manpower, and the difficulty of setting up the machine again for the same job as well as economic factors.

Mold repairs should be carefully evaluated. Since mold repairs may effect the customer and the economies of the job, they should be approved by management rather than left to the discretion of operating personnel.

Mold records are essential. Figure 2-32 shows the front of a typical mold record card. The other side of the card is left blank for specialized information.
Figure 2-32  Typical mold record card.

Figure 2-33 shows a "mold out" form. This is filled out every time a mold is removed after a molding run. It is countersigned by the molding foreman and head of the tool shop. This permits them to discuss what has to be done before
Mold Out Form

Mold __________________ Machine __________________ Date _____
Shift __________________ Removed by __________ Foreman ______
Authority for Removal ________________

Removal Procedure—Initial Each Operation as Performed:

1. ___ Save last four shots prior to shutting down. If mold becomes inoperative, submit shots taken last for inspection purposes. Final shots are to be complete to include runners and sprue.

2. ___ Close mold, remove all water lines, and blow out all lines until no evidence of moisture is present.

3. ___ Open mold. Allow to come to room temperature if cooled. Dry completely if moisture is present and use antitrust on all interior surfaces—no grease.

4. ___ Close mold, coat with antitrust, place dust caps or plugs into all water lines, and remove mold from press.

5. ___ Put special parts and fixtures into box and label. List parts on the reverse of this sheet. Parts stored in location ____________.

6. ___ Note on reverse side of this sheet any discrepancies not listed on Molding Control Sheet attachment

7. ___ Return Molding Requirements Form and Inspection Sheet to file.

8. ___ Note on reverse side all repairs that have to be made on the mold.

Figure 2-33  Mold out reminder form. (Robinson Plastics Corp.)
Figure 2-34  Mold repair ticket.

the mold is run again. A copy of this form and samples of the molded shot are given to the tool room when the maintenance is scheduled. They fill out the “repair ticket,” Figure 2-34, which is evaluated and filed with the original copy
of the "mold out" form. Periodic inspection of these files will reveal molds causing trouble and suggest remedies. It is interesting to observe how often the same repair is required on a mold.

CHECK LIST FOR MOLDS

The mold design is the final stage in the engineering and planning of a plastic part. A good mold is prerequisite to the economic production of quality parts. If the mold is able to consistently produce parts that are dimensionally within tolerance, flash free, and mechanically and esthetically acceptable, the need for supervision and quality control is reduced greatly though not eliminated. The nature of operating molding machines is such that it is almost impossible to have every operator, on every shift, able enough to make adjustments, sort parts, and do whatever else is required to nurse a poor mold. It is for this reason that mold design and its implications are extremely important. "Savings" in mold engineering and mold costs are illusory.

The purpose of this check list, which has been successfully used and expanded for many years, is to force systematically, consideration of the important parts of mold design. Certainly an experienced mold engineer will automatically consider all of these without the formalized need of going through them one by one. In practice the author has found that the more experienced the designer, the happier he is about a list of this kind. It has been an indispensable training device and is of significant help to the sales engineer. His involvement with the customer or user must be directed to eliminate as many difficulties as possible before the mold is designed.

Brief comment has been made on certain questions. Other questions are covered more fully in the text. Still others are amplified in the bibliographical material.

Piece Parts

1. Is this piece part drawing approved? Often there is more than one drawing made for the part. Drawings might be changed. Samples might have been made and the drawing not changed. The final drawing might have been verbally modified by the parties concerned. It is always desirable to have the piece part drawing from which the mold is being built approved, initialed, and dated. Often the toolmaker redraws the part. It is good practise to have this drawing approved also. The final print should be signed by the moldmaker, molder, and customer.

2. Have you read all the notes pertaining to the job? Notes are just as important and binding as dimensions. If a note reads, for example, "this part must fit — part," it is incumbent upon the molder and toolmaker to understand
enough of the other part so that he can meet the specification. If he cannot then the limitations should be approved or the note removed.

3. *Is the type of plastic materials indicated?* Many times there is a possibility of running the part in another material. If so, it might be necessary to have runner bars and gates removable. Modifications in the cooling and knockout mechanisms might have to be planned.

4. *Is the function, location and use of the piece understood?* This is one of the most important items. It is part of the plastic fabricator’s responsibility to interpret plastic properties for the specific application. This is true even if a piece part drawing for the plastic is submitted. While the moldmaker may not be economically responsible, the difficulties and delays must eventually harm his relationship with his customer. Knowledge of the parts use influences the mold design. The end user might not be fully aware of the significance of parting lines selection, gate location, draft, surface finish, tolerances, weld lines, and so on. The plastics engineer should have these explained to the end user, who should agree to the final decision.

5. *Can any changes be recommended to make a simpler or better piece?* Such suggestions are always in order. Sometimes the people involved in the design of the part and/or system have lost a certain amount of perspective. The mold designer may have a fresh viewpoint which can be most helpful.

6. *Are the number of cavities correct?*

7. *Are tolerances indicated on all critical dimensions?*

8. *Can these tolerances be maintained?* Tolerances are discussed on p. 145, 275. The tolerances referred to in steps 7 and 8 are those of the molded plastic part. The mold drawing will give the mold dimension whose tolerances are very different. One cannot overemphasize the importance of establishing moldable tolerances. The mold must be designed so that it can be adjusted. It is almost always easier to remove metal than to add to it. Many times it is desirable to leave too much metal on the mold, try the part, and then remove enough metal to bring the piece into tolerance. While maintaining the tolerances during molding it is not strictly a moldmaker’s problem, it should be reviewed here. If they cannot be maintained, and the part will not function unless they are, provision must be made for a postmolding operation. If this cannot be done and there is no other solution, then there is no point to building the mold.

9. *Are the dimensions given including or excluding shrinkage?*

10. *What shrinkage factor is to be used?* This should be specified by the molder. See p. 280, 284.

