

# Polymer Processing: An Overview

*Polymer processing is dominated by laminar and creeping flows and chemical processing by turbulent flows. In the following, polymer processing is discussed in terms of mechanisms, equipment, and transport and reaction phenomena.*

This review on polymer processing has been prepared by senior staff members of the Polymer Processing Institute, a free-standing institute hosted by Stevens Institute of Technology, Hoboken, New Jersey. The authors of the various sections of the review are:

## Overview

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## Handling of Particulate Solids

Melting, Softening and Solidification of Polymers

## Pressurization and Pumping

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## Devolatilization and Reactive Processing

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## Overview

**P**olymer processing is the series of operations that are carried out on polymeric systems to increase their utility by changing them to shaped and internally structured (oriented) finished products. The molten and deformable state achieved by thermoplastic polymers at elevated temperatures, and possessed by thermosetting polymers before being chemically "set," allows them to be shaped into a myriad of simple and complex finished products in a continuous or batch fashion. Since the operations can be carried out relatively quickly and easily, they are superbly fitted for mass production. Without a doubt, the use-

fulness of polymeric materials and their profound impact on modern life and technology are due just as much to the versatility and ease of the available shaping methods as to the inherent properties of the polymers.

In preparing polymers for the final shaping process, the

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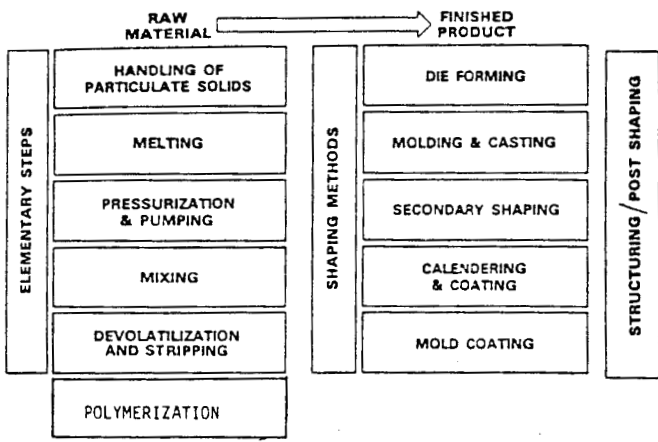


Figure 1. Conceptual breakdown of polymer processing (1).

following operations, called *elementary steps (1)*, are carried out in polymer processing machinery: handling of particulate solids; melting of compressed particulate beds; flow and pressurization of the resulting polymer melts; mixing primarily by laminar flow; devolatilization and stripping; and on occasion, chemical or physical modifications by chemical reaction such as polymerization and foaming.

The elementary steps are typically carried out in a single piece of processing equipment operating in a continuous (extruder) or a batch fashion (injection molding) machine. Every polymer processing machine represents an engineering solution as to how each of the elementary processing steps will be carried out by specific mechanism(s) and in given geometry, taking advantage of polymer properties and being mindful of their limitations. A conceptual breakdown of polymer processing is given in Figure 1.

Chemical engineers deal daily with the phenomena involved in the elementary steps of polymer processing: handling of powders and flakes; melting of solids; flow, pressurization and mixing of liquids; removal of volatiles from solids and liquids; and chemical reactions. The difference between chemical engineering and polymer processing problems is that the mechanisms utilized in effecting the elementary steps in the two disciplines differ necessarily because of the profound differences in the natures of monomeric and polymeric substances. Primary differences are the very high viscosity (and non-Newtonian nature) of polymer melts that dictates laminar mixing, drag-induced flow, dissipative melting (heating), and devolatilization in laminar flow across free surfaces. Notable are the susceptibility of polymers to degrade thermally and their very low thermal diffusivity that require the removal of newly formed polymer melt away from hot surfaces, usually by drag flow. While classical chemical engineering is dominated by processes involving turbulent flows, polymer processing is dominated by laminar and creeping flows.

The purpose of this article is to familiarize chemical engineers with polymer processing by noting both the common roots of the transport and reaction phenomena involved and the differences in mechanisms, and therefore the equipment used, by which the corresponding processes are carried out in the two fields.

## Polymer processing line

A blown film production line, Figure 2, is used to provide an overview of the operations and transport phenomena involved in polymer processing.

The extruder, the primary processing equipment, is fed continuously with a mixture of virgin polymer (pellets or powder) and recycled polymer processed in the granulator, originating from the necessary trimming of the product, as well as from off-specification film rolls. A blender mixes the polymer streams, together with other additives, in this case color concentrates. The blender, in turn, feeds the blend into the extruder hopper in a controlled fashion.

The particulate feed is accepted by the helical channel formed by the screw of the extruder rotating inside the stationary barrel, which is maintained cool in the feed region. The dragging action of the screw compresses the particulates and moves them forward in the helical channel, despite the steep positive pressure gradient created. At the end of the feed region, only a few turns long, the barrel is heated to temperatures well above the melting or glass transition temperature of the polymer.

A thin film forms next to the barrel from the conductive heating that initiates the melting process. As soon as this film is formed, it gets sheared by the relative velocity between the compressed solid bed and the barrel. Shearing of this high-viscosity melt results in a large viscous dissipation of energy, contributing appreciably to the rate of melting. When the film thickness exceeds the clearance between the screw flight tip and the barrel, the pushing end of the flight acts as a doctor blade, forcing the melt away from the hot barrel region into a melt pool circulating side-by-side with the compressed particulates. The hydrody-

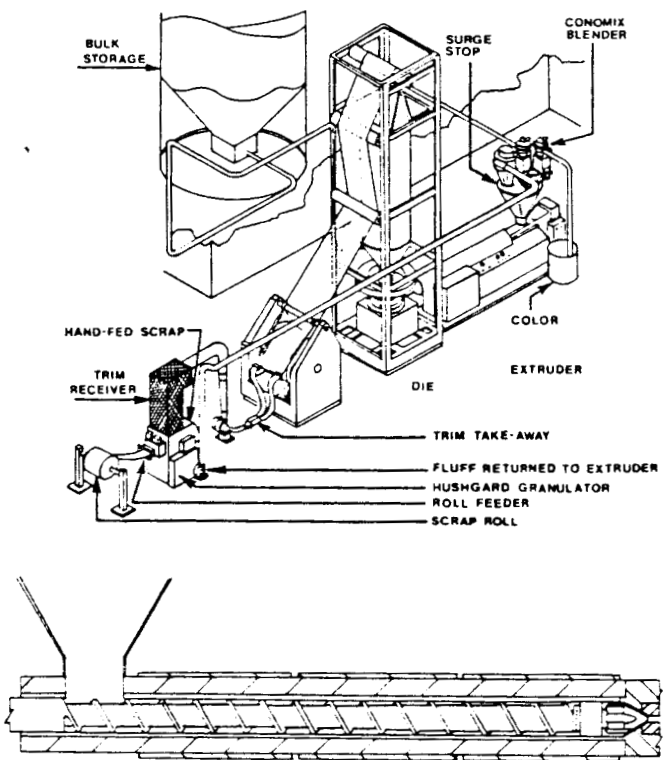


Figure 2. Blown film extrusion line and cross section of the extruder.

copolymer structures. It is important to note that starting with a given monomer or copolymerizing monomers, one can obtain chemically an infinity of structures that results in products of different physical properties.

Since polymers are large chain-like molecules containing many single covalent bonds, polymers are permitted, to degrees that depend in the quiescent state on temperature and steric factors, to assume a great many conformations. Conformations are shapes of the chain molecules resulting from rotations about single primary bonds. They may be viewed locally (random, zig-zag, helical), or as long range, describing the entire chain (random coil, folded or extended). Long-range conformations, such as the degree of chain extension and the period of chain folding, can be induced by imposing shear or tensile deformations or by specific thermal treatment such as annealing. Polymer processing steps that orient and anneal polymer melts affect the long-range

conformations of the polymers and, consequently, their properties. The folded chain conformation is characteristic of polymer crystalline regions; random coil and strained (oriented) random coil conformations characterize amorphous polymers in the molten liquid, flexible rubbery or solid (rigid coils) state.

Each mer unit in a polymer molecule is a site for intermolecular bonds. Since the number of mer units within each polymer molecule is so large, the level and structural significance of intermolecular bonding between chains is large. Polymer substances satisfy the following relation:

$$\sum_{\bar{x}_n} \left( \begin{array}{l} \text{strengths of inter-} \\ \text{molecular forces} \\ \text{in each mer} \end{array} \right) > \left( \begin{array}{l} \text{strength of any one} \\ \text{type of primary bond} \\ \text{present} \end{array} \right)$$

The above holds for  $\bar{x}_n > 200$  for strong hydrogen bonding and dipole forces and for  $\bar{x}_n > 500$  for weak dispersion forces. The implication of this relation is that polymers are either very viscous liquids or solids, increasing in viscosity and modulus with increasing molecular weight. At elevated temperatures, thermal degradation or chain scission occurs, not vaporization. In addition to intermolecular bonding, chain entanglements contribute, above a certain chain length, to the polymer melt and solid properties acting as additional intermolecular forces.

The degree to which intermolecular forces are utilized depends on the distance between the units creating the bond, since, to a first approximation, these forces depend inversely on the seventh power of this distance. There are two broad classes of polymers: amorphous and semicrystalline. Amorphous polymers are composed of coiled or strained coiled chains, randomly packed, characterized by a major second-order transition, the glass transition at a temperature range reported as  $T_g$ . Below  $T_g$ , the chains are rigid; above it, flexible and, of course, ever changing in conformation due to thermal motions. Semicrystalline polymers, below the melting point  $T_m$  of the crystalline portion form both amorphous and crystalline regions. The amorphous portion responds to temperature changes as noted above, *i.e.*, it has a  $T_g$ .

The crystalline regions are folded chain crystallite aggregates often in the morphology of spherulites. The size and number of spherulites, the degree of crystallinity, and the rate of crystallization depend strongly on the crystallization and annealing temperature as well as orientation of the macromolecular chains during crystallization. Polymer processing can affect the crystalline morphology of semicrystalline polymers and, therefore, their properties. Crystallization of highly oriented and extended chains results in anisotropic, and anisotropically strong, morphologies from row nucleation along lines parallel to the extension direction (4). These structures are common in fibers and at the surface of injection-molded (5) semicrystalline articles.

Figure 3 shows the specific volume of amorphous and semicrystalline polymers. The specific volume values at various temperatures indicate strength of secondary bonds. Relative to the glass transition and melting temperatures, polymers can be classified as follows:

- Elastomers are polymers with crosslinks, or intense en-

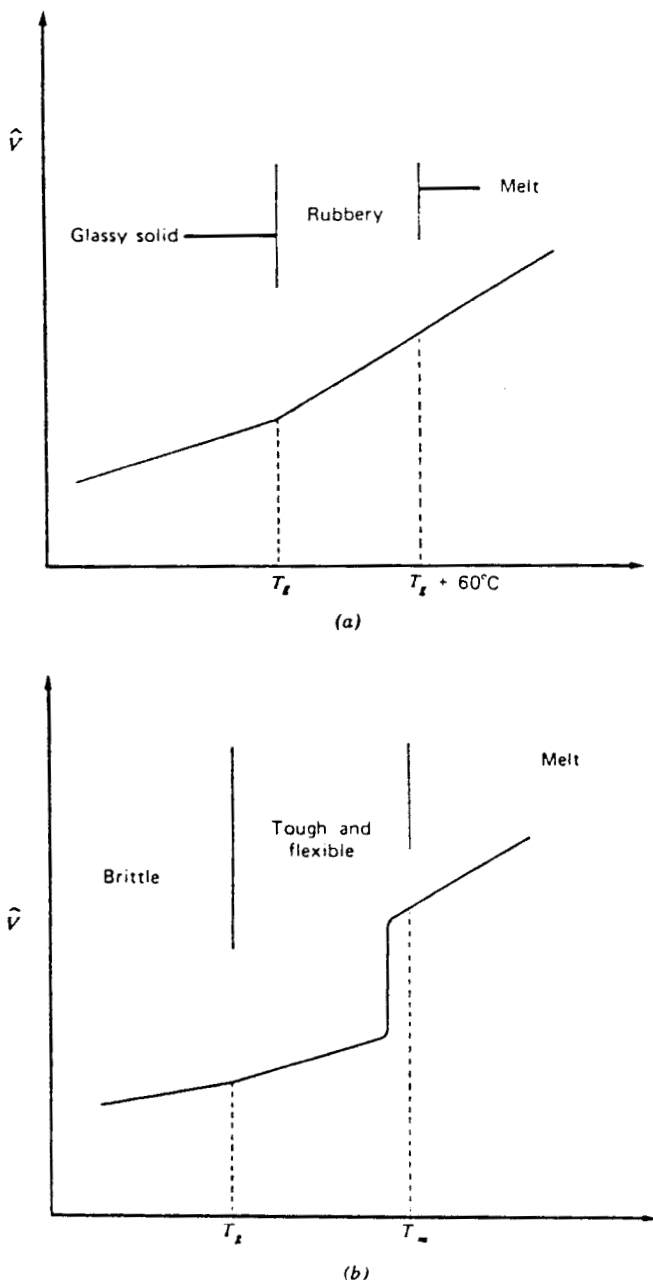


Figure 3. Temperature dependence of the specific volume of polymers: (a) amorphous; (b) semicrystalline.

**Table 1. Tensile moduli of polymers and other materials: approximate ambient values.**

Material	Modulus $E$ (N/m <sup>2</sup> $\times 10^9$ )	Density, $\rho$ (kg/m <sup>3</sup> $\times 10^{-3}$ )	Specific Modulus, $E/\rho$ ( $\times 10^6$ )
<b>Polymers</b>			
Commonly processed HDPE	1-7	1	1-7
"Extrusion drawn" HDPE fibers <sup>a</sup>	~70	1	~70
Specially cold drawn HDPE fibers <sup>b</sup>	68	1	68
DuPont "Kevlar" fibers	132	1.45	92
Theoretical limit of polymers other than HDPE and PVA—fully extended <sup>c</sup>	<140	~1	<140
Theoretical limit of HDPE and PVA—fully extended <sup>d</sup>	240-250	1	240-250
<b>Other Engineering Materials</b>			
Aluminum alloys	<70		
"E" glass fiber <sup>e</sup>	63	2.54	35
Steels	~200		
RAE carbon filaments <sup>f</sup>	420	2.0	210

<sup>a</sup>Southern, J. H., and R. S. Porter, *J. Appl. Poly. Sci.*, 14, p. 2305 (1970).

<sup>b</sup>Capaccio, G., and I. M. Ward, *Poly. Eng. Sci.*, 15, p. 219 (1975).

