supplied in bulk form or as a cylindrical extrudate. BMC is molded by conventional compression or transfer molding; it is also molded in reciprocating screw injection presses equipped with a piston stuffer attached to the barrel to force-feed the material into the screw flights. Other injection-moldable thermoset formulations in granular form (phenolics, amino, epoxy, and diallyl phthalate compounds) are fed through standard gravity hoppers. In thermoset injection molding, screws with low compression ratios are used to convey the material through a short barrel heated typically up to 120° C and decrease its viscosity; this is followed by injection into a hotter mold (typically up to 220° C) where chemical cross-linking takes place. Total cycles may range from 10 to 120 s, depending on part thickness and formulation characteristics.

Transfer molding is a combination of compression molding and injection molding. A measured charge is heated in a reservoir, from which it is injected or transferred through runners to the mold cavity. Forcing the polymer through the entry gate results in a rise in temperature that may promote flow but also accelerates curing. The molten polymer is held at temperature while the crosslinking reaction proceeds to completion.

Open-Mold Processing. Common open-mold processes are hand or mechanized methods such as lay-up and spray-up, that use a single cavity mold and produce one finished surface (90). These techniques are used to produce fiberreinforced structures containing the reinforcement in the form of cloth, chopped strands, mat, continuous roving, woven roving, etc. Thermosetting resins of choice are liquid unsaturated polyester or epoxy resins. In lay-up, catalyzed resin is used to impregnate the reinforcement that is preplaced on the mold. A spray-up system consists of a resin spray gun, a fiber chopper, and a pumping system; the catalyst is combined with the resin just before deposition with the fibers onto the mold surface. Open-mold processes use little or no pressure during the curing cycle. Cross-linking usually takes place at room or slightly elevated temperature through a proper combination of curing agents. A variety of products such as boat hulls, automotive components, tanks, etc are made by open-mold processing (91). Types of emissions and U.S. environmental regulations for thermoset components and cure reaction by-products are included in Reference 19.

In another open-mold process, filament winding, continuous fibers such as glass, carbon, or aramid are wound on a mandrel surface in a precise geometric pattern (92). Fibers are usually preimpregnated with a low viscosity resin containing a suitable cross-linking agent for room or higher temperature curing. Most common resins are polyesters and epoxies. A tubular component with the fibers in angle-ply arrangement results after curing and the mandrel is withdrawn. The

process, originally developed as a rapid method to manufacture pipes and cylindrical vessels, has expanded to allow more complicated geometries. Products include, among others, helicopter rotor blades, external fuel tanks, pressure bottles, and pipes.

Pultrusion. In pultrusion, reinforcing fibers in a combination of styles are wetted by a resin containing a high temperature cross-linking agent and then pulled through a forming system that positions the fibers into the desired packed structural arrangement; the material then moves through a heated die where curing takes place (93). The process can in principle produce continuous profiles of any length; rods, bars, and other more complex profiles such as I-beams and channels are mostly made from continuous glass fibers and polyester or epoxy resins (94). Glass content can be very high (50–70%) at production rates of about 1.5 m/min (91–93). An analogous method has been used to produce continuous composite lengths by impregnation of fiber bundles with molten thermoplastics which can be chopped to long fiber pellets that are used in injection molding (95).

Reaction Injection Molding. Reaction injection molding (RIM) is used for the production of solid or partially foamed polyurethane moldings by rapid injection of metered streams of polyol and isocyanate into a mold. RIM has been developed around polyurethane and polyurea chemistry; other chemical systems of lesser commercial significance can be processed by RIM (96,97). Articles are produced on a cycle of 3 min or less. The two liquid streams are mixed by impingement before entering the mold. The mold is filled at 0.35–0.70 MPa (50–100 psi), which is a very low pressure compared to that used in standard injection molding. Equipment, and in particular mixing head design, is critical. The cost of the mold and press are less for RIM than for conventional injection molding and the process is particularly suited to the production of large parts.

A wide range of formulations can be used in the RIM process. A typical polyol stream contains 75–80 wt% polyether polyol, 17–20 wt% 1,4-butane-diol, 2–6 wt% blowing agent, and amine and metal catalysts. The most commonly used isocyanates are proprietary products made from 4,4'-methylenedi(phenyl isocyanate). Processing conditions and physical properties depend on the formulation. Often, parts are removed from the mold before curing is complete; then, additional curing is required at elevated temperatures in an oven. Glass fibers and other fillers added for reinforcement and to control shrinkage are dispersed into the polyol component. Another approach is to place continuous fiber mats directly in the mold cavity and inject a low viscosity, reactive mixture through the mat (structural RIM) (98).

Resin Transfer Molding. In resin transfer molding (RTM) a piston-type positive displacement pump injects a premixed resin–catalyst stream into a closed mold thoroughly impregnating a preplaced reinforcement pack. Glass, graphite, or aramid fibers in the form of continuous strand mat, woven rovings, and their combinations are typical reinforcements (99). RTM differs from structural RIM in that it uses slower reacting formulations and injects under lower pressures components that are premixed or homogenized by passing through static mixers. Molds are made of lower cost materials and cycles are longer (10–60 min). RTM machines have been adapted for a variety of resins including polyesters, epoxies, polyurethanes, and isocyanurates (100,101).

Polyurethane Foam Processing.

Flexible Foam. These polyurethane products have varying densities and a relatively low degree of cross-linking (102). They are made from trifunctional polyols (mol wt 3000) and TDI, a mixture of 2,4- and 2,6-toluene diisocyanates, in the presence of tin and amine catalysts, surfactants as foam stabilizers, water, and blowing agents. Physical blowing agents are Freons; CO_2 , the reaction product of water and isocyanate, is a chemical blowing agent. Flexible foams are resilient open-cell structures with densities varying from 25 to 650 kg/m³, depending on the choice of the raw materials. Most flexible foams are produced in the form of a slab or bun in a continuous process in widths up to 2.4 m and thicknesses up to 1.2 m. A liquid foamable mixture is pumped onto a conveyor, which moves through a tunnel where reaction and foaming occur (103). Similar mixtures can be placed in a mold and allowed to foam. This process is used in the manufacture of automobile seats (see Foamed Plastics).

Rigid Foam. These are closed-cell foams with excellent thermal insulation characteristics (104). Most rigid foams are made from a high functionality polyol with ca 500 mol wt and poly(methylene)–poly(phenyl isocyanate), yielding a mixture with a high functionality of 2.7; hence, the foams have a higher degree of cross-linking than the flexible foams. The formulations include blowing agents, catalysts, and foam stabilizers. Rigid foams can be made as continuous slabs that are cut into panels. Other production methods include coating suitable substrates to produce laminated products used for architectural insulation; spraying, as for insulation during construction; and pouring or pumping the foamable mixture into place, as in the manufacture of refrigerators.

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