11. *Has adequate draft (taper) been specified?* The purpose of draft is to ensure that the part can be ejected from the mold. This is a function of many other things. See p. 114, 128. Many times drawings do not have any taper specifications at all. These should be selected by the molder and mold maker and approved by the end user.
12. Has the parting line been approved? See p. 95.
13. Has the gate location been approved? See p. 123.
14. Is the gate location in the best possible place for maximum physical properties?
15. Is the gate location in the best possible place for finishing?
16. In designing gate location, will anticipated weld lines prove objectionable esthetically or mechanically? In considering steps 13, 14, 15, and 16, do not lose sight of the ultimate consideration whether the gate is in a position which will permit molding.
17. Will the piece hang on the injection side? It is not always safe to assume that the part will remain on the ejection side. The mold should be designed so that tapers can be changed and undercuts provided to hold the part on the right side of the mold. It might be necessary to design an ejector mechanism on the injection side of the mold. For a discussion on ejection, see p. 114, 128.
18. Has the ejector mechanism(s) been decided?
19. Have the location of the ejector mechanism(s) been approved?
20. Is the ejection mechanism(s) sufficient?
21. Has polish been specified? This should have been specified before the mold was quoted as it strongly influences its cost. See p. 114.

Machine. While steps 22 to 26 seem obvious, they are often overlooked. If the mold is being designed to be operated at a specific molding plant, the machines in which the mold will fit should be indicated on the blue-print. This information should be permanently recorded and passed on to the molding room.

22. Will the molds physically fit into the presses being used?
23. Is the mold thicker than the minimum thickness required of the presses? If the mold is too thin, bolster plates can be added. It is usually easier to increase the spacer bars of the mold.
24. Is the stroke of the machine long enough to allow for part removal? This should be critically reviewed. When there is a minimum amount of room the overall cycle may be longer and this should be considered when quoting the piece part.
25. Is the ejection stroke of the machine long enough to allow for part removal? If the stroke is insufficient it may be overcome by extending the knockout plates and attaching pneumatic or hydraulic cylinders to it on both sides, with the rod end toward the movable platen. When pressure is applied to the head end of the cylinder the knockout plate will move. If the rod is attached to the platen the knockout system will be hydraulically controlled and can be made to move in either direction at any time.
26. Can the mold be clamped into the press? Sometimes additional holes might have to be drilled in the platen. If cylinders or other equipment are to be
attached to the mold they should be mounted so that they will not interfere with the clamping of the mold.

27. Is the clamping capacity of the machine enough for the parts?
28. Is the injection capacity of the machine enough for the parts?
29. Do the ejector holes correspond to the ejection mechanism of the presses to be used? Molds may be run in several presses. Not all presses have the standard SPI ejector hole pattern. After the types of presses upon which the mold may run have been listed, it should be determined whether the mold can be made so that its ejector holes will accommodate them all.

30. Are knockout mechanisms needed on the injection side? It is strongly suggested that holes be drilled through the injection platen and hydraulic cylinders be mounted on each side. When such hydraulic ejection is available, mold design may often be simplified, particularly when three plate molds and ejection on the stationary side is used.

31. Are water lines located so that they will not be in the way of the operator, or the removal of the part and gate? When water lines are externally connected they can be in the way of the operator or catch the gate or piece as it falls. When the mold is heated, the connection should be out of the operator’s reach so that he will not be burned. When refrigerated water is used the mold should be designed so that condensation does not fall where it can cause damage.

32. Do water lines interfere with tie bars or other mechanisms?
33. In the event of requirements for heating the mold, are the heating elements and control units placed safely to be out of the operators way?
34. Have the dimension of the locating ring been shown?

Mold Design

35. Have the materials for cavities, cores and other parts been specified? There are other things beside economics which dictate the material choice. For example, if dimensional changes caused by hardening could cause trouble, prehardened steel might be used. Another method might be to use hardened steel and finish the cavity with EDM. Beryllium copper might be chosen because of its high thermal conductivity. Stainless steel might be chosen because of its low thermal conductivity, or its resistance to rusting. Parts moving against each other should be of different hardness or material to prevent galling.

36. Are the mold plates and component parts strong enough for the piece?
37. Is there sufficient steel surrounding the cavities and cores? This is particularly important in multicavity molds. They are usually inserted in milled out sections of the retainer plate. Unless there is sufficient steel retaining them on the outside there will be a tendency for the mold to spread. There is no practical way to calculate the requirement. It is better to have more steel than less.
38. Are there sufficient support pillars? See p. 92.
39. Is one leader pin and bushing unsymmetrical? The reason for this is to prevent the mold from being assembled in the press or on the table incorrectly.
40. Will the leader pin enter before any other part of the mold? This is very important. In the event a mold slips during assembly or on the press, the leader pin will hit the other side of the mold rather than the core. If the leader pin hits a noncritical area no damage will result. If it is the force that hits any part of the other side of the mold there is good possibility of damage.
41. Is there ample clearance for leader pins in the other side of the mold? In addition the hole into which the leader pin goes should be vented.
42. Is there sufficient travel for the ejector plate?
43. Is the ejector plate strong enough?
44. If a stripper mold, is the stripper plate properly supported?
45. Have push back pins been provided?
46. Does the sprue bushing fit the machine? This is a good opportunity to reexamine the size and length of the sprue, and cold-slug. The mold designer should know the maximum depth into which the machine nozzle can penetrate into the mold. The length of the sprue bushing should be kept to a minimum. The diameter of the sprue bushing should be large enough to provide free flow but not that large where the cycle will be held up because of its cooling.
47. Have the dimensions of the sprue bushings been recorded?
48. Are there sufficient cooling channels in the mold and cavities? This is exceptionally important. It should be reviewed again after the mold has been completely designed. See p. 160.
49. Do the knockouts clear the water holes? While knockout pins can be sent through water holes using “0” rings, it is not desirable. If extra knockouts might have to be added in the future water lines should be kept clear of the sites.
51. Have gates been specified? See p. 123, 279.
52. Have run offs been provided when required? See p. 141.
53. Has venting been specified? See p. 131, 141.
54. In cam acting molds, have provisions been made for hardening moving parts? See p. 135.
55. In cam action molds, have provisions been made for replacing worn parts and tightening cams?
56. In cam action molds, can cam pins be replaced without removing the mold from the machine? The purpose of steps 55 and 56 is to minimize mold down time. This should be a constant thought throughout the mold design stages.
57. If there are electrical heaters or devices on the mold, have they been made safe? Since molds are subject to vibrations, shock, water, and mechanical actions, the requirements for electrical safety are rigorous. One should attempt
to visualize what could go wrong and design to prevent it. Electrical shocks are dangerous as well as unpleasant.