<sup>c</sup>Watt, W., N. Phillips, and W. Johnson, *The Engineer* (May 27, 1960).

<sup>d</sup>Sakurada, I., T. Ito, and K. Nakamae, *J. Poly. Sci.*, C15, p. 75 (1966).

entanglements. The viscosity ranges from  $10^5$  to about  $50 \text{ N} \cdot \text{s}/\text{m}^2$  making it  $10^4$  to  $10^6$  larger than the viscosity of monomeric liquids. The viscosity decreases with increasing shear rate and decreases with increasing temperature, the temperature sensitivity or flow activation energy decreasing with increasing shear rate.

Let us try to understand this in terms of the Deborah number: The time allowed by the experimenter for flow motions,  $t_{exp}$ , is equal to  $(1/\dot{\gamma})$ . The lower the shear rate, the longer the time allowed for chain motions; the more motions against secondary forces and entanglements, the larger the internal frictional dissipation and therefore the viscosity. The Newtonian plateau observed for all temperatures on Figure 5 is indicative of a Deborah number that is for all practical purposes zero,  $\lambda \ll 1/\dot{\gamma}$ .

As the shear rate increases, the viscosity decreases; the polymer melt shows shear thinning or pseudoplasticity. Macromolecular motions, which take long times compared to the allowed  $t_{exp}$  at increased shear rates, do not take place fully. Consequently, the viscosity drops as the melt dissipates less and stores more (in terms of retained orientation) of the applied mechanical energy. If the flow at these shear rates is interrupted, the melt will recover some of the applied strain.

The terms viscoelastic, shear-rate-dependent, and pseudoplastic denote for polymers the occurrence of the same

phenomena: flowing macromolecular structures (but not flowing to their fullest extent) that become oriented during flow and therefore possess entropy elastic properties.

The effect of temperature on the melt viscosity can be explained in terms of classical rate theory

$$\eta|\dot{\gamma} = A \exp(\Delta G/RT) \quad (6)$$

where  $A$  is a preexponential constant and  $\Delta G$  is the free flow activation energy. For monomers  $\Delta G$  is a constant independent of the shear rate. In polymer melts it depends on the shear rate applied, since with increasing shear rate chain motions that result in flow do not take place and a fluid which is less viscous and more elastic is created: the fluid is changed. As the shear rate is increased, the resulting smaller range motions require a smaller  $\Delta G$  to occur. This results in a polymer melt viscosity that is less temperature-sensitive at high shear rate. Furthermore, the Newtonian plateau extends to higher shear rate at higher temperatures because of the decrease of the relaxation times with increasing temperatures; molecular motions occur more easily in higher-temperature, more-loosely-bonded polymer melt chains.

The shear rate range of interest to polymer processing is approximately 1 to 1,000. Log-log plots of viscosity against shear rate exhibit, Figure 5, a pronounced linearity in the region of processing interest; for common polymers the slopes are between  $-0.3$  and  $-0.85$ . This linearity implies a power law, rheological, constitutive equation of the form

$$\tau = -\eta(\dot{\gamma}) \cdot \dot{\gamma} \quad (7)$$

where  $\tau$  is the shear stress and

$$\eta = m \dot{\gamma}^{m-1} \quad (8)$$

in which  $m$  (with units of  $\text{N} \cdot \text{s}^m/\text{m}^2$ ) is the consistency index, a temperature-dependent constant denoting the viscosity at  $\dot{\gamma} = 1$ , and  $\eta$  is a dimensionless quantity called the power law index. As Bird *et al.* (7) states, "This simple expression is, without a doubt, the most well-known and widely used empiricism in engineering work; many specific flow problems and heat transfer problems have been solved using it and the results have been proven to be useful."

### Effects of polymer nature on processing

The nature of polymers briefly described in this article has profound effects on both the processed products and the nature of the elementary processing steps used.

**Structuring of Polymer-Processed Products.** During the forming and post-forming steps in polymer processing, orientation can be imparted in the molten state that can be locked in, at least partially, if the experimental time for solidifying the melts is small compared to the relaxation times, *i.e.*, if  $De > 1$  or  $De \gg 1$ . Structuring occurs when the desired orientations are locked in and imparted to a final product.

It is difficult to avoid structuring of processed polymers since the products are usually thin and heat transfer pro-

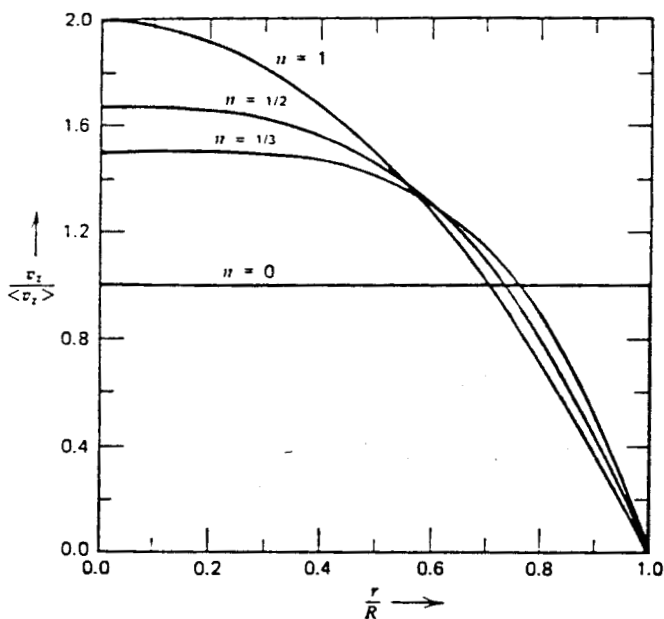


Figure 8. Tube flow velocity profiles for Newtonian and power-law fluids.  $n = 0$  corresponds to plug flow; the Newtonian (parabolic) profile is shown as  $n = 1$ .

For power law fluids

$$\tau = -m\dot{\gamma}^{n-1} \cdot \dot{\gamma} = -m\dot{\gamma}^n \quad (14)$$

and

$$VED = m\dot{\gamma}^{n+1} \quad (15)$$

If  $\mu$  is taken to be larger or equal to  $m$ , which is always the case, the energy dissipated by Newtonian fluids at high shear rates is higher than that with power law pseudoplastic fluids. This is good news for polymer processing that operates at high shear rates.

This good news has to be qualified by the fact that the smaller amount of energy dissipated in pseudoplastic fluids is distributed more unevenly; it is spent almost entirely in shear heating of the layers of the fluid next to the tube wall. This can spell trouble, since these layers are slow flowing, have long residence times in the tube and, therefore, get appreciably heated. Furthermore, since the thermal diffusivity of pseudoplastic polymer melts is very low (of the order of  $10^{-3}$  cm<sup>2</sup>/s), the heat generated in the outer layers does diffuse to the cooler fluid layer of the core, remaining trapped. Calculated results indicate that temperature rises of 80°C for the exiting wall layers of a fluid are possible, Figure 9.

While temperature inhomogeneity of the exiting melt is not desirable, the real concern of high levels of shear heating is with thermal degradation. Polymers, because of their macromolecular nature, are susceptible to thermal degradation. There is, for every melt temperature, an induction time  $\theta(T)$  before degradation begins; it decreases exponentially with increasing temperature and can be prolonged with the addition of higher levels of stabilizers. For times greater than  $\theta(T)$ , the rate of degradation increases exponentially with temperature. Exposure times of just a few minutes are needed for thermal degradation when the polymer melt is hot. In polymer processing, in addition to wor-

rying about high melt temperatures generated by viscous dissipation, one must avoid regions of stagnation even at moderate temperatures. This is why all transitions from wide to narrow channels are tapered; this helps avoid the gross circulatory flows that can result in long hold-ups.

*Effects of the Nature of Polymers on the Elementary Step of Melting.* The thermal energy balance in Eq. 16 sums up all the possible mechanisms of heating (melting) and cooling of an incompressible substance

$$\rho C_v \frac{DT}{Dt} = \nabla \cdot k \nabla T + \eta \dot{\gamma} : \dot{\gamma} + \dot{S} \quad (16)$$

where  $\rho$  is the density;  $C_v$  is the heat capacity at constant volume;  $k$  is the thermal conductivity;  $\eta \dot{\gamma} : \dot{\gamma} = -\tau : \dot{\gamma} = VED$ ; and  $\dot{S}$  denotes any source of heat, such as a chemical reaction. The temperature of a substance can be changed by conduction at an external surface with the resulting heat flux thermally penetrating the substance with time or by forcing the substance to flow, thus creating  $VED$  that is proportional to viscosity, and finally by the presence of a chemical source.

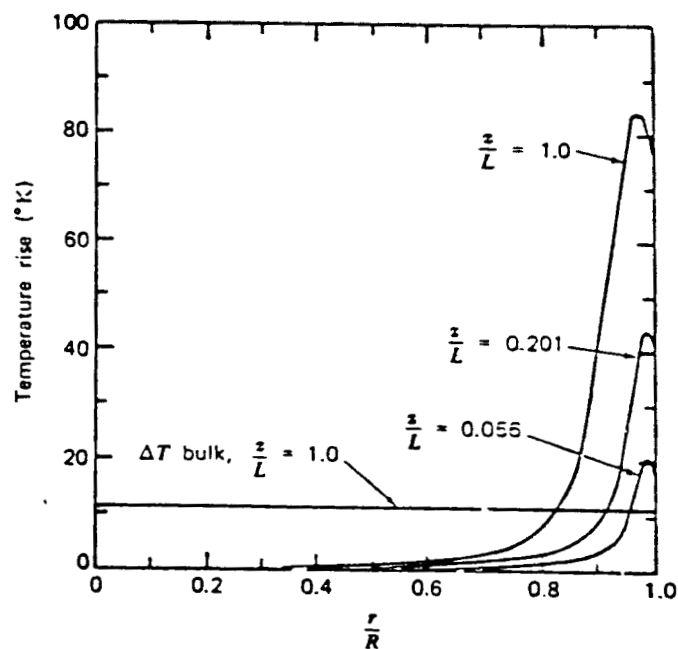


Figure 9. Temperature profiles calculated for ABS Cycloac T in tube flow.

Reprinted from AIChE J., 20, p. 785 (Sept., 1974).

When Eq. 16 is translated to the task of heating a polymeric substance and taking into consideration the nature and properties of polymers, we can arrive at some "do's" and "don'ts," which allow us to use sensible and hopefully optimal methods for heating polymers. Conduction *per se* is not an effective mode of heating polymers. For this to be effective, since the thermal conductivity is very low (polymers are thermal insulators), the temperatures of the hot surface in contact with polymers have to be very high. Yet conduction can generate a thin layer of melt (necessary for flow to occur), which when forced to flow will automatically supply heat at high rates, assisting conduction.

Again, by forcing the molten layer to flow, high melt vis-

cosity can be made, an asset, not a liability to heating. Furthermore, if we force the melt layer to flow away from the hot surface, we achieve two more important tasks for efficient and safe melting: 1. the opportunities for thermal degradation are diminished; 2. it allows for fresh solid polymer to come into contact with the hot external surface and have a chance to be melted without a layer of insulating melt. All of the above describe the mechanism of melting in polymer processing, termed *conductive melting with forced melt removal*.

*Effect of the Polymer Nature on the Elementary Step of Mixing.* Mixing is an operation intended to reduce the non-uniformity of a mixture. This can be accomplished only by inducing physical motion of the ingredients. Three basic types of motions are involved in mixing. Brodkey (13) calls these motions diffusions and classifies them as molecular diffusion, eddy diffusion, and bulk diffusion. Molecular diffusion is a process that is spontaneously driven by a concentration (chemical potential) gradient. It is the dominant mechanism of mixing in gases and low-viscosity liquids. In turbulent mixing, molecular diffusion is superimposed on the gross random eddy motion, which in turn may occur

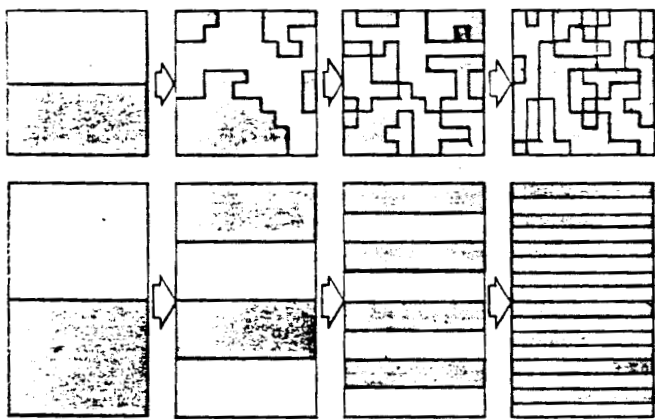


Figure 10. Distributive mixing: (a) random rearrangement such as what takes place in a V-blender; (b) ordered rearrangement such as what partially takes place in motionless mixers.

within a larger scale of bulk diffusion or convective flow process.

In polymer processing, because of the very high viscosities of polymer melts, eddy diffusion is rarely reached and molecular diffusion is almost insignificant in that it occurs extremely slowly. Therefore, we are left with convection as the dominant mixing mechanism. Convection is also the only mixing mechanism for solid-solid mixing.

However, if one of the components is a low molecular weight material (e.g., certain antioxidants, foaming agents, dyes used for fibers, slip additives), molecular diffusion may be a significant factor in the mixing process. Moreover, the utility of such additives in the finished product depends on molecular diffusion. Molecular diffusion plays, of course, an important role in such mass transfer dominated processes as stripping and devolatilization.

Convection involves movement of fluid particles, blobs of fluid, or clumps of solid from one spatial location in a system to another. Convection results in mixing either if the

interfacial area between the minor and the major component increases (14) or if the minor component is distributed throughout the major component without an increase in interfacial area (15). The former criterion is relevant primarily to liquid-liquid mixing, and the latter to solid-liquid and solid-solid mixing. Convective mixing can be achieved by a simple bulk rearrangement of the material through a plug flow and requires no continuous deformation of the material. Therefore, it can be termed bulk-convective mixing, plug-convective mixing or simply distributive mixing. Spencer and Wiley (14) have referred to this kind of mixing as repetitive mixing, and McKelvey (16) has used the term simple mixing. This kind of mixing, through repeated rearrangement of the minor component, can in principle reduce nonuniformities to the molecular level. The repeated rearrangement in distributive mixing can be either random or ordered. The former is the process that takes place, for example, in V-blenders and many other solid-solid mixers, whereas the latter forms part of the mixing mechanism in certain motionless mixers. Figure 10 shows these two types of distributive mixing.