58. Can the electrical parts be replaced without removing the mold?

59. Have provisions been made for closing opening and depressions which might be filled up by flashed shots? This is particularly important on three plate molds. Often screw holes are filled when a shot flashes and are never cleaned out properly. This causes depressions in the mold and flashing. It is usually easy to keep openings away from the plastic surfaces.

60. Are all steel and metal specifications shown? Items 60, 61, 62, 65, and 66 are extremely helpful for the molding and mold maintenance department. It is rather frustrating to try to properly weld or reheat treat an unknown steel.

61. Have the heat treating specifications been shown?

62. Have the surface treating specifications been shown (including chrome plating)?

63. If the mold has to be heated, have provisions for difference in expansion been made? In hot runner molds provisions will automatically be made for expansion and contraction of the hot runner block. If one expects to run one side of the mold at a significantly different temperature than the other, provisions might have to be made to prevent galling of leader pins and other malfunctions.

64. Have eye bolts been provided on both halves of the mold? This permits each half of the mold to be safely handled by means of a crane. Many plants drop molds in from the top rather than slide them in on the side. It permits each side of the mold to be handled separately, not only at the machine but also during repairs and maintenance in the mold shop.

65. Where there are expendable parts such as springs, “0” rings, and switches, has a specification chart been provided? This is exceptionally valuable for maintenance in the plant, as anyone trying to measure a badly damaged “0” ring can attest. It also permits ordering spare parts without having to disassemble the mold to find out what these specifications are.

66. Are bolt sizes specified?

67. Are mold parts (sprues, etc.) standard? It is much more expensive for a molder to make a sprue bushing, leader pins, knockout pins, and other standard parts, than it is to purchase them from companies who specialize in their manufacture. Therefore, standard parts should always be specified. This is particularly important when purchasing molds built in other countries. Most countries have these standard American parts available. If not, they can be purchased here and sent to the moldmaker.

68. Have any spare parts to be furnished with the mold designated?

69. Can mold and cavities be disassembled within a minimum of time?

70. Are all the component parts numbered so as to allow for proper reassembly?

71. Has the mold been properly marked for identification?
72. Are the dimensions on the prints the same as the dimensions on the mold? This happens so rarely that the mold drawings are seldom used without rechecking dimensions. However, when a dimension has been checked it should be so marked on the print.

73. Is there a schedule of completion dates for stages of the mold work? If one is concerned about prompt mold deliveries, it is too late to expedite when the mold is scheduled for completion. The only way to find delays in time for remedial action is to have a schedule from the mold maker. Periodically this should be checked visually. With good reasons, mold makers are notoriously optimistic about the time it takes to perform a task.
CHAPTER 3

Theory and Practice of Injection Molding

This chapter develops a theory of injection molding and is concerned primarily with the qualitative aspects of plastic flow after the material leaves the injection cylinder. Practical applications that logically follow the theory are presented, where possible, immediately thereafter. Therefore, the presentation of theory is not limited to this chapter, but given in logical places in the book. For example, the theory of plastification can be found with the discussion of the screw in the first chapter.

A mathematical expression of injection molding process has not yet been accomplished. The reasons become clear when we analyze the machinery, materials, and process. Most factors that affect the process—material temperature, temperature profile, pressure, material velocities in the cylinder and mold, and mold temperature and flow patterns—are not measured at all or noncontinuously at isolated points. There is no feedback of the processing variables to the molding machine to compensate automatically for changing conditions.

Plastic material is never the same. It has different heat histories, molecular weights, molecular weight distributions, degrees of polymerization, and impurities. In processing, the material is exposed to moist air and compressed with it, in the heating cylinder, with varying amounts of oxidation. It is heated by convection, conduction, and shearing. The heat content of the plastic changes as it moves through the cylinder and mold. Pressure changes from 0 to possibly 30,000 psi.

The physical properties of the material are generally not linear with respect to temperature and velocity. The plastic is compressible, stretchable, elastic, and subject to changing properties after removal from the mold. It changes its dimensions and properties after processing, and these properties may differ,
depending on the direction of the material flow in the mold. It has
time-dependent properties which are strongly altered by its environment. In
some materials varying degrees of crystallinity are neither predictable nor
reproducible.

Therefore, one should not be surprised if injection molding has not yet
yielded to mathematical analysis with the same accuracy attained in bridge
building or motor design. However, the qualitative understanding of plastic
behavior and the mathematical treatments (based on certain simplifying
assumptions) are sufficiently advanced to permit a reasonably accurate under-
standing of the process.

BASIC THEORETICAL CONCEPTS AND THEIR RELATIONSHIP TO
PROCESSING

Rheological data, concepts of energy levels, molecular structure, molecular
forces, theory of heat transfer, and the theory of flow can be combined to
develop a cohesive picture of what happens during the injection molding process.
This conceptual catalogue can be of great value in preventing problems and
solving difficulties. Furthermore, it is extremely helpful in understanding the
literature.

A picture of this kind will contain certain generalizations. While existing
theory and experimental evidence may slightly limit or modify these concepts,
they do not limit their usefulness for our purposes. The picture is essentially a
simple one and can best be explained by starting with certain fundamental
concepts.

Phase Changes

Materials exist in three forms—solid, liquid, and gas. As heat is applied to a solid
a point is reached where the solid is in equilibrium with the liquid. This is the
melting point. Continual application of heat will not raise the temperature of the
mixture until the heat energy required to convert the solid to the liquid is
absorbed. This amount of energy is called the latent heat of fusion. After all the
solid is melted, the application of heat will raise the temperature of the liquid
until it reaches its boiling point and begins to vaporize. Similarly the liquid will
remain at the same temperature until enough heat is supplied to completely
vaporize the liquid. The amount of energy to convert the liquid to vapor at
constant temperature is called the latent heat of vaporization.

Melting Points

In plastics processing we are concerned with the liquid and solid phases. In
crystalline materials the change from solid to liquid is abrupt and easily
discernible. In an amorphous (noncrystalline) polymer the change is not abrupt
or readily apparent. The material softens over a wide temperature range and
there is no dramatic visible change in its flow properties at any given point, such
as found at the conversion of ice to water. If we plot certain properties of the
plastic such as specific volume or heat capacity against the temperature, we
notice at a point an abrupt change of the slope of the line. In the
thermodynamic sense it is called a second-order transition, although there is
evidence to suggest it might be a first-order transition (1). In polymer science,
this point is called the glass transition point \( T_g \). Below the glass transition
temperature the polymer is stiff and dimensionally stable behaving like a solid. It
has brittle characteristics with little elasticity and its properties are relatively
time independent. Above \( T_g \) the polymer will behave as a viscous liquid. It will
evidence elastomeric properties depending on the chemical structure, cross
linking, and degree of crystallinity. Its properties are now highly time
dependent. (The glass transition mechanism will be discussed subsequently.)
Additional heat applied to the polymer brings it to its melting range.

In a crystalline polymer the upper limits of the melting range is the melting
point. This is the temperature above which crystals cannot exist. The melting
point of an amorphous polymer is more difficult to determine. Since melting is
accompanied by considerable changes in properties, a comparison of them with
temperature is used for determining the melting point.

How Solids Behave

The differences between the three forms of matter can be explained in terms of
molecular attraction. In a solid, the closeness of the molecules to each other
permits the strong cohesive force of molecular attraction to limit their motion
relative to each other. While solids can be deformed, it takes a comparatively
large amount of energy to do so. If the solid is stressed below its elastic limit, it
will be deformed. An ideal solid obeys Hooke's law which states that the amount
of strain (movement) is directly proportional to the stress (force). The constant
of proportionality, \( E \) (stress/strain) is called Young's modulus or the modulus of
elasticity. When the stress is removed the molecular bonds which have been
stretched contract, bringing the solid back to its original position.

Plastics are not ideal solids. They exhibit both Hookean elastic properties and
delayed elastic responses, which are combined with viscous or flow properties;
hence they are called viscoelastic materials.

There are two energy systems to consider within a material. One is the
potential energy of a Newtonian gravitational nature and is a measure of the
forces between the molecules. The other is kinetic energy which is the energy of
motion and is related to the thermal or heat energy of the system.
Ionic bond. Electron given from one to another. Not usually found in polymers.

Coordinate bond. Electron to be shared donated by one donor. Not usually found in polymers

x = Hydrogen electron:  \( \Delta \) = First carbon electron:  \( \Delta \) = second carbon electron

Cova lent bond. Electrons shared. Primary bond in polymers. Bond distance is 1.54 Å; dissociation energy is 83 Kcal/mole.

Hydrogen bond. Between Hydrogen attached to an acidic group (-NH\(_2\), -COOH, etc.) and to an oxygen, halogen, or a nitrogen in a basic group. Bond distance is 2.4-3.1 Å; dissociation energy is 3-7 Kcal/mole.

Van der Waals Forces. Result of interaction of electrostatic fields. Varies inversely as the sixth power of the distance. Dissociation energy is 2-5 Kcal/mole.

Figure 3-1 Nature of bonding forces.
Heat is energy in transit. When it flows over into the boundaries of the system it is called internal energy which is related to the random motion of the molecules—Brownian movement. The higher the internal energy (heat) of the system, the more the random motion. If we heat a solid of a given number of molecules, it is safe to assume that the increased internal energy has been used to increase the intermolecular distances.

In a solid, the potential energy (forces of attraction between the molecules) is larger than the kinetic energy (energy of movement tending to separate the molecules). Hence a solid has an ordered structure, with the molecular attraction strong enough to limit their motion relative to each other.

As more energy is put into the system the solid turns into a liquid where the potential and kinetic energy are equal. The molecules can move relative to each other but the cohesive forces are large enough to maintain a contiguous medium. Additional thermal energy results in the kinetic energy becoming larger than the potential energy. This separates the molecules to the extent they repel each other and will fill the container with equal density throughout. This is called the gaseous state.

**Bonding Forces.** It is appropriate here to review briefly the nature of the bonding forces in the polymer (Figure 3-1). The atom consists of a relatively small nucleus which contains most of the atom’s mass and the positive charges. If the atom were the size of a house, the nucleus would be a pinhead at its center. Atoms are a few angstroms (10⁻⁸ cm) in diameter. The nucleus is some five orders of magnitude smaller, a few ten-trillionths of a centimeter in diameter. The orbits of the electrons form outer concentric shells each of which have certain stable configurations. The outermost, most loosely bound electrons (valence electrons) are involved in chemical reactions and primary bond formation.

When one element donates an electron to another to complete the stable configuration we have a strong electrostatic bond called an ionic bond. This is characteristic of compounds of metallic elements, such as sodium chloride (NaCl).

The covalent bond is of a different nature. Here the electron in the outer shells of two atoms are shared between them. This is typical of carbon-carbon bonds and is the primary bond found in polymers used commercially. The C-C bond is 1.54 Å long with a disassociation energy of 83 Kcal/mole.

A coordinate bond is one in which the electrons that are shared are donated by only one of the atoms. The strength of the coordinate bond is between that of the ionic and covalent ones.