Convective mixing also can be achieved by imposing deformation through laminar flow, otherwise known as laminar convective mixing, as streamline mixing (14), or as simply laminar mixing (16). Liquid-liquid and liquid-solid mixing in processing are accomplished by laminar convective mixing through various types of flow: shear, elongation (stretching), and squeezing (kneading). However, shear, often circulatory, flows play the major role in processing.

If a liquid-liquid system is to be mixed by a laminar convective mechanism, permanent deformation or strain (14) must be imposed on the system. The term strain in the context of laminar convective mixing does not include elastic or delayed elastic strains and certainly not rigid body rotation and translation. Furthermore, it should be obvious that for the interfacial surface to increase, both phases must undergo flow. Therefore, the viscosity ratio (as well as the viscoelasticity of the phases that would bring about strain recovery) plays an important role in laminar mixing.

The foregoing discussion implies that in laminar mixing the decisive variable is the strain and that the rate of application of strain and stresses plays no role. This is indeed the case for all operations that do not involve materials that exhibit a yield point (and are miscible) (17). In these cases, shear stresses are irrelevant as far as the degree of mixing is concerned (it is not irrelevant, of course, to power requirements). When there is a component that breaks only upon reaching a certain yield stress, however, local stresses do play a very decisive role in the mixing operation. Examples of such components are carbon black agglomerates and viscoelastic polymer blobs. Moreover, with viscoelastic systems in particular, the rate of stress buildup or local stress histories may be very important. This kind of mixing is referred to as dispersive mixing (16) for solid-liquid mixtures and homogenization for liquid-liquid mixtures.

In polymer processing, nondispersive and dispersive mixing can also be referred to as extensive and intensive mixing. The basic type of motion in extensive mixing is obtained by convection: the mixing may be either distributive

or laminar. The mechanism through which the extensive mixing is imposed on the material may be either an ordered or a random rearrangement process; intensive mixing (*i.e.*, laminar mixing) is achieved by deforming the material in various laminar flow patterns such as shearing, squeezing, or elongational flows.

**Devolatilization and Chemical Reaction.** Chemical reactions can be carried in polymer processing, such as reactive extrusion (REX) (18) and forming, such as reactive injection molding (RIM) (19). In RIM, a relatively low-viscosity, intimately-mixed bicomponent system is pressurized externally to fill a mold, the mold-filling flow field being laminar. Some of the reaction occurs during mold filling, requiring the specification of the viscosity of the reacting mixture over the whole path lines for each particle. Polymerization is completed in an *in-situ* fashion after filling has been accomplished.

Polymer processing equipment such as extruders, through dynamic viscous pressurization, has a powerful mechanism for effecting laminar flow of very viscous reactive systems. They are in principle ideal equipment for carrying out advanced polymerizations. The key design problem is to provide for the necessary residence times for polymerization. Since the design task is difficult, only some polymerization systems are good candidates for reactive extrusion.

Devolatilization for reactive and nonreactive systems is subject to two key properties of polymer melts: the high viscosity allowing for only creeping laminar flow and the low diffusivity of small molecules in viscous melts. Nevertheless, this elementary step can be efficiently carried out in drag-induced flow fields where polymer melts fill the processing equipment flow channels only partially, thus creating free surfaces. In a partially filled extruder, the circulating pool renews the free surface material, bringing small-molecule-rich layers to the free surface, thus increasing the devolatilization rate ( $\dot{E}_v$ ). The thin film on the barrel surface, which also gets renewed at least partially, contributes significantly to the process ( $\dot{E}_v$ ).

We have given an overview of polymer processing from the standpoint of how the multifaceted and unique nature of polymers dictates specific mechanisms for the elementary steps involved in polymer processing operations. ■

## Handling of Particulate Solids

In polymer processing, most of the raw materials and intermediate products are in the form of particulate solids, which require storage, transportation, feeding into machinery through bins and hoppers, and compaction. They are further processed in various batch and continuous operations involved in polymer industries. Solid particulates are generally classified as granules (usually larger than 1 mm in diameter) and powder (usually less than 100  $\mu\text{m}$  in diameter).

Prior to the 1880s, the designers of bulk storage facilities and transportation systems for particulate solids assumed that they behaved like fluids and determined pressures on

the basis of the apparent fluid density (20). However, it was soon realized that the properties of particulate systems are quite complex and lie between those of a fluid and a solid. When a bed of particulate solids is deformed, no simple relationships exist between the deformation field and the distribution of stresses acting on the particulate bed.

### Transport of momentum

The stress distribution in particulate solids arises from the following (21):

- Transport of momentum accompanying the translation of particles between layers of particulate solids in relative motion
- Transport of momentum by collisions between particles from layers in relative motion
- Forces between particles at points of sustained contact

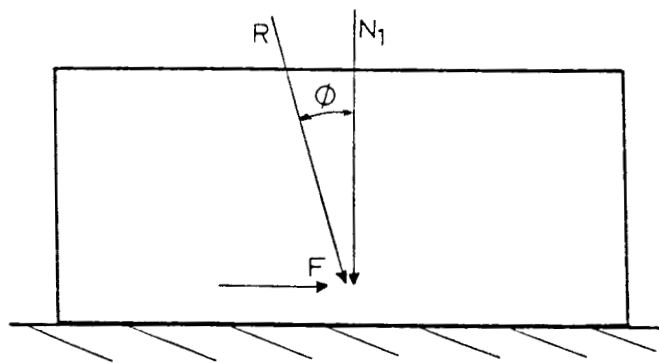


Figure 11. Forces acting on a sliding block.

Transport of momentum by collisions between particles is similar to molecular momentum transfer in liquids. The forces between particles at points of contact are most significant and give particulate solids their unique nature. The behavior of particulate solids is strongly affected by their frictional properties as well as their bulk densities, which in turn depend strongly on the applied stress field.

Particulate solids can sustain shearing stresses as manifested by their ability to form piles. However, when the shearing stress goes above a yield value, sliding at particle-particle contact points occurs. This is shown in Figure 11, where a block of solid material is resting on a surface of the same material. The shear stress,  $F/A = \tau_{12}$ , is increased until the block begins to slide. During shearing if the normal stress,  $N_1/A = \tau_{11}$ , is increased, a greater shear stress value will be required to cause slippage.

The resultant force,  $R$ , makes an angle,  $\phi$ , with the normal and is referred to as the friction angle. A linear relationship exists between the shear stress,  $\tau_{12}$ , and the normal stress,  $\tau_{11}$ :

$$\tau_{12} = \tau_{11} \tan \phi = \tau_{11} f \quad (17)$$

where  $f$ , the coefficient of sliding friction, characterizes the shear resistance of the polymer upon yielding. The coefficient of friction is a material property and depends on the microscopic roughness of the surface of the solid, the presence of contaminants on the surface, surface chemistry, and

**Table 2. Sliding friction coefficients of polymeric resins.**

	Coeff. of Friction between Poly. and Steel*	Coeff. of Friction between Poly. and Poly.
Nylon	0.25	0.25
Teflon	0.04	0.04
Polyethylene	0.15-0.25	0.10-0.25
Polystyrene	0.4-0.5	0.4-0.5
PVC	0.5	0.4-0.6
Polymethylmethacrylate	0.44-0.5	0.4-0.8
Saran	0.22-0.24	

\* Polished steel  
Reprinted from (28).

temperature. Typical values of the sliding friction coefficients of some polymeric resins are given in Table 2.

Although the coefficient of friction is a material property, the shear resistance of the same material in bulk (as an aggregate of particulate solids) depends on other factors. Especially important is the degree of interlocking between individual particles that determines the internal friction coefficient of a particulate bed. This highlights the importance of the bulk density of a particulate solid: its variation with loading and deformation is critical to the development of frictional forces between particles.

The bulk density and the internal friction coefficient of particulate solids are in turn affected by (21):

**Composition.** Composition basically determines the deformation characteristics of individual particles.

**Particle Size Distribution.** In a particulate solid system with a broad particle size distribution, the smaller particles fill the gaps between larger particles. This gives rise to a greater bulk density. A broad particle size distribution will give rise to more contact points between particles. This generates better interlocking between particles, leading to a greater internal friction coefficient.

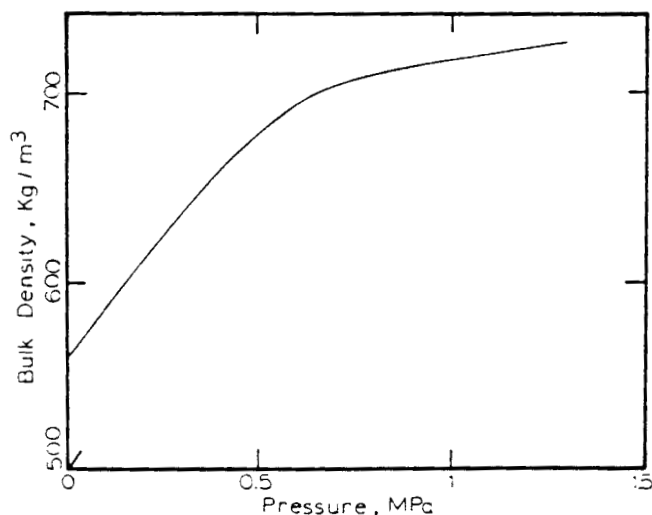


Figure 12. Bulk density vs. pressure of a phenol-formaldehyde molding powder at 25°C under one-dimensional consolidation test.

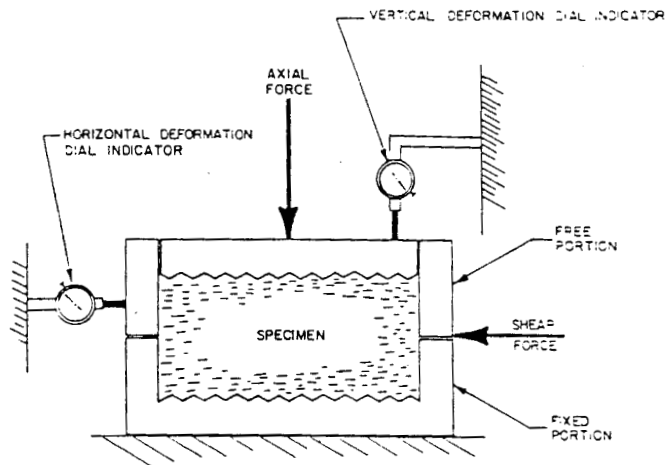


Figure 13. Translational shear box (28).

**Particle Shape.** Polymer particulates composed of more rounded grains will exhibit lower internal friction coefficients than those composed of angular particles. More angular particles generate greater interlocking.

### Stress-strain behavior

One of the experimental methods used for the determination of stress-strain behavior of bulk particulate solids is the one-dimensional consolidation test. In this test a cylindrical specimen is compressed axially, while lateral strains are prevented. The lateral stress to axial stress ratio in such a test is not unity.

Typical results from a one-dimensional consolidation experiment with a phenol formaldehyde molding powder are shown in Figure 12. Pressure increases exponentially, when bulk density is increased. The deformation is primarily plastic. Reduction of axial stress results in the recovery of only the elastic deformation, which is relatively small. In this configuration, the specimen never reaches shear failure. The strain is due to volumetric strain, *i.e.*, axial strain that is small due to the lateral constraint.

It is also possible to design a direct shearing apparatus, where the particulate bed is compressed in one dimension, while simultaneously being sheared along a horizontal plane. In the translational shear box method, Figure 13, the specimen is confined in a box which is split horizontally (22). While the axial stress compresses the specimen, the horizontal shear is applied to the free portion of the box. The free portion slides over the fixed portion upon the yielding of the particulate bed.

Typical stress-strain behavior of high and low bulk density particulate solids in direct shear is shown in Figure 14. The shear stress value increases up to a maximum, where the particulate bed yields. This point defines the shear strength or shear failure of the bed. Figure 14 further indicates that there are differences in the shearing behavior exhibited by particulate solid samples that initially had different bulk densities.

The role of the initial bulk density can be understood by noting the volume changes upon deformation, Figure 15. It appears that the high bulk density material exhibits an anomalous behavior since it initially expands in volume

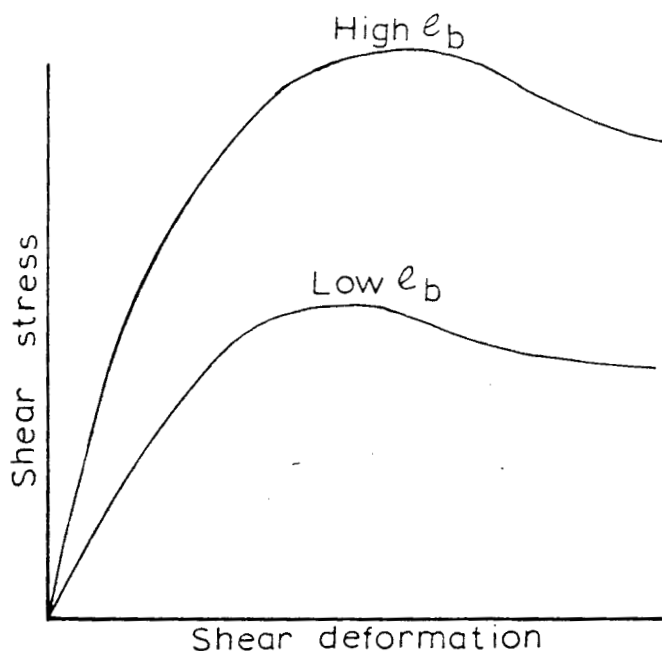


Figure 14. Shear deformation of particulate solids.

upon compression. The major portion of the deformation in direct shear is a result of sliding, rolling or rearrangement of the particulates relative to one another. When the particles are tightly interlocked as in high bulk density resins, it is necessary for the particles to roll up over one another in order for the bulk solid to shear, giving rise to dilatation. On the other hand, for low bulk density materials the smaller particles will move into open spaces as the solid bed deforms. Therefore, compression will be accompanied by a volume decrease.

The shear strength of particulate solids depends on the packing or degree of interlocking of individual particles. This suggests that granular solids may either strengthen or weaken during deformation (21). Deformation of a material of low initial bulk density under relatively high loads will lead to compaction and strengthening. On the other hand, deformation of high bulk density material under relatively low loads is accompanied by dilatation and weakening.

In addition to the internal shear resistance of a bed of particulate solids, the interactions with the walls of the container are also important. These interactions are controlled by the roughness of the container surface as well as the properties of the particulate solid.