There is another bond of importance in polymers which is not fully understood. Hydrogen should theoretically only be able to form one covalent bond. However, there is another weaker covalent type bond found primarily on hydrogen atoms attached to acidic groups (COOH, NH₂) which bond with
oxygen, nitrogen, chlorine, and fluorine atoms attached to basic groups in the
same or different molecules. Typical hydrogen bonds have a bond length of 2.4
to 3.1 Å and disassociation energies of 3 to 7 Kcal/mole.

There are secondary bonding forces in polymers which are sometimes called
Van der Waals forces. Their disassociation energy is 2 to 5 Kcal/mole. They are
between molecules and molecular segments and vary as the sixth power of the
distance. They are much weaker than the primary bonds, and are part of the
resistance to flow. The energy attracting molecules is sometimes called the
“cohesive energy,” and is that energy required to move a molecule a large
distance from its neighbor.

If we take a cubic inch of a plastic and raise its temperature, its volume will
increase. Since we are not adding any molecules to the cube, it is reasonable to
believe that the distance between the molecules has increased. The Van der
Waals forces decrease with the sixth power of the distance. Therefore, the
molecules and their segments become much more mobile. Since these forces are
decreasing as the sixth power of the distance, there will be a relatively narrow
range in which the polymer properties change from “solid” to a “liquid.” This is
the glass transition point ($T_g$). Also since these cohesive forces form a major
portion of the strength of the polymer, we can expect polymer properties to be
very temperature dependent. This is the case.

**Structure of a Plastics Molecule**

It is important to have a physical concept of a plastic molecule. This will make it
easier to understand its flow properties and characteristics. As an example, let us
consider the polyethylene polymer. It is made by linking ethylene molecules.
The double bond between the carbons in ethylene are less stable than the single
bond in polyethylene. We can, with appropriate temperatures, pressures, and
catalysts, cause the ethylene molecules to react with each other to form
polyethylene. The idealized reaction is

\[
\begin{align*}
&H \quad H \quad H \quad H \quad H \quad H \quad H \\
&\text{C} = \text{C} + \text{C} = \text{C} + \text{C} = \text{C} + \cdots \rightarrow - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \\
&H \quad H \quad H \quad H \quad H \quad H
\end{align*}
\]

If the number of molecules of ethylene in a reaction was one hundred, the
polymer would have an approximate molecular weight of 3200. A typical
Ziegler-type polyethylene polymer might have 7000 ethylene molecules with a
molecular weight of approximately 200,000. The polymerization does not
proceed as simply as the above indicates. Each polymer molecule will not be the
same length or configuration.

When we discuss molecular weight of polymers we mean the average molecular
weight. The molecular weight distribution is an important characterization of
the polymer. If the molecular weight is spread over a large range (broad spectrum material) its properties will differ from those whose molecular weight distribution is narrow. For example, a wide spectrum material will show more elastic effects and extreme pressure sensitivity. Viscosity, solubility, and stress crack resistance are some of the other properties effected. Molecular weight and molecular weight distribution are discussed in greater detail later.

To get some idea of the size of a polyethylene molecule imagine that the methyl (\(\text{CH}_3\)) group is 0.25 in. in diameter. A typical polyethylene molecule would be one city block long. A molecule of water would be about the size of the methyl group. When one considers the possibilities of entanglement, kinking, and partial crystallization of the huge polyethylene molecule, compared to the small size and simplicity of the water molecule it would not be unexpected to find considerable differences in flow properties. Flow of water is relatively simple (Newtonian). Viscoelastic flow (of polymers) has been qualitatively described but not yet mathematically defined in a quantitative manner.

When ethylene molecules polymerize they could theoretically do so and produce a straight line of carbon linkages, as shown in the top of Figure 3-2. It is also possible for the polymerization to take place so that the carbon atoms attached to each other in a nonlinear fashion, branching out to form chains, as shown in the bottom section of Figure 3-2. The amount of branching will depend on the method of manufacture. Polyethylene made with high pressure processes has more branching, with a typical polymer having 20 to 25 methyl side groups per 1000 carbon atoms. Polyethylene made under low pressure conditions (Ziegler, Phillips) might have from 1.5 to 4 methyl side groups per 1000 carbon atoms.

To understand further the nature of the polymer molecule it should be noted that the carbon atoms are free to rotate around their bonds and can bend at angles less than 180°. This swiveling and twisting permits the molecules and segments of the molecules to twist and entangle each with the other. This cohesive force consists of Van der Waals type attraction. The other type of force in the polymer is, of course, the carbon-carbon (C-C) linkages.

With our simple concepts of molecular structure we should be able to predict the different properties of the linear and branched materials.

**Density.** The linear structure should permit the polymer segments to get closer to each other than the branched structure so that it is denser. Obviously the branched side chains will keep the main polymer backbones further apart from each other in those areas where the chains exist. The longer the chains the greater this effect. There are three density ranges in commercial polyethylene, low density 0.910 to 0.925 g/cc, medium density 0.926 to 0.940 g/cc, and high density 0.941·to 0.965 g/cc. The high density polyethylene is commonly called linear polyethylene, recognizing the linear quality of the polymer chain. Some of the properties that we may predict from our model (Figure 3-2) follow.
**Product Yield.** The higher the density the fewer pieces of molded parts per pound of polyethylene can be produced. This is not an unimportant consideration in material selection.

**Permeability to Gases and Solvents.** Since the branching effect of a low density polymer provides more space between the atoms, one would expect that molecules of gas or solvent would diffuse more readily through the low density material. This is the fact. For example, the permeability of 0.92 density polyethylene film to oxygen or carbon dioxide is five times that of 0.96 density. The percentage weight gain tested for 7 days at 73°F in 5% acetic acid is 0.20% for low density, 0.16% for medium density, and 0.06% for high density. Similarly, for turpentine it is 11% for low density, 9% for medium density and 1.9% for high density.
**Tensile Strength.** One would expect that the linear material being closer together would have higher intermolecular forces and therefore greater tensile strength. A 0.915 resin has a typical strength of 1400 psi as compared to a 0.96 resin with a tensile strength of 4300 psi.