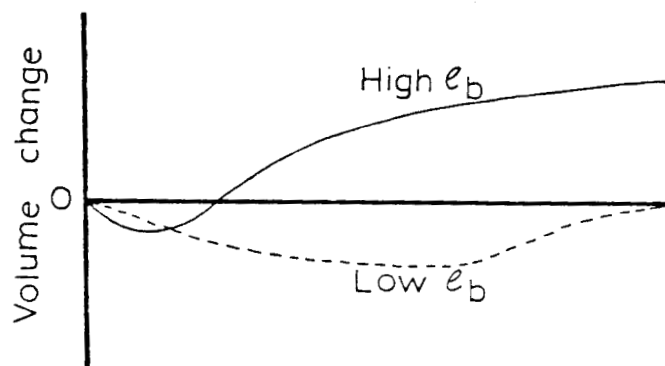


Figure 15. Volume change during deformation of particulate solids.

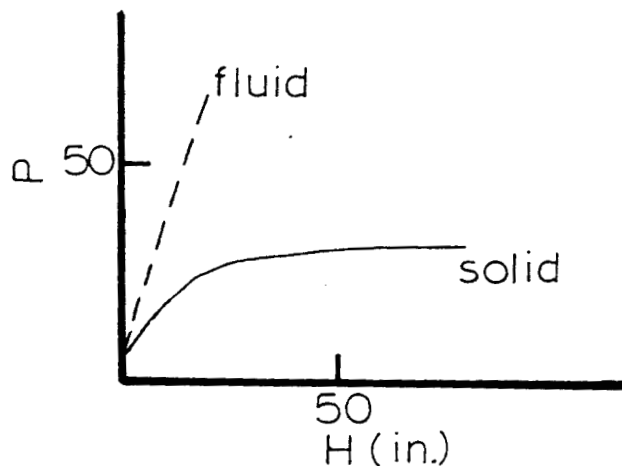


Figure 16. Pressure at the base as a function of height of cylindrical bin.

### Storage and transport design equations

These salient features of particulate solids can be applied in a number of simplified analyses to establish the storage and transportation design equations for particulate solids in polymer processing. Examples of such equations include pressure distribution in bins and hoppers, compaction, mechanical displacement flow, and the drag-induced flow of particulate solids (1).

The pressure distribution in a cylindrical and vertical bin of diameter,  $D$ , and height,  $H$ , has been derived by Janssen (23,24) assuming that vertical stresses are constant over any plane, the ratio of horizontal and vertical stresses is a constant,  $K$ , and constant bulk density,  $\rho_s$ . The force balance gives the pressure,  $P$ , as a function of height,  $h$ , from the bottom of the bin as:

$$P = \frac{\rho_s D}{4fK} \left\{ 1 - \exp \left[ \frac{4fK(h-H)}{D} \right] \right\} \quad (18)$$

where  $f$  is the friction coefficient. The maximum pressure at the base approaches a constant value as height,  $H$ , goes to infinity

$$P_{max} = \frac{\rho_s D}{4fK} \quad (19)$$

indicating that the pressure will level off above a critical height. This is shown in Figure 16 for a cylindrical hopper filled with polystyrene cubes. The frictional forces between the particles and between the walls and the particles give rise to a pressure profile, which reaches an asymptotic value above a critical height. Obviously, the pressure-height relationship for fluids is linear.

In mechanical displacement flow and compaction, the variation of axial stresses with distance can be determined with the same assumptions employed in Janssen's analysis.

## The shear strength of particulate solids depends on the packing or degree of interlocking of individual particles.

The relevant geometry is shown in Figure 17 (1). A force balance on a differential volume element with length,  $dx$ , and wetted perimeter,  $C$ , and cross-sectional area,  $A$ , leads to (2):

$$F_x - (F_x + dF_x) - C\left(\frac{F_x}{A}\right)Kf dx = 0 \quad (20)$$

Upon integration the pressure profile during mechanical displacement or compaction is given as:

$$P_x = P_0 e^{-KfCx/A} \quad (21)$$

Equation 21 indicates that pressure drops exponentially with distance in particulate solids. In flow of a fluid the

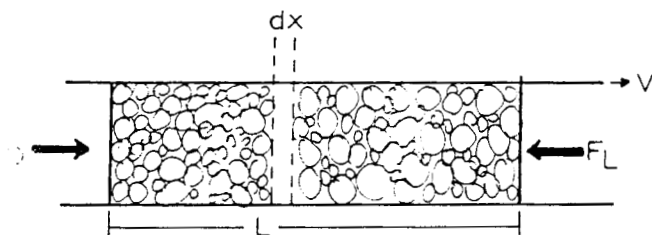


Figure 17. Mechanical displacement flow of particulate solids.

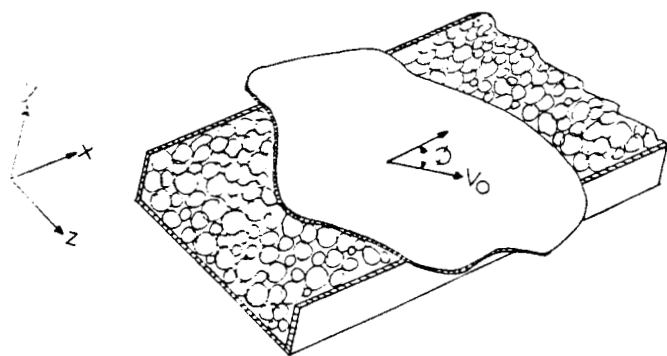


Figure 18. Drag-induced conveying of particulate solids.

pressure change would have been linear. The exponential drop in pressure has significant ramifications in the development of machines to compact and convey polymer solids. Generally, mechanical displacement is avoided in solids conveying and drag-induced methods are preferred.

The general mode for conveying of solids in processing machines, including plasticating simple screw extruders, intermeshing co-rotating and non-intermeshing (tangential) twin screw extruders, various types of continuous mixers, and reciprocating injection molding machines, is the drag-induced mechanism. It is shown in Figure 18. The solid bed moves in the down-channel direction,  $x$ , due to the fric-

tional drag exerted by the top plate moving at an angle,  $\theta$ , to the down-channel direction. Those familiar with plasticating extrusion will recognize that the top plate represents the unwound barrel and  $\theta$ , the helix angle of the screw, and the velocity of the top plate is the linear screw speed.

The simplified pressure distribution in drag-induced flow is:

$$\frac{P_x}{P_0} = \exp \left\{ \left[ C_1 f_1 \cos(\theta + \phi) - C_2 f_2 \right] \frac{K_x}{A} \right\} \quad (22)$$

where  $f_1$  and  $f_2$  are friction coefficients at the moving top plate and the stationary plates;  $C_1$  and  $C_2$  are the wetted perimeters of the moving plate and the stationary plates; and  $\phi$  is the solids conveying angle that increases with increasing volumetric flow rate of the solids. This expression suggests that the drag-induced flow is very suitable for pressurization, compaction and conveying of particulate solids in polymer processing. The friction coefficients of the moving and the stationary surfaces,  $f_1$  and  $f_2$ , play a significant role in drag-induced flow. Pressurization capability with drag increases with high values of the friction coefficient of the moving plate,  $f_1$ , and low values of the friction coefficient of the stationary plate,  $f_2$ . This explains why, in plasticating extrusion, the barrel surface is roughened and the screw surface is smoothed.

Although in principle very high values of pressure can be obtained on the basis of Eq. 22, high values are rarely attained in drag-induced solids conveying. This is because frictional drag also gives rise to energy dissipation that is proportional to the pressure in the channel (25). The heat flux,  $q_w$ , at the plate and solid bed interface generates a film of molten polymer. As this film develops, the solid-solid frictional drag mechanism is converted into a viscous drag mechanism governed by the shearing stresses developed at the molten film. ■

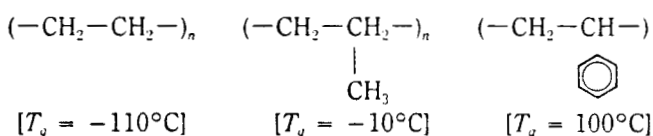
## Melting, Softening and Solidification of Polymers

In some polymer processing operations, polymers need to be softened or molten to a state that allows them to be pumped and pressurized. Pressurization is necessary for shaping through extrusion dies or for filling of mold cavities. Upon shaping, the thermoplastic polymer needs to be cooled and solidified.

The processing temperatures are about 80-150°C above

the glass transition temperature of amorphous polymers and 10-100°C above the melting temperature of semicrystalline polymers. (The glass transition temperature is that temperature below which no large-scale molecular motion is possible and the amorphous polymer exhibits the characteristics of a glass.) At temperatures above the glass transition temperature, amorphous polymers behave like viscous liquids if their molecular weight is small and rubbery if their molecular weight is high. The glass transition temperature of a polymer is affected by the molecular structure as well as its molecular weight distribution.

The effect of the molecular structure can be dramatic: a rigid aromatic group, for example, increases the glass transition,  $T_g$ , of polystyrene significantly as compared to polyethylene and polypropylene.



Increasing molecular weight increases the glass transition temperature as shown in Fox and Flory equation:

$$T_g = T_{g\infty} - K/\bar{M}_n \quad (23)$$

where  $T_{g\infty}$  is the glass transition temperature for infinite molecular weight and constant,  $K$ , is a parameter of the polymer.

Drastic changes in the mobility of the polymer molecules and the viscosity occur at temperatures over the glass tran-

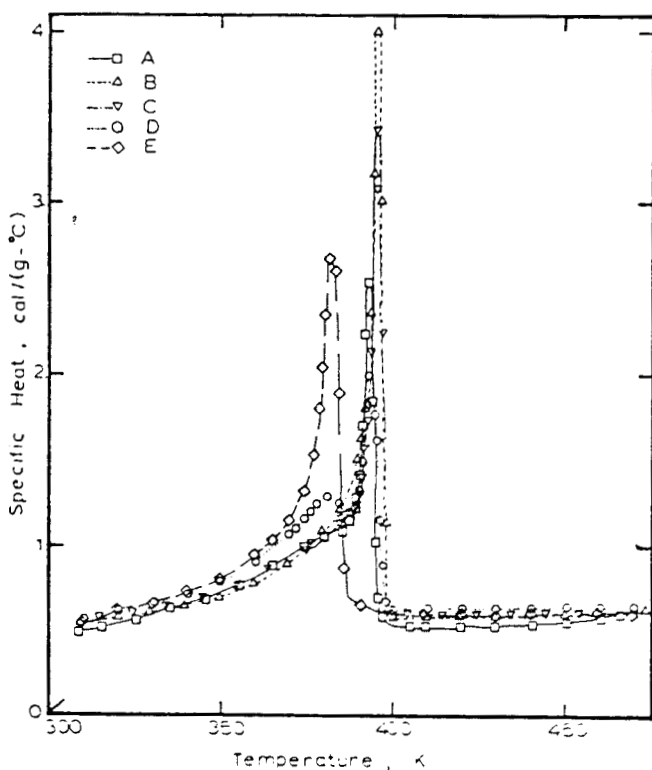


Figure 19. Specific heat capacity vs. temperature of polyethylene resins, various densities.

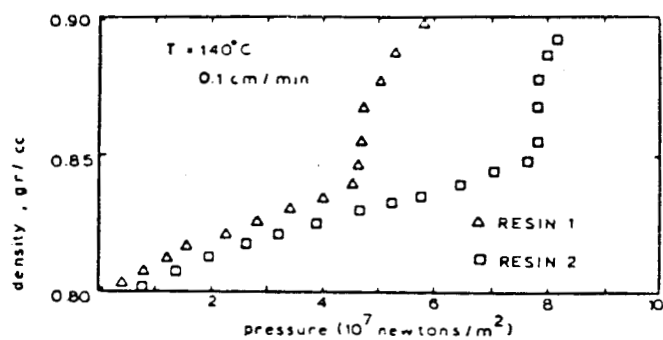


Figure 20. Pressure-induced crystallization under pressure-volume-temperature experiment (26).

sition. The change in viscosity can be represented by the empirical Williams-Landel-Ferry (WLF) equation:

$$\log(\eta/\eta_{T_g}) = \frac{-17.14(T - T_g)}{51.6 + (T - T_g)} \quad (24)$$

This equation is valid up to 100°C above the glass transition temperature. It suggests that the ease of processing increases significantly as one moves upwards away from the glass transition temperature, where shear viscosity is of the order of  $10^{12}$  Pa·s.

On the other hand, for semicrystalline polymers that possess some degree of structural regularity, the first-order transition temperature, the melting temperature needs to be known if a suitable processing temperature is to be selected.

The typical specific heat capacity-temperature behavior of various commercial polyethylenes is shown in Figure 19. The deviation from the baseline denotes the heat of fusion,  $\Delta H$ , given by:

$$\Delta H = \int_{Tm_1}^{Tm_2} C_p dT \quad (25)$$

where  $Tm_1$  corresponds to the onset temperature of melting and  $Tm_2$  is the temperature at which the last trace of melting disappears and is referred to as the melting temperature. For homopolymers, the melting temperature again depends on the molecular weight of the polymer:

$$\frac{1}{T_m} - \frac{1}{T_{m\infty}} = \frac{2R \cdot M_0}{\Delta H \cdot M_0} \quad (26)$$

where  $T_{m\infty}$  is the melting temperature for an infinite length polymer, and  $M_0$  is the molecular weight of monomer.

The melting temperature of polymers also depends on the hydrostatic pressure through the Clausius-Clapeyron relationship:

$$(T_m)_p = (T_m)_{atm} \exp\left(\frac{(\hat{V}_c - \hat{V}_a)(P - 1)}{\Delta H_f}\right) \quad (27)$$

where the melting temperature at pressure,  $P$ , is shown to be an exponential function of the hydrostatic pressure.  $\hat{V}_c$  and  $\hat{V}_a$  denote the specific volumes of amorphous and crystalline phases of the polymer. The effect of pressure on melting temperature is shown in Figure 20, where a high-

The low thermal conductivity and stability of polymers require the continuous removal of the layer of molten or softened polymer from the interface.

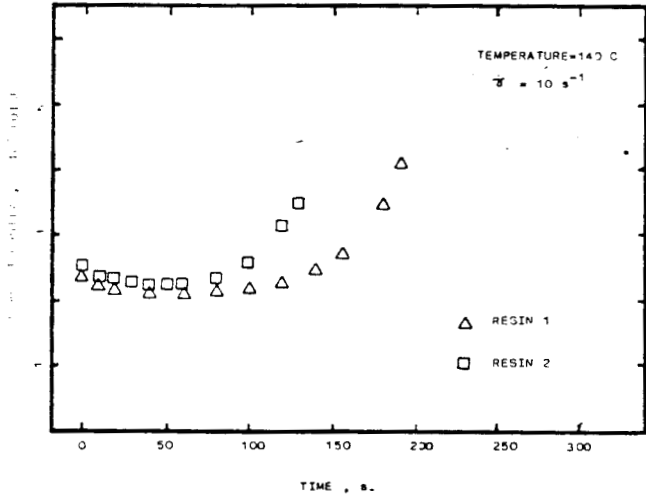


Figure 21. Stress-induced crystallization in steady shear flow under one and plate.

density polyethylene sample is kept at 150°C and its melt density is determined versus pressure (26). Rapid increases over a critical pressure indicate that the sample is crystallizing. A temperature of 150°C is comfortably above the melting temperature of high-density polyethylene under ambient pressure, which is about 134°C.