**Percentage Elongation to Failure.** Since the linear molecules can entwine and kink more than branched molecules, one would expect that it would be more difficult to separate them, so that applying a strong tensile force would rupture the molecule rather than causing it to flow and elongate. The branched material having lower intermolecular forces would slide considerably more before rupturing. High density polyethylene (HDPE) breaks at 30% elongation. Low density PE breaks at 450% elongation.

**Stiffness.** Linear PE being closer together would allow less room for segmental motion of the chains and bending of the backbone. Therefore it should be stiffer; 0.915 density PE has a stiffness or flexural modulus of 19,000 psi; 0.960 density has a modulus of 150,000 psi.

**Heat Distortion.** The heat deflection temperature under load is that temperature at which a specified bar under given conditions loaded to produce an outer fiber stress of 66 psi or 264 psi will deflect, (ASTM D-648). At a given temperature the molecular forces binding a high density material are higher than a low density material because the segments are closer together. Therefore, it will take a certain amount of heat energy (temperature increase) to separate the linear configuration so that it will have the same binding forces as the branched configuration. The more dense the material the more heat will be required to separate the molecules for equivalent strength. A low density PE will have a heat distortion temperature of approximately 110°F, a medium 130°F, and a high density of 160°F.

**Softening Temperature.** For similar reasons the softening temperature of the high density material is higher than that of the low density.

**Hardness.** Since the linear molecules are closer together, one would expect them to be more resistant to penetration. Hardness is measured by a penetration test. Hardness as measured on the Shore D scale is 67 for linear PE and 48 for branched PE.

**Resistance to Creep.** Creep is the amount of flow (strain) caused by a given force (stress). One would expect the higher intermolecular forces of the linear material to be more resistant to strain. The 100-sec tensile creep modulus at 68°F for a 1% strain is 20,000 psi for a 0.918 density and 125,000 psi for a 0.957 density. The stress required to produce a 1% strain is 170 psi for the 0.918 density PE material, 620 psi for a 0.939 density, and 1020 psi for the 0.957 density (2).
Flowability. Again, because of the stronger molecular attraction, the linear should be more difficult to flow. The standard test of flowability is the melt index (MI). This melt index and its limitations are discussed shortly. One would expect that the branched material, having less molecular attraction, would flow much more readily. As a practical example low and high density PE of similar MI were used to mold a rectangular dishpan. The minimum injection pressure to fill the mold, using low density PE, was 7600 psi, and for high density 11,500 psi (3).

Compressibility. Since there is a lot more open space in the branched PE it should compress more easily. At 15,000 psi the linear material compressed 1% and the branched material 3%. At 30,000 psi the linear compressed 3% and the branched 6 1/2% (4).

Impact Strength—Stress Cracking. One would expect from the molecular structure that the linear material would have a higher impact strength. This is not the case. Polyethylene is a crystalline material. Because linear material can get closer together there is an increased likelihood of crystallization. It can have so few branches that the crystallinity may reach the 90% level. On the other hand low density material can be so branched that the level of crystallinity can be as low as 15%. The formation of crystal structures brings the CH₂ units closer together. In addition, the formation of the crystal structure itself requires energy. The closeness of the CH₂ units and the energy of formation of the crystal structure should make the impact strength of the linear polymer much higher than the branched polymer whose CH₂ groups are much further apart. This is not so because of the characteristic of crystalline materials which permits the propagation of a crack very readily along the crystal structure. The energy of impact in a branched material will be absorbed by elongation in the amorphous phase. In a crystalline material the energy which won’t be absorbed as readily follows the crystal and break it. For this reason, too, the resistance to stress cracking is higher in a branched material. Crystallinity can be controlled to some degree by the molding conditions. We shall therefore consider the effects of crystallinity although in some instances they are parallel to the effects of density.

The effects of density on some polymer properties are summarized in Table 3-1.

CRYSTALLINITY

The properties of crystalline materials such as polyethylene, polypropylene, nylon, and acetal are affected by the amount of amorphous material, the amount and nature of the crystalline phase, and the orientation. In a given
Table 3-10  Effect of density on polymer properties — Increasing density causes the indicated change in the property listed in the first column

<table>
<thead>
<tr>
<th>Increasing density changes the</th>
<th>Increase</th>
<th>Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (pcs/lb)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Permeability to gases and solvents</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Percentage elongation to failure</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Stiffness</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Heat distortion</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Softening temperature</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Resistance to creep</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Flowability</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Compressibility</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Impact strength</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

polymer these properties will be strongly affected by the molding conditions and post molding treatment.

When a polymer is melted, the molecules are separated to the extent that there no longer is an ordered structure. Large molecular segments vibrate and rotate to give a totally disordered structure. When the plastic is cooled a point is reached where the forces of attraction are strong enough to prevent this free movement and lock part of the polymer into an ordered or latticed position. The segments can now rotate and oscillate only in a small fixed position. Since the molecular configuration is the same throughout, the intermolecular distance for this phenomena should be the same throughout the polymer. This distance is controlled by the temperature. At a given temperature the effect is extreme and the material starts to crystallize. This is known as the crystallization temperature. This is usually 10\(^0\) or more below the equilibrium melting point.

Crystalline polymers have a latent heat of fusion which is a measure of the energy required to form or melt the crystal. The heat of fusion of high density PE is 104 Btu/lb, acetal 70, low density PE, 56, and nylon 66, 56. For example, it takes approximately 180 Btu/lb to bring acetal to its molding temperature. Of this, 70 Btu (about 40\%) are for melting the crystalline structure. In contrast polystyrene, which has no latent heat of fusion, requires only 160 Btu/lb, because there are no crystals to melt (4a). It should be noted that cylinder output ratings are usually given in polystyrene, and produce considerably less output for crystalline materials unless additional heat can be delivered to the polymer.

As one would expect the crystalline or ordered structure occupies much less space. The sharp decrease in volume is indicative of the onset and amount of
crystallization. Amorphous materials do not have any volume change caused by crystallization. Therefore, all crystalline polymers show greater shrinkage than amorphous ones in going from a hot liquid to a room temp solid.

Since the amount of crystallinity varies with molding conditions, it is usually more difficult to maintain tolerances in highly crystalline materials.

The measurement of the amount of crystallinity has theoretical and practical significance. It is done by measuring a particular intensive property of the polymer. The following properties have been used: specific volume, specific heat, specific enthalpy, specific enthalpy of fusion, infrared extinction coefficients, specific line widths in nuclear magnetic resonance, and specific X-ray diffraction intensities (5). The properties of the polymer with different degrees of crystallization can be measured and correlated with the processing conditions (5a).

Crystalline materials, on the other hand, have a considerable degree of rigidity between \( T_g \) and the melting point, ranging up to a relatively rigid solid. The amount of "rigidity" depends on the amount of crystallinity.

For example, amorphous polystyrene, which is commercial, has a modulus (stiffness) of about 100,000 psi at 175°F. Just above its \( T_g \), 190°F, it drops to close to 0. Crystalline polystyrene which is a laboratory product follows the value of amorphous polystyrene until \( T_g \), but instead of dropping precipitously, continues decreasing slowly so that it has a modulus of about 1000 psi at 385°F. As it approaches its melting temperature, its remaining modulus disappears rapidly. Polyethylene at 75°F has a modulus of 15,000 psi when 40% crystallized and 110,000 psi when 70% crystallized.

These results are not unexpected in terms of our concept of molecular structure. The crystalline state has a more compact structure so that the Van der Waal's forces are stronger. Thus more force is required to move the polymer segments, that is, the polymer is "stiffer." This is another way of saying that the crystalline structure is at a higher energy level (the heat of fusion) and that more energy is required to move the segments than at the lower amorphous level.

**Structure of the Crystalline Polymer**

We now consider the structure of the crystalline polymer. There are several excellent summaries of polymer morphology. Reference 6 is primarily concerned with the structure of the polymer crystal. Reference 7 considers the structure of the crystallite, orientation, and the effect on polymer properties. Reference 8 (47 pages) is a fine presentation of the theory of polymer crystallization including nucleation, and Reference 9 questions the formation of regularly folded interfaces. A full presentation of polymer single crystals will be found in Ref. 10, and a discussion of crystallinity is found in Chapter 5 of Ref. 11 and Chapter 10 of Ref. 12. Discussion of the structure of crystalline polymers is also found in Ref. 13 and 14. Measurement of crystallinity is reviewed in Ref. 15.

The initial concept of crystalline structure was a series of almost perfectly formed crystals surrounded by an amorphous region. A single molecule might be part of several crystalline structures. The part of the molecule not in the crystal
consisted of the amorphous region. This "fringed micelle" concept was not questioned until 1957 when single crystals of polyethylene made by slow crystallization from dilute solutions showed a folded chain structure. This was the only structure that could fit the X-ray diffraction patterns and the known size of the crystals and molecules.

Figure 3-3 Schematic view of crystal structure, showing plate-like lamella, amorphous connections and section of spherulite.
The chain-folding theory of crystalline structure is illustrated in Figure 3-3. The crystalline part of the polymer consists of lamellae (platelets) which are plates of crystal material. They consist of chains of molecules folded into the flat plates (lamellae) which are between 100 and 500 A° units thick (l). It is generally agreed that the chain segments reenter in adjacent positions rather than randomly jumping to other parts of the crystal. The crystals grow on the pointed front end of the lamellae. The lamellae are held together by polymer chains going from one to another. These are randomly located and are the amorphous part of the plastic. When the polymer is oriented, either by processing conditions or stretching, the amorphous part tends to become parallel and to straighten out the lamellae.

Crystal growth requires measurable time and high mobility of the chain so that the molecular segments can get close together. Therefore, the slower the cooling (high mold temperatures) particularly as the polymer passes thru its melting temperature, the higher the degree of crystallization. Anything that affects the polymer mobility should affect its crystallinity. High pressure on the material decreases crystallinity and reduces density. Using a high density Phillips type PE at a mold temperature of 230°F, the density with 5000 psi injection pressure was 0.962, and with 20,000 psi 0.955 (16).

Most polymers under the conditions of processing form spherulites (Figure 3-3). As the polymer cools, crystallization starts at a nucleus which may vary from several tenths of a micron to several millimeters in diameter. The crystalline structure spreads out more or less in a spherical manner. The crystalline part (lamellae) consists of stacks of thin blades radiating from the nucleus. They branch and rebranch at small angles to the radius to fill the volume of the spherulite. They may twist in a regular manner. The polymer chain axis are approximately perpendicular to the spherulite radius. Unless quenched rapidly enough the spherulites will grow until they touch each other filling the volume of the plastic.

The spherulites may fill the whole structure. There is no reason to believe that the amorphous content between the lamellae in the spherulite is any different than that between the spherulites. The properties of the plastic will depend in part on the number and quality of the spherulites.

The type and size of the crystallite also have a strong influence on polymer properties. As the polymer cools from above its melting point, crystallites form around the nucleus. The spherulitic growth continues until the temperature drops to the point where the lack of chain mobility prevents crystallization. The rate of crystallization affects the size of the spherulite, and this rate is highly temperature dependent. It is a combination of the rate of nucleus formation and of crystal growth. They are each affected differently by temperature. The rate of nucleation increases continually as the temperature falls. The rate of crystal growth increases as the temperature falls and then decreases. When the
crystallization rate is low, such as in isotactic* polystyrene, rapid cooling, such as quenching in water, will prevent crystallization. High density polyethylene, on the other hand, has such a high crystallization rate that it is not possible to cool it quickly enough to prevent some crystallization.

**Nucleation.** Therefore, at higher temperatures the nucleation is relatively slow and the crystallization relatively rapid, so that large spherulites form. The rapid quenching of the material gives much smaller spherulitic structure. The importance of this is evidenced, for example, in that the Gardner impact strength of a linear polyethylene with a 4.2 - \( \mu \) - diameter spherulite is 104 ft/lb. While the same material with a 6.8 - \( \mu \) - diameter spherulite drops to an impact strength of 13 ft/lb (17). As we shall see, other properties are affected by the character and number of the spherulites.