Furthermore, the first-order crystalline/melt-phase transformation of polymers depends on the deformation history. This is shown in Figure 21, where a high density polyethylene sample at 140°C is undergoing steady shear. Orientation of the macromolecules during deformation results in crystallization as manifested by the increase in shear viscosity.

All possible modes of raising the temperature of a solid

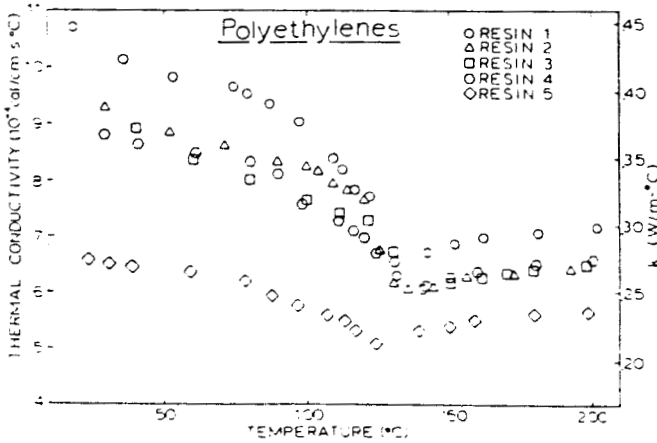


Figure 22. Thermal conductivity vs. temperature of various polyethylene resins.

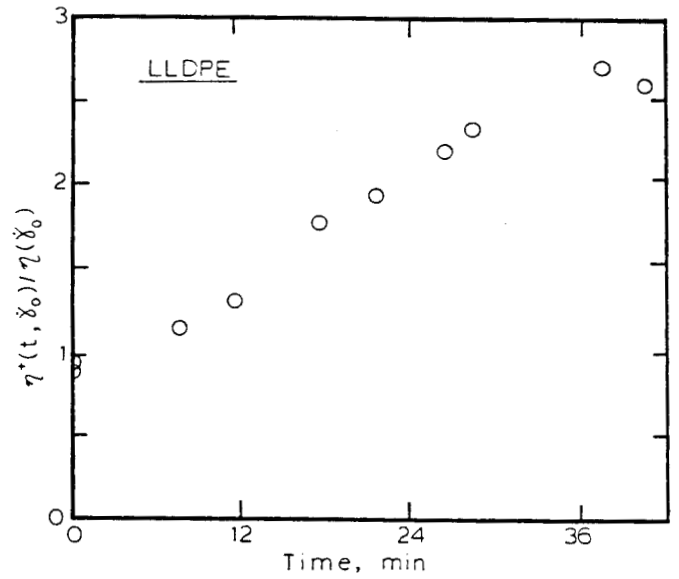


Figure 23. Oxidation of a linear polyethylene resin under steady shear.

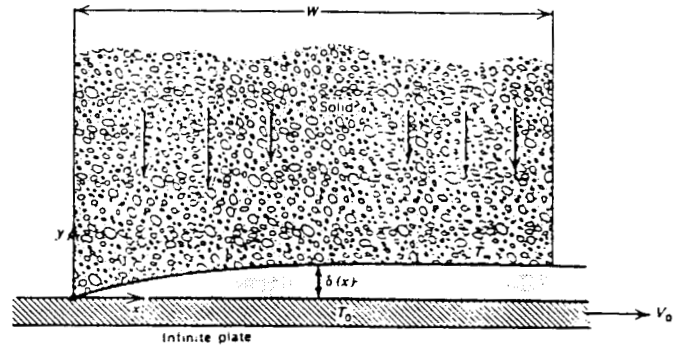


Figure 24. Drag-induced melt removal.

polymer to the optimum processing temperature are given by the thermal energy balance given in Eq. 16. One can raise the temperature of a solid polymer by conduction, compression, viscous dissipation, and with heat from an external source. Practically, only conduction and an external heat source can be used as vehicles to raise the temperature of solids to the melting temperature.

While ultrasonic or dielectric heating (external sources) have been used, conduction heating is primarily used for melting polymeric solids. The following are typical boundary conditions:

- Conductive heat flux through the surfaces, where polymer is sandwiched between hot platens
- Convective heat flux such as circulation of hot air at the surface

- Radiation-based heat flux from infrared or microwave heaters at the surface

- Viscous energy dissipated at the interface of a molten and moving film of polymer

While significant heat fluxes can be provided through surfaces, the ability to heat the bulk polymer is limited by the relatively low thermal conductivity values for polymers. Typical values for polyethylenes are shown in Figure 22. Moreover, most polymeric resins are not very stable at high temperatures. Thermal degradation, oxidation or cross-linking reactions, which adversely affect the properties of the product, can occur. The oxidation behavior of a polyethylene is shown in Figure 23. Occurrence of oxidation is manifested by an increase in viscosity under simple shear flow.

The low thermal conductivity and stability of polymers require the continuous removal of the layer of molten or softened polymer from the interface by either:

- Drag-induced melt removal
- Pressure-induced melt removal

Drag-induced melt removal is the most common mode in polymer processing, Figure 24 (I). Here a bed of particulate solids is compressed against a hot surface at temperature,  $T_w$ , and moving at a velocity,  $v_w$ . The melt is dragged off by the moving plate permitting further melting. The molten film is initially generated from conduction through hot surfaces and from the frictional heat generated at the particulate solids and moving wall interface. The interface temperature between the solids and the molten film is the melting temperature,  $T_m$ . Over the molten film, the viscous energy dissipation term is significant.

This mode of melting is widely employed in polymer processing including plasticating single- and twin-screw extruders and in reciprocating injection molding machines. In a single-screw extruder, the solid bed is confined between two flights, a barrel surface and the screw root. The relative velocity between the polymer and the barrel surface drags the polymer melt toward the pushing flight, where it grows in volume and circulates. Obviously as one moves in the down-channel direction, the percentage of solids in the channel decreases, whereas percentage of the melt increases. ■

## Pressurization and Pumping

An elementary step for the shaping of polymeric resins is the pressurization and pumping. For example, in injection molding the melt needs to be pressurized to high pressures, in the order of thousands of psi, to flow through the nozzle and the flow distribution channel, and to fill the mold cavity. In extrusion, the melt needs to be pressurized to flow through the die at the desired volumetric flow rate. The pumping and pressurization characteristics of polymers are

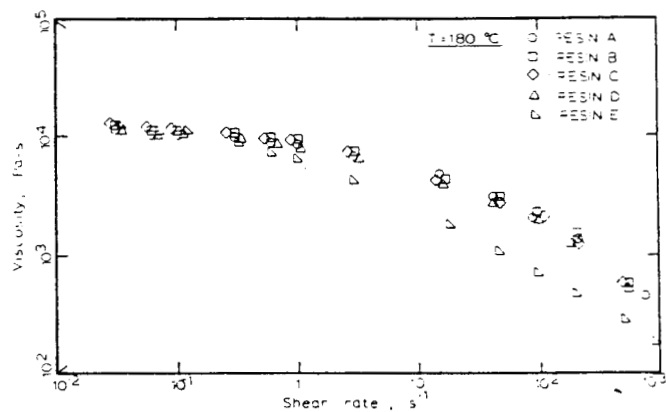


Figure 25. Shear viscosity as a function of shear rate of polyethylene resins.

affected by their non-Newtonian rheological behavior. They generally exhibit:

- A shear viscosity material function that depends strongly on the rate of deformation, i.e., shear rate in simple shear
- Development of normal stresses on deformation, indicative of their elasticity
- Fading memory, which suggests that the behavior of the fluid is affected most by the recent events

Moreover, rheological behavior can be strongly affected by the thermomechanical history and by changes in molecular structure upon oxidation and cross-linking.

### Shear viscosity and stress

Typical shear viscosity and first normal stress difference values of various polyethylene resins are shown in Figures

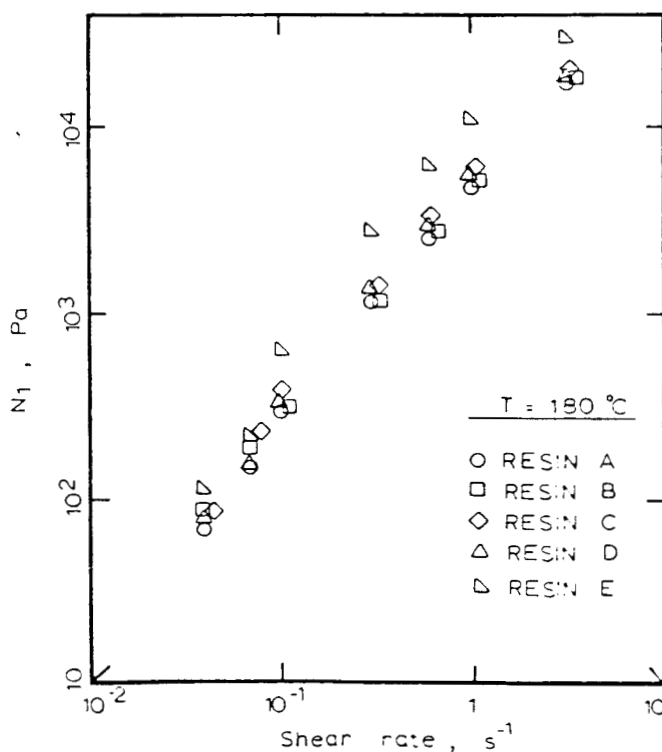


Figure 26. First normal stress difference of polyethylene resins.

The pumping and pressurization characteristics of polymers are affected by their non-Newtonian rheological behavior.

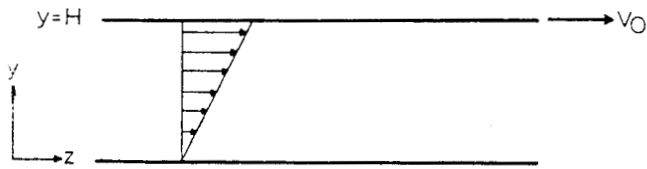


Figure 27. Pure drag flow between parallel plates.

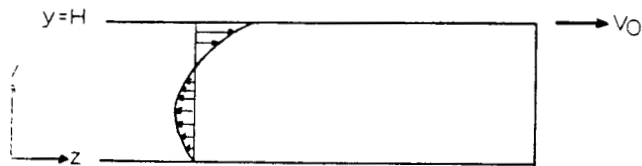


Figure 28. Parallel plate drag and pressure flow.

25 and 26. The relatively high viscosity values of  $10^2$ – $10^3$  Pa·s, the strongly shear thinning nature and the high values of the first normal stress difference, shown in Figures 25 and 26, are characteristic of most polymeric melts.

The methods available for pumping and pressurization of polymer melts are given by Eq. 9, which indicates that a melt can be pressurized through acceleration, gravity, and the application of external stresses ( $I$ ). Acceleration and gravity are generally not effective, although exceptions arise in processes like centrifugal casting, rotational molding, and low-pressure structural molding. On the other hand, the generally high shear viscosity and the elastic nature of polymer melts make viscous forces (Eq. 11) most important. This term must be considered whenever the melt is dragged by a moving surface or is displaced mechanically.

In general, one can distinguish between ( $I$ ):

- Dynamic pressurization through an external moving surface that drags the polymer
- Positive mechanical displacement as in a plunger cylinder arrangement

Both modes of pressurization are commonly used in polymer processing.

Dynamic pressurization can best be understood by considering the isothermal, fully-developed flow of an incompressible melt in between two parallel plates, separated by distance,  $H$ , and with the top plate moving at velocity,  $V_0$ , Figure 27. If there is no down-stream restriction, the volumetric flow rate per unit width of the channel of the fluid,  $q_0$ , is given by:

$$q_0 = \frac{V_0 H}{2} \quad (28)$$

This configuration will obviously not generate pressure, although high volumetric flow rates can be attained. How-

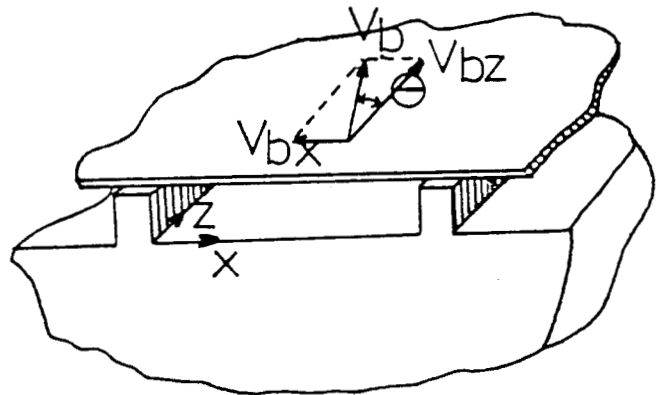


Figure 29. Single-screw extrusion.

ever, if a restriction such as a valve or closed discharge is placed down-stream, Figure 28, the  $z$  component of Equation of Motion becomes:

$$\frac{\partial p}{\partial z} = \frac{-\partial \tau_{xz}}{\partial y} \quad (29)$$

where  $\tau_{xz}$  is the shear stress. In this configuration, the drag mechanism will generate a pressure gradient, the absolute value of which will be equal to the absolute value of the pressure drop over the restriction. This pressure generation capability arises from the power input moving the top plate at velocity,  $V_0$ .

Various ways of bringing about drag-induced pressurization and pumping in polymer processing are shown in Figures 29-34. Figure 29 shows the unwound channel for sin-

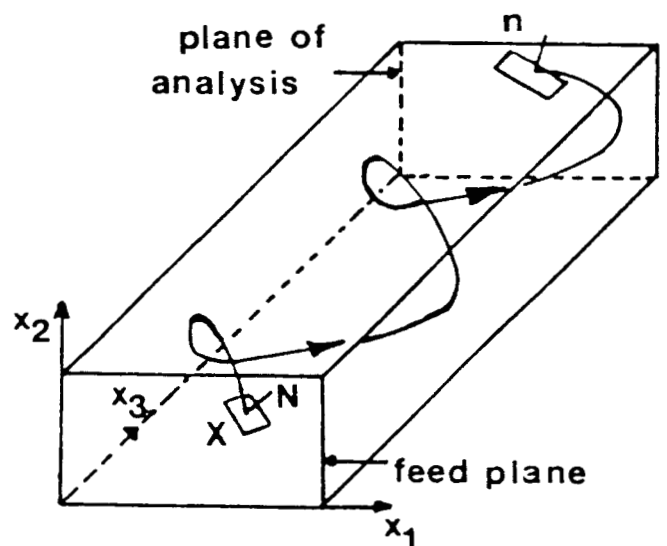


Figure 30. Flow of melt in down-channel direction in single screw (21).

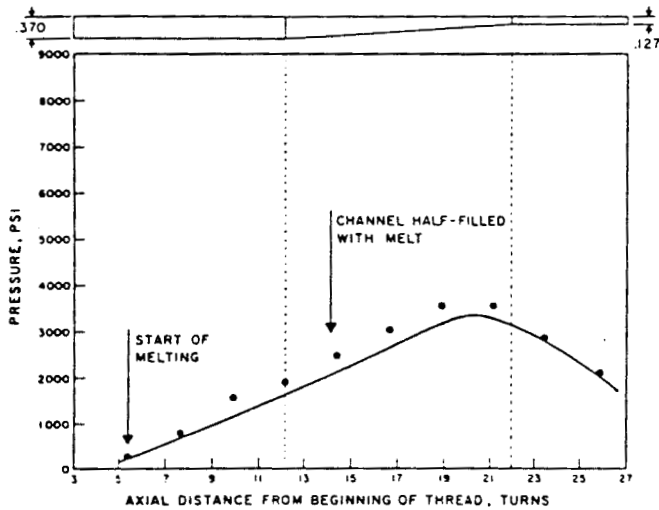


Figure 31. Pressure vs. distance in plasticating extrusion of a LDPE resin extruded in a 2.5 in. (64 mm), 26 L/D extruder (28).

gle-screw extrusion, where the barrel is moving at an angle  $\theta$  to the down-channel flow direction of the melt. Component  $V'_{bx}$  of the barrel drags the fluid in the cross-channel direction and gives rise to a circulatory motion between the pushing and trailing flights. On the other hand, the down-channel component of the barrel velocity,  $V'_{bz}$ , drags the fluid in the down-channel direction. As a result, the melt is pumped and flows in the down-channel direction as a "helix in a helix," Figure 30 (27).

The typical pressure profile in a plasticating extruder is shown in Figure 31 (28). In absolute values the total pressure rise generated in the plasticating extruder is equal to

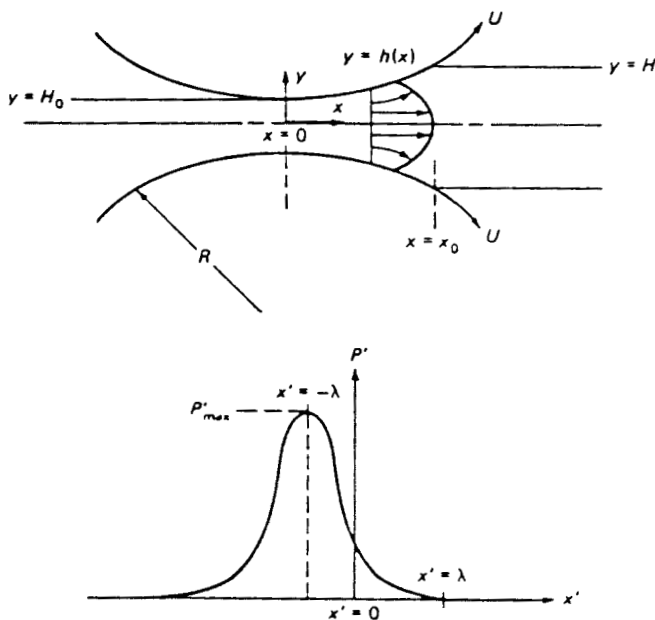


Figure 32. Pressure distribution in between two rotating rolls (29).

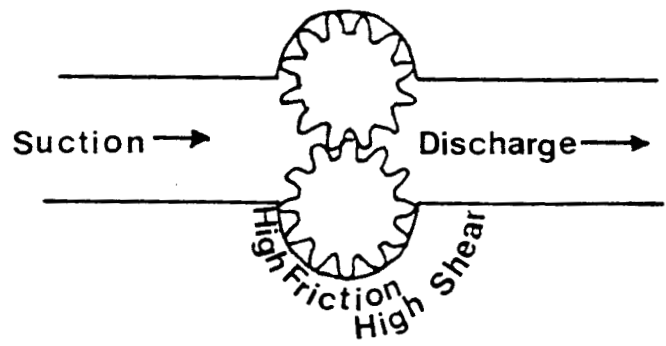


Figure 33. Gear pump.

the pressure drop of the melt in the die at the same flow rate. The pumping characteristics of regular flighted, non-intermeshing, counterrotating twin-screw extruders and corotating, intermeshing twin-screw extruders are similar to the single screw. However, their extensive and intensive mixing characteristics are quite different. On the other hand, corotating disk extruders pump the melt with two moving and drag-inducing surfaces, and can thus pump at higher rates.

For pumping and pressurization of the polymeric melt, the two bounding surfaces need not be parallel. This type of nonparallel plate flow is the basis for extruders with tapered sections, where the channel depth changes as a function of helical distance, in roll mills and calenders, and in coating flows. The typical pressure distribution for the flow of a polymer melt in between two rolls of equal diameter rotating at the same angular speed is shown in Figure 32 (16,29). High pressures can be generated by dragging of the melt with the two rolls, where the cross-sectional area for flow decreases to a minimum at the nip.

The second mechanism available for pumping and pressurization of polymeric liquids is the positive mechanical displacement. This mechanism is used in piston-cylinders, gear-pumps, and fully-intermeshing, counterrotating twin-screw extruders.

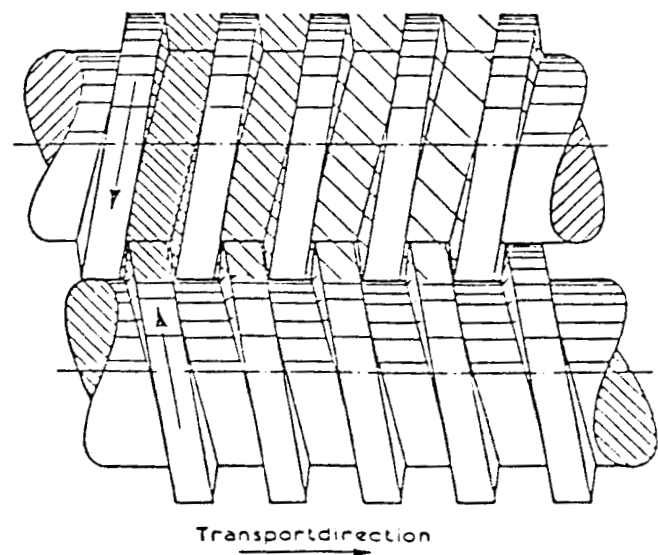


Figure 34. Intermeshing, counterrotating twin-screw extruder with regular flighted elements.

The gear pump ideally displaces an exact volume of melt per revolution, and its volumetric flow rate can be adjusted by varying the speed of rotation. Figure 33. Gear pumps can handle shear viscosities of 200,000-300,000 poise. Furthermore, mass flow rates of up to 100,000 lb/h (45 Mg/h) and pressures to 15,000 psi (103 MPa) can be generated. Gear pumps can also be placed in series with plasticating extruders to pressurize the melt to feed the die at the desired volumetric flow rate.

The mechanical displacement mechanism is also used in the intermeshing, counterrotating twin-screw extruder. The schematic representation of the cylindrical type of intermeshing, counterrotating twin-screw extruder is shown in Figure 34. The bulk of the melt is pumped in the downstream direction in isolated C-shaped segments, with the flights acting as positive displacement pumps. Neglecting leakage flows, the volumetric flow rate is a function of geometry and screw speed if the channel is full of melt.

The drag-induced pumping and pressurization mechanism capitalizes on the high shear viscosity values of polymeric melts. On the other hand, the high values of first normal stress coefficient that they exhibit can be employed to design pressurization devices like the normal stress extruder (12). The design equations for the various types of pumping and pressurization processes are discussed in detail in References (1,16,28,29).

## Mixing

From the viewpoint of the material user and manufacturer, mixing is a processing step designed to tailor a polymer to desired performance criteria. To achieve this goal one or several minor components must be dispersed in a major component, generally a polymer in the liquid or rubbery state at the operating temperature. The minor component can be liquid, rubbery, or solid in nature. If the minor component is in the liquid or rubbery state, compatibility of the components plays an important role. In the solid state, a distinction has to be made between solids with a particle size larger than 10  $\mu\text{m}$  and those with smaller-size particles.

Large particles are free flowing. In such instances as reinforcing fibers, breakage during the mixing process must be avoided. Small particles tend to form agglomerates that must be broken up into the ultimate particle size during the mixing action. Basically the equipment used for mixing can be employed to change the polymer structure for the modification of its properties in a desired way by changing molecular weight distribution and aligning branches.

### Measure of efficiency

The ultimate measure of the efficiency of a mixing process is whether the desired properties have been achieved:

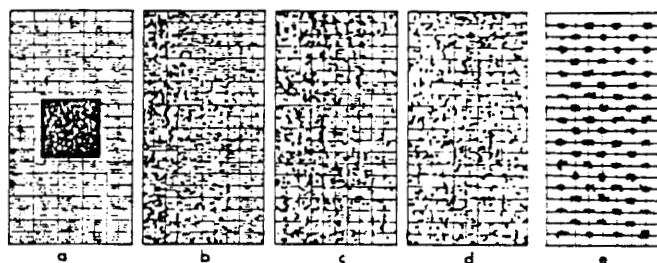
- Uniformity of color of the mixture after a pigment has been added
- Uniformity in size and distribution of bubbles after a foaming agent has been applied

COMPLETELY  
UNMIXED STATE

PERFECTLY  
MIXED STATE

$$\Omega = 1$$

$$\Omega_{\text{mixed}} = \frac{(N_1 + N_2)!}{N_1! N_2!}$$



COMPONENT: A, B

VOLUME FRACTION:  $\alpha, \beta$

ULTIMATE PARTICLE SIZE:  $\infty, \beta$

Figure 35. The mixed state.

- Physical and wear properties of rubber compounded with carbon black
- Modification of the properties of a base polymer as a result of blending it with a semicompatible polymer as well as other properties.

Originally the development of mixing equipment was based solely on empirical information. F.H. Banbury, for example, invented the first and still foremost internal mixer based largely on experience gained from mixing on two-roll mills.

The first step in developing a scientific theory of mixing is a general definition of the mixed state. To transform a system of separate components into a perfectly mixed state, the ultimate particles must be moved into positions that satisfy the definition of such a state. Figure 35. Since an enormous number of particles are involved in mixing it is necessary to define the perfectly mixed state in a statistical fashion.

One perfectly mixed state of a component *A* in a component *B* is achieved if the probability of finding an *A* particle is the same at all points in the mixture and is equal to the volume fraction  $\alpha$  of *A* in the mixture. Assume that  $N_A$  and  $N_B$  are the number of particles of components *A* and *B*; the particles of component *A* differ from those of *B*, but particles within each component are not distinguishable from one another. Under these conditions, there is just one distinguishable arrangement where the components of *A* and *B* are in the unmixed state (Figure 35a  $\Omega_u = 1$ ). The number of distinguishable arrangements that are perfectly mixed, as defined in Figure 35, is

$$\Omega_m = \frac{(N_A + N_B)!}{N_A! N_B!} \quad (30)$$

The number is obviously very large; Figures 35d and 35e represent only two possibilities.

The arrangement shown in Figure 35e is a special one, the so-called regular random arrangement. The probability of approaching such a state with present-day mixing equipment exists only for two compatible components with ultimate particles of molecular size. The intermolecular forces

that are developed during the final phase of mixing facilitate the development of this state.

If  $Va_1$  and  $Vb$  are the volume fraction of  $A$  and  $B$  in the mixture, the perfectly mixed state can be expressed as the probability of finding a concentration  $X_s$  of component  $A$  within a sample volume  $V_s$ ,

$$P(X_s) = \exp \frac{-1/2 \frac{(X_s - a)^2}{\sigma^2}}{\sqrt{2\pi\sigma^2}} \quad (31)$$

If  $\alpha$  is the size of the  $A$  particles, then the  $\eta$  variance  $\sigma^2$  is:

$$\sigma^2 = a \cdot b \frac{\alpha}{V_s} \quad (32)$$

where  $\alpha/V_s$  is the ratio of the volume of the ultimate particle of component  $A$  to the volume of the sample that was drawn.

The distribution of the concentration of a great number of samples of a given size drawn from a perfectly-mixed state will follow Eqs. 31 and 32, Figure 36. Any deviation indicates a less-than-perfect mixture.

Several methods have been proposed to quantitatively define the quality of the mixture. The variance of  $N$  samples is:

$$S^2 = \frac{1}{N-1} \sum_1^N [X_{s_i} - a]^2 \quad (33)$$

where  $X_{s_i}$  is the concentration found in the drawn samples. A mixing index can then be defined as:

$$I = \frac{\sigma_0^2 - S^2}{\sigma_0^2 - \sigma^2} \quad (34)$$

With  $\sigma^2 = a \cdot b$  being the variance of the completely unmixed state. This index assumes the value of 1 for the perfect mix and the value 0 for the completely unmixed state. To study a mixture, the quality of mix is established by drawing large samples to examine gross uniformity and smaller samples to examine texture and the local structure.

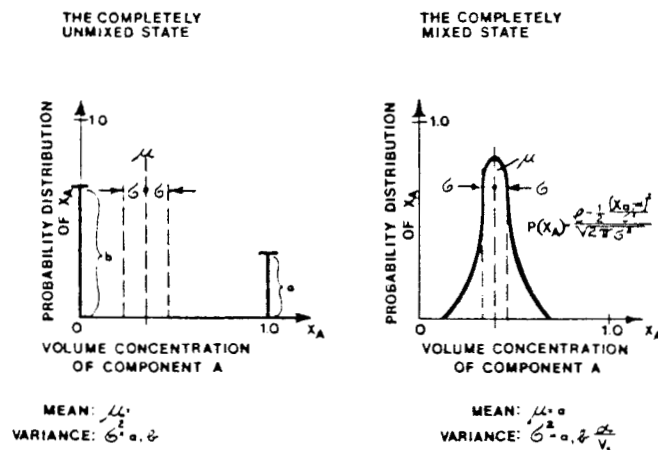


Figure 36. Statistical definition of the state of mixtures.

P. V. Danckwerts (30) introduced measures of scale of segregation and intensity of segregation to characterize texture and local structure. Segregation is a measure of the size of segregated regions; intensity is a measure of the relative differences in concentration between segregated regions. Danckwerts (30) derived mathematical expressions for both measures; however, application requires an automatic image analyzer. Various methods for evaluating quality of mixtures have been developed, each one tailored for a specific class of materials. All methods of arriving at a quantitative rating of the mixture start with the fundamental statistics outlined previously.

### Quality of mixture

A model of the mixing process that enables one to follow that process as performed in a given apparatus and to predict its outcome — the quality of the mixture — would be highly desirable. To achieve that objective one would have to follow every ultimate particle throughout the process; this is a task beyond our capability.

Mixing actions have been investigated by following small domains of materials (cells) through the process. The increase of the interfacial area between the components is being used as a measure of the progress of mixing.

Our approach into mixing will treat the materials as a continuum. While this is a simplification, the results can nonetheless lead to at least a qualitative understanding of more complex conditions. A simplified approach can be justified since the ultimate particles of each component are indistinguishable from one another; therefore it makes little difference which ultimate particle assumes a specific position.

Three basic types of motion have to be considered in mixing:

- Molecular diffusion
- Eddy diffusion (turbulent flow)
- Convection

In polymer processing we are handling at least one high viscosity component, and diffusion is only of significance during the final mixing phase when the minor component is rather uniformly distributed. Since the Reynolds numbers characteristic of turbulent flow cannot be attained with polymer systems, mixing by eddy diffusion is not significant. Consequently, convection is the only type of flow that needs to be considered for mixing of polymers.

Two kinds of convection to be considered in mixing processes are: bulk convection (plug convection) and laminar convection. Convection involves the movement of fluid particles. In bulk convection, blobs of fluid are distributed with or without an increase in the interface between the components. In the latter case, the blobs of material are hardly deformed during their change in position.

Bulk convection can be random: an operator on a two-roll mill cutting the sheet off one roll and folding it, and then reintroducing it into the nip, or ordered bulk convection as in a motionless mixer (31). Bulk convection, as it takes place between the nonintermeshing rotors of an internal mixer, is often referred to as random and is difficult to model. For a given apparatus and operating conditions,

The ultimate measure of the efficiency of a mixing process is whether the desired properties have been achieved.

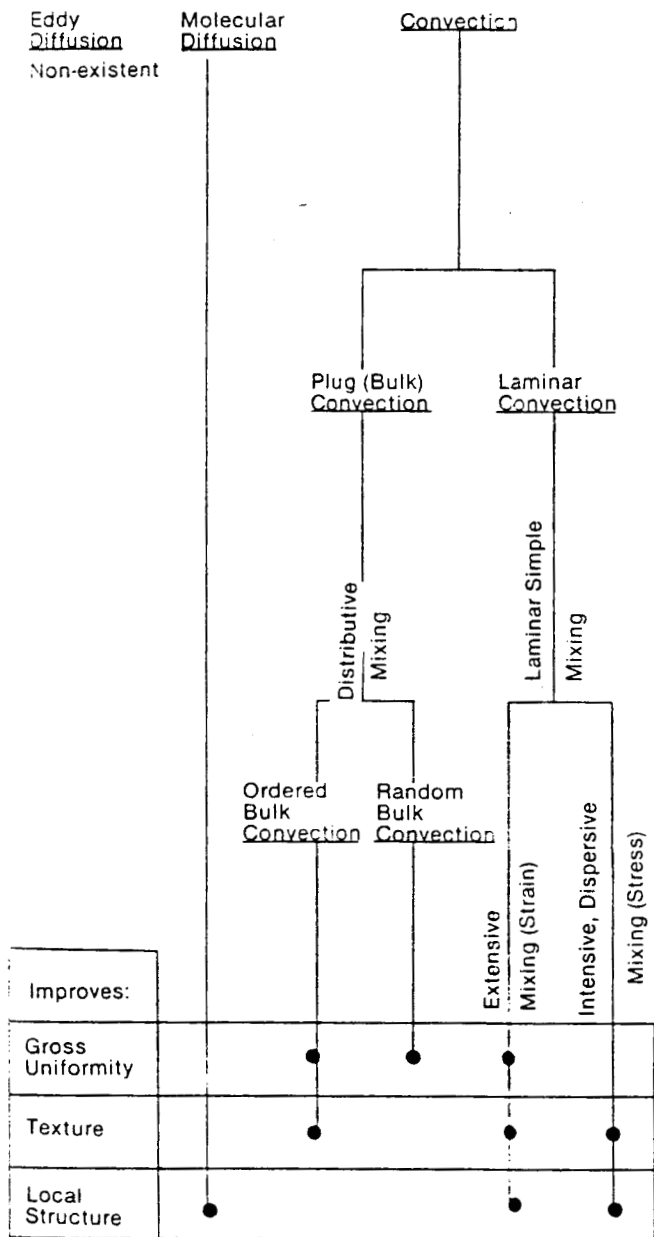


Figure 37. Mixing mechanisms.

however, it will only be a matter of time until techniques have been developed to solve this problem.

Laminar convection is the result of laminar flow imposing deformations on a system. Liquid/liquid and liquid/solid mixing are accomplished by laminar convection mixing through various flow mechanisms: shear, elongational and squeezing. However, shear flow plays a major role in commercial processes since it is easy to attain in industrial machinery. In laminar mixing the viscosity ratio plays an important role and the decisive variable is the strain applied. The rate at which the strain is applied affects only the tem-

perature increase that occurs as a result of the application of a given amount of strain. Even in a shear thinning fluid such as a power law fluid, the total energy absorbed and with it the temperature increase with increasing shear rate for the same total strain (31).

The viscosity of the components affects not only the mixing process but also their elasticity. Including elasticity in the mixing model results in time entering the model as a variable since viscoelastic fluids are capable of storing energy as potential energy and dissipating it as kinetic energy. Modeling of simple mixing processes of viscoelastic materials is now possible using finite element techniques.

These considerations can be extended also to mixtures of a major liquid component and a minor component consisting of free-flowing solid particles. In these cases shear stresses are also irrelevant as far as mixing is concerned.

For minor components of solid particles that form agglomerates which have to be broken up by exceeding a specific yield stress, the rate of strain which determines local stresses plays a decisive role. Considerable additional research is required before it will be possible to predict the break-up of agglomerates of known properties and shape in a given flow field. This mixing is referred to as dispersive or intensive mixing in contrast to extensive or distributive mixing.

In laminar mixing, streamlines never cross. Initial non-uniformities of the distribution of the minor component across the streamlines of the mixing flow can be eliminated only if laminar mixing is combined with plug convection. Figure 37 shows the mixing mechanisms and their impact on the mixing process.

Figure 38 shows the progress of mixing in shear flow between two parallel surfaces and between two concentric cylinders (couette flow). The nonuniformities of the minor component across the stream lines cannot be improved by laminar mixing although the degree of mixing improves. The importance of the initial orientation of the minor component is also shown. Spencer and Wiley (32) were the first to develop the equation of interfacial growth for simple shear flow. They concluded that the increase in the degree of mixedness at large shear deformation is proportional to the shear strain. This result is widely used to predict the degree of mixing in industrial equipment. As a rule of thumb a shear strain of 8,000 to 10,000 units is considered to be the minimum for good mixing.

A volume of fluid in laminar flow undergoes both translation elongation and a rotation. Figure 39 illustrates this for shear flow between parallel plates (in this situation the translation is suppressed); the elongation increases the degree of mixing. Rotation orients the deformed body toward the direction of the shearing action, reducing the rate of progress of mixing. If shearing at half the shear strain is in-

To study a mixture, the quality of mix is established by drawing large samples to examine gross uniformity and smaller samples to examine texture and the local structure.

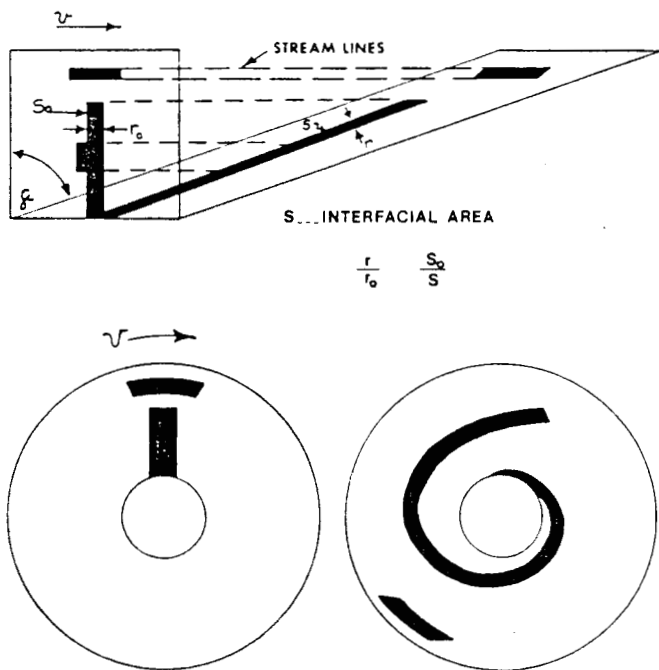


Figure 38. Laminar mixing.

rupted and continued in the perpendicular direction, the degree of mixing achieved for the same strain is considerably larger than that for shearing.

Figure 40 shows the progress of mixing in planar elongational flow, which is free of rotation and mixing is faster than in the previous examples. Erwin (33) showed that simple shear mixing can be optimized by changing the direction of the instantaneous shearing action so that it always maintains angles of  $45^\circ$  with the direction of the principal axis of deformation. Studies on laminar mixing emphasize

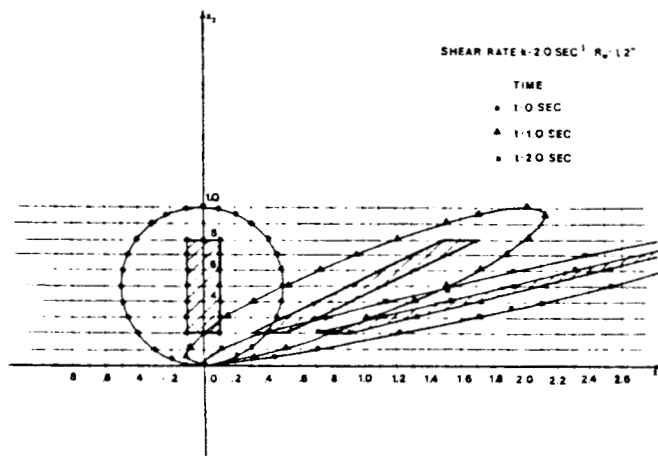


Figure 39. Simple shear field.

the importance of plug flow in combination with laminar flow. This not only evens out any initial nonuniformity in the distribution of the minor component but it also changes orientation to the shearing action.

An important feature of continuous mixing devices is the residence time distribution. To ensure a uniform product, achieving a narrow residence time distribution is important. Equal residence time of all particles is a requirement for a uniform quality distribution of the mixture. Often polymer systems with a very high temperature sensitivity or with temperature-activated reacting additives have to be processed. Extrudates can contain varying amounts of gels resulting from excessive residence time of small fractions. Also the time to purge a mixing system is determined by its residence time distribution.

### Mixing devices

The oldest mixing device is the two-roll mill. It is a very effective mixer still used in laboratories and in the rubber industry for small special lots. The Banbury mixer with its two counterrotating, nonintermeshing rotors was the first internal mixer. It is still the most important mixing device in the rubber industry.

A number of mixers following basically the same design concept use both nonintermeshing or intermeshing rotors. During the 1960s the first continuous mixer was developed by The Farrel Company. A number of continuous mixers with nonintermeshing, counterrotating rotors of different geometries have been developed and introduced to the market since. They are competing with the fully-intermeshing, corotating twin-screw extruder. With the introduction of high shear mixing sections and other modifications of the screw geometry, the corotating twin-screw mixer has be-

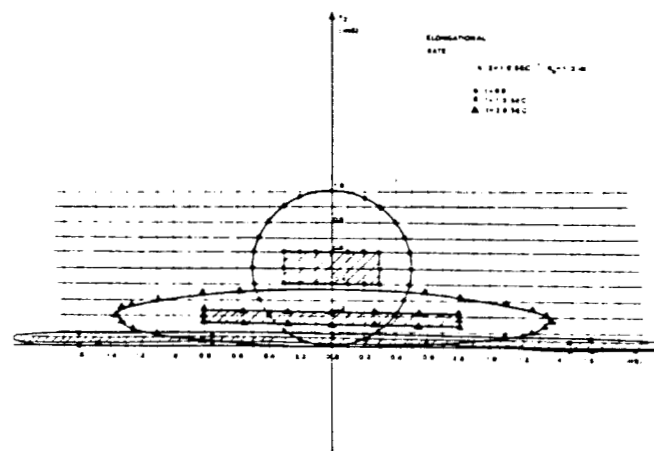


Figure 40. Planar elongational flow: pure shear flow.

come a very efficient mixer that can be easily adapted to the requirements of a large number of polymers. Both the continuous mixers and the corotating twin-screw mixer are generally not designed to generate significant exit pressures. This allows a greater flexibility in the selection of the operating variables.

The mixing efficiency of the counterrotating, intermeshing twin-screw extruder is not good. However, mixing can be improved by introduction of special mixing sections. With its narrow residence time distribution, the twin-screw extruder is used for compounding of heat-sensitive material.

A relatively new addition to the industrial mixing machinery is the Disk-Pack, which is a good mixer for small and medium output rates. It is also capable of melting, devolatilization, and pumping.

Single-rotor extruders are basically for melting, devolatilizing, and pumping. Through the introduction of devices that break the laminar flow pattern in the channel, limited mixing efficiency can be obtained. ■

## Devolatilization and Reactive Processing

Polymers discharged from the reactor sometimes contain high percentage of volatile components and require purification down to a few parts per million. The degree of purification is dictated by the ultimate use to which the resin will be put. High-purity requirements, for example, are needed to meet health and safety standards for food-packaging materials and end-use mechanical properties, both of which can be adversely affected even by small amounts of residual contaminants.

### Devolatilization

Since the contaminants in most cases are volatile relative to their polymeric hosts, they are removed from the condensed phase (polymer) by evaporation into a contiguous gas phase. Such separation processes are commonly referred to as devolatilization (DV). The polymer to be devolatilized may be in the form of a melt or particulate solid. Separation is effected by applying a vacuum or by using inert substances, such as purging with nitrogen gas or steam.

Devolatilization is an important unit operation in the processing of polymeric materials, perhaps second only to mixing and compounding. Knowledge about its mechanism is fragmentary and imprecise; mathematical models and design algorithms are incomplete and inadequately tested.

It is convenient to identify two distinct DV regimes. In flash evaporation, the molten feed stream contains large amounts of solvent. Application of vacuum causes foaming; the evaporation rate is determined by the rate of heat transfer to the polymer that replaces the latent heat of vaporization of the volatile component. In the second regime, the feed is solid or, if molten, dilute enough to afford a diffusion-controlled DV rate.

In most industrial operations, three process elements are distinguishable:

- Solid particles when the polymer is in the rubbery state, *e.g.*, polyethylene
- Solid particles when the process temperature,  $T$ , is at or below the glass transition temperature,  $T_g$ , of the polymer, *e.g.*, PVC

- A stationary melt film or pool and a rotating melt pool, sometimes called a rolling bank when  $T > T_g$ .

The rotating melt pool and stationary melt film coexist in various proportions in all DV equipment containing rotating blades or flights.

*Equilibrium.* The ultimate separation attainable is determined by a thermodynamic partition law relating to the equilibrium composition of the polymer to the equilibrium partial pressure of contaminant in the contiguous gas phase,  $P_c$ . The partition law,

$$P_c = P_c^0 \gamma_c \phi_c \quad (35)$$

stems from Flory-Huggins theory, where  $\phi_c$  is the volume fraction of the contaminant;  $P_c^0$  is the vapor pressure of the pure contaminant; and  $\gamma_c$  is the activity coefficient.

$$\gamma_c = \exp [(1-\phi_c) + \chi (1-\phi_c)^2] \quad (36)$$

where  $\chi$  represents an interaction parameter. For sufficiently small contaminant concentrations, Eq. 35 takes the form of Henry's law,

$$P_c = K_w w_c \quad (37)$$

where  $w_c$  is weight fraction and

$$K_w = P_c^0 (\rho_p / \rho_c) \exp (1 + \chi) \quad (38)$$

$\rho_p$  and  $\rho_c$  are the densities of the polymer and contaminant, respectively.

*Inert Substances.* Introduction of an inert substance enhances DV in several ways. Its presence in the vapor phase reduces  $P_c$  and the attainable contaminant composition. Furthermore, the presence of an inert substance in the polymer melt as a separate (dispersed) phase allows flashing of the contaminant at higher pressures through the additivity of vapor pressures. In addition, the vaporization of an inert, dispersed liquid, *e.g.*, water, greatly increases the interfacial area for mass transfer. However, it does enhance foaming.

*Foam-Enhanced DV.* In principle, bubbles form when the polymer melt is exposed to a reduction in pressure  $P$  such that  $P$  is less than  $P_c$  by  $2\sigma/R$ , where  $\sigma$  is surface tension and  $R$ , the initial radius of a bubble. A supersaturated solution results and initiates boiling or foaming. In practice, however, vacuum levels below supersaturation are often not required to induce foam formation in polymer melts; indeed foaming has been observed at surprisingly low contaminant concentrations.

Even in the absence of added inert substances, bubbles are probably nucleated heterogeneously by metastable

pockets of undissolved gases, trapped within cracks and crevices of the particulate matter present in the polymer. These gas pockets are liberated by a reduction of external pressure. Entrained air has the same effect. Entrainment can occur through the interstitial voids in the feed hopper of a pellet-fed extruder or by drag flow into the nip formed by the convergence of a rolling pool and the polymer adhering to a contiguous stationary wall in a rotating machine, such as an extruder or a thin-film evaporator.

**Power.** Thermal energy is introduced into molten polymers by direct transfer of heat through equipment walls and transformation of mechanical energy (shaft work) into thermal energy via viscous dissipation.

The rate-controlling step in flash evaporation, where the concentration of volatile contaminants is high, is frequently the rate of heat transfer through equipment walls. This is partly because of the large amount of latent heat required and partly because of notoriously poor heat transfer coefficient of the polymer. Mechanical introduction of heat is significant only when the polymer melt viscosity is high. This occurs at low volatile concentrations where large amounts of latent heat are no longer present. Then DV might even be diffusion-controlled. Therefore, an important design consideration, especially for vented extruders, is how much of the evaporation energy in a given composition-viscosity range can be obtained from drive power.

## Staging

Reduction of the applied vacuum level,  $P$ , results in two competitive effects. On the one hand, the lower  $P$  is, the greater the separation potential, a condition that can be explained from both an equilibrium viewpoint (a lower effluent  $P$ , and therefore ultimate  $w_i$ ) and from rate viewpoint (larger driving force, feed  $P_i - P$ , for foaming). On the other hand, the lower  $P$ , the lower is the amount of contaminant vapor removed per unit volumetric displacement of vacuum pump.

These competing effects suggest that vacuum should be staged; higher pressure (low vacuum) should be used when most of the volatile component is removed. Lower pressures (high vacuum) should be used to attain a low final contaminant composition. While staging can minimize the required total vacuum displacement, it requires the use of larger equipment (a longer vented section on an extruder, for instance), for equivalent target separations and throughput rates. An optimum design, of course, will call for a cost comparison between the relative benefits of smaller vacuum pumps as compared to smaller extruders.

## Transport properties

The analysis and design of most DV processes require a knowledge of molecular diffusivities not only in the diffusion-controlled condition, but also in the foam condition. Bubbles presumably grow by absorbing volatile contaminant from the surrounding polymer melt. Contaminant molecules are transported by diffusion to the bubble-melt interface. Therefore, it is conceivable that diffusion is the rate-controlling step in foam DV, although diffusion distances be-

tween bubbles are small and interphase transport surfaces large.

In the absence of bubbles, DV rates may be enhanced by surface renewal or mixing steps. In general, it is far better to expose the melt periodically to many short evaporation cycles (or stages) with intermittent mixing than to a single cycle of equal total duration without intermittent mixing.

All DV processes whose rates are ultimately determined by molecular diffusion become limited by the inordinately small molecular diffusivities. The diffusivities of small-molecule solutes in polymer melts diminish considerably with concentration level to values that can be orders-of-magnitude below those for conventional liquids. Corresponding diffusivities in solid polymers are even lower, a deficiency sometimes offset by small diffusion distances, as is the case for polymer particles of very small diameter from emulsion or suspension polymerizations.

## Equipment

It is convenient to classify DV equipment in accordance with the physical state of the polymer (melt vs. solid) and with transport conditions (high vs. low percentage contaminant).

When the polymer is a liquid of relatively low viscosity and the driving force ( $P_i - P$ ) is large, simple flash evaporation is the most appropriate process. The necessary equipment consists of an expansion tank with an overhead vent for vapor removal and a suitable discharge pump (a gear or screw pump) for the removal of viscous bottoms. Foaming is promoted by subjecting the feed stream to a sudden reduction in pressure.

Differences among equipment configurations stem primarily from alternative procedures for generation of the interfacial mass transfer surfaces. In the falling-strand devolatilizer, strands of melt are extruded through a manifold and allowed to fall by gravity, while flashing, into a melt pool for subsequent removal. In a thin-film evaporator, a thin liquid film flows by gravity down the inner wall of a vertical cylinder and contacts a vapor stream passing through its center. Mass transfer takes place across the gas-liquid interface perpendicular to the cylinder axis. To accommodate the higher viscosities of the liquid phase, pitched scraper blades mounted on a rotor through the cylinder axis provide the polymer film with a downward component of motion assisting its flow toward the exit.

When a polymer is a viscous melt and difficult to pump, vented extruders particularly of the twin-screw variety can be used as devolatilizers. Melt is conveyed from hopper to exit by a combination of drag and pressure flow in single-screw and nonintermeshing twin-screw extruders, and by positive displacement and leakage flow in closely intermeshing twin-screw extruders (corotating and counterrotating). To facilitate evaporation and subsequent removal of contaminant, a continuous vapor space adjacent to the melt is generated by increasing the depth of the screw channel and the degree of leakage between channels in twin-screw extruders.

Heat is introduced by transport through the barrel wall

“ Since the contaminants in most cases are volatile relative to their polymeric hosts, they are removed from the condensed phase by evaporation into a contiguous gas phase. ”

and generated by viscous dissipation, especially in the clearance between the screw flight and barrel wall. Here a film of melt is deposited during each revolution of the screw and recombined, at least in part, with the melt pool flowing down the helical screw channel.

Certain resins emerge from their reaction vessels in particulate form. They are most economically devolatilized directly in solid form avoiding additional melting and pelletizing operations.

At least one DV process for polyethylene consists of charging a silo with resin beads and passing a stream of gas, such as nitrogen, through the packed bed to extract the contaminant (ethylene) by diffusion. This process is best suited to extracting contaminants with large vapor pressures such as ethylene.

### Reactive processing

Traditionally, the manufacture of products made from synthetic polymers (plastics, rubbers, fibers, films) involved two separate and distinct operations: reaction and processing. Polymerization reactors made monomer molecules into polymer molecules, and polymer processing equipment transformed the polymer molecules into shaped products.

Reactive processing attempts to combine these operations by conducting polymerizations and polymer modification reactions in processing equipment, such as molds and extruders. Two examples are currently receiving wide attention: reactive injection molding (RIM) and reactive extrusion (REX).

### Reactive extrusion

In the history of materials evolution, we have entered a period that some refer to as the age of polymeric alloys. In the search for so-called engineering thermoplastics with enhanced mechanical, thermal, electrical and chemical properties, the focus of research has shifted away from synthesizing new polymers toward combining existing polymers with one another and with various fillers and reinforcing agents. The resulting blends and composites are frequently modified chemically to improve their compatibility and stability. An early example is ABS and a recent one is toughened nylon.

The following polymer modification reactions are representative of REX:

- Polymerizing monomer *A* in the presence of polymer *B* to give an intimate physical mixture (blend)
- Grafting monomer *A* on polymer *B* to give copolymer blocks or branches
- Coupling polymer *A* chemically with polymer *B* to give a block or graft (branched) structure

- Copolymerizing small amounts of *A* and *B* (block, graft, other) to produce a compatibilizing agent that stabilizes blends of polymers *A* and *B*

Synthesis of new materials by REX is limited only by our imagination; their production demands the application of nontraditional process engineering concepts. Rather than solution or emulsion polymerization, economic factors, particularly the cost of energy and capital equipment, dictate a preference in many cases for bulk reaction, and therefore extrusion-type equipment.

The extruder is especially suitable as a polymer reactor. Operating on the principle of drag flow, it is capable of pumping and mixing viscoelastic materials while generating high pressures and maintaining high temperatures. Moreover, it has the ability to sequence process steps such as melting, mixing, pressure reduction or generation, and sidestream addition. Sidestream addition is accomplished by isolating stages from one another with melt seals which permit the pressure to be reduced, and solid, liquid or gaseous sidestreams can be metered into the extruder. In addition, one has the opportunity to combine one or more downstream processing operations, such as compounding and shaping, and reaction in the same machine.

Twin-screw extruders, in particular, are constructed with segmented screw and barrel elements, permitting melting, mixing, pressurization and venting operations to be arranged in any desired sequence with relative ease.

### Reactive injection molding

One important motivating aspect of the RIM process as opposed to conventional injection molding is the substantial reduction in pumping costs by the use of low-viscosity prepolymer feeds. If the filling phase can be completed prior to advanced reaction, a reduction in conventional injection pressures typically from greater than  $10^3$  psi (6.9 MPa) to as little as 10 psi (69 kPa) can be realized. However, in the interest of diminished cycle times, the closed mold curing time can not be excessively long. Effective design requires treading a fine line between delaying reaction sufficiently long to preclude excessive pressure rise during fill, while still attaining a high enough conversion rate to achieve a short cycle time.

Although pressure-driven tubes may not have wide applicability as polymerizers, pressure flow is nonetheless important in RIM processes. Runners and sprues leading to a mold can be treated as pressure-flow tubular reactors; the mold itself may be viewed as a parallel-plate reactor.

An important distinction between molding and conventional flow reactors is the transient nature of the flow. As the melt front advances through the runners and ultimately

*In the search for engineering thermoplastics with enhanced mechanical, thermal, electrical and chemical properties, the focus of research has shifted away from synthesizing new polymers toward combining existing polymers.*

through the mold cavity, the length of the flow path continually increases. At the same time, if the fluid is reacting, its material properties change significantly with both time and position. When the time to fill the mold is appreciably less than the reaction time, a RIM process can be subdivided into two parts for convenience. The first is flow without reaction (mold-filling) and the second is reaction in a stagnant medium (curing). Since RIM processes demand fast reactions to minimize cycle time, in practice fill time and reaction time are often of the same order of magnitude.

Urethane polymerizations, which are sufficiently rapid, are most widely used in RIM processes. Other reactions such as anionically catalyzed amide polymerizations and certain epoxide polymerizations have also been carried in RIM processes.

### Reaction viscosity

The design of conventional (nonreactive) polymer processing equipment is complicated by the non-Newtonian nature of polymer melt viscosity. When attempting to design equipment to process reacting fluids, one is faced with an even more formidable task: accounting for changes in viscosities with conversion, temperature and molecular weight as well as nonuniformities within the equipment.

Difficulties can be experienced when attempting to mix or pump polymerizing fluids with rapidly rising viscosities that accompany reaction. To understand the associated flow phenomena, it is necessary to deal with the coupling between extent of reaction and viscosity. Reaction viscosity appears to be much more sensitive to concentration and molecular weight than to temperature as shear rate.

Polymer concentration must increase with extent of reaction when the product is soluble, as does temperature from the rapid reaction exotherm and poor heat transfer. Rising reaction viscosities can be, mitigated somewhat by rising temperatures. Molecular weight, on the other hand, could increase or decrease with reaction, depending on the nature of the polymerization. Consequently, the shapes of viscosity growth profiles are varied and diverse.

Reaction viscosity profiles can profoundly affect the design strategy for a polymerization process. Decisions concerning the pumping mode (external vs. internal pressurization) and the mixing mode (turbulent vs. laminar) to be used critically depend on reaction viscosity.

The viscosity of a reaction going from a monomeric feed to a polymer melt product may change seven decades or more in magnitude. While significant effort has been devoted to describing the flow behavior of dilute polymer solutions as well as that of polymer melts, relatively little at-

tention has been paid to the broad range of polymer concentrations between these extremes. Nonetheless, this is the region of importance for reacting mixtures. Coupled with the temperature gradients created by highly exothermic reactions, drastic spatial variations in viscosity can be expected for reacting mixtures. An additional complication arises when one considers the contrasting molecular weight growth characteristics of condensation step-addition, and chain-addition polymerizations and copolymerizations. ■

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