Spherulite formation can start in three ways:

1. The random motion of the polymer chains produces a crystal of sufficient size so that the surface energy thereof will propagate continued crystalline growth. This is called spontaneous or homogeneous nucleation and is the vastly predominant mechanism.

2. The polymer is not completely melted and the unmelted portions form nuclei.

3. Foreign substances are deliberately added which are called nucleating agents. A nucleating agent for nylon, for example, may be colloidal silica at a concentration of about 0.1%. Nucleating agents for polypropylene may be finely ground higher melting polymers, silica, and some metal salts of organic acids.

In a molded part it is desirable to have as homogeneous a structure as possible. Rapid cooling tends to produce more and smaller spherulites. Nucleating agents normally produce more uniform development of the spherulite in terms of growth, size, and distribution. It usually will produce more crystallinity, and some of the effect of nucleating agents are in reality the result of higher crystallinity. Some of the effects of nucleating agents follow:

1. Nucleation raises the temperature at which the crystallization rate is maximum. A nonnucleated polypropylene has a crystallization rate peak at about 240°C. With nucleating agents it can be raised as high as 287°C (18). The

*The term "isotactic" refers to the spatial or stereo configuration of a regularly repeating unit in a polymer chain such as the methyl group in polypropylene. Isotactic polypropylene has the methyl groups all on one side of the polymer chain. Syndiotactic polypropylene has the methyl groups alternating from one side to the other. Atactic polypropylene has the methyl groups located randomly. Isotactic polypropylene crystallizes readily, while atactic cannot crystallize at all and is a soft rubbery material which can be extracted with hydrocarbon solvents to leave the desired percentage of isotactic material.
amount of crystallinity determines the stiffness of the material which determines the length of time a part must cool in the mold before it is stiff enough to eject. Since the crystallization temperature is higher, the setup temperature (stiffness) is higher, and the part can be removed at a higher temperature, significantly lowering cycles. Depending on the shape of the piece cycle reductions of 3 to 30% have been reported (19).

2. The fine spherulitic structure of nucleated polypropylene significantly reduces the dispersion of transmitted and reflected light giving a marked increase in transparency and surface gloss (18).

3. Because of the small spherulite size nucleated materials tend to shrink more uniformly. As the spherulitic size is less temperature dependent the polymer tends to be more uniform. A nonnucleated material will have larger spherulites in the center where the temperature remains higher longer. It has been found that nucleation permits molding thicker sections without voids. Similarly the tendency for sinks to form on the surface is reduced.

4. Nucleation tends to reduce warpage particularly in olefins. Probably this is caused by a more uniform material and the higher tensile modulus. The latter effect might be due to more crystallinity rather than the size of the crystals.

5. Nucleation increases the hardness slightly, and also the abrasion resistance.* Tensile strength, rigidity, and the tensile yield strength are moderately increased. Conversely the elongation decreases and the impact strength drops. These effects are probably predominantly caused by the increase in crystallinity. It is interesting to note the effect of nucleation, spherulite size, and crystallinity on the impact properties of compression molded polypropylene (Table 3-2).

6. Nucleation of the polymer raises the heat distortion temperature of the molded part. For example, a nonnucleated nylon 6 has its heat distortion temperature raised from 152 to 180°F by nucleation.

7. Water absorption is slightly lower for nucleated materials, probably due to the increased crystallization.

8. Nucleated polymers seem to shrink more (higher crystallinity) than nonnucleated materials. This can be used to advantage if a part is molded in a nonnucleated material and is sticking in the cavity. Sometimes the additional shrinkage of the nucleated material will keep it on the force.

Summarizing, nucleation generally results in the following:

Shorter cycle time
Increased cost of material
Less voids
Minimum sink marks
Reduced flow lines
Increased surface smoothness

*A description of plastic properties is found in Chapter 4.
<table>
<thead>
<tr>
<th>Crystalization Conditions</th>
<th>Nucleation</th>
<th>Spherulite Diameter (μ)</th>
<th>Crystallinity Measured from Density (%)</th>
<th>Impact Data at 23°C Energy (kg·cm⁻¹·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water quenched</td>
<td>No</td>
<td>~2</td>
<td>52</td>
<td>11.34, 940-2600</td>
</tr>
<tr>
<td>Cooled slowly</td>
<td>No</td>
<td>~20</td>
<td>67</td>
<td>4.2, 540</td>
</tr>
<tr>
<td>Water quenched</td>
<td>Yes</td>
<td>&lt;2</td>
<td>62</td>
<td>4.4, 510</td>
</tr>
<tr>
<td>Cooled slowly</td>
<td>Yes</td>
<td>&lt;2</td>
<td>73</td>
<td>3.6, 470</td>
</tr>
</tbody>
</table>
Improvement in see through clarity
Reduction of warping
Increased shrinking
Increased flexural modulus
Increased tensile modulus
Increased tensile yield strength
Increased hardness
Increased abrasion resistance
Increased heat distortion temperature
Decreased elongation
Decreased impact strength

How to Regulate Crystallinity. The molder has a limited ability to regulate the percentage and type of crystallinity in polymers. This is done primarily by using the following variables:

1. Mold temperature.
2. Cooling method after removal from the mold.
3. Cycle time.
4. Injection and holding pressure.

As the polymer in the mold is well below its melting temperature, we would expect the higher the mold temperature the more molecular and segmental motion of the chains. This condition increases the probability of bringing the molecules close enough together to be frozen into a crystalline state. Therefore, the higher the mold temperature the more the crystallinity. Similarly, the quicker the part is cooled outside the mold the less the crystallinity. Pressure increases the rate of crystallinity because it brings the segments closer together. A 1/2-in.-diameter high density polyethylene rod was molded with a melt and mold temperature of 400°F. The mold was cooled at a rate of 10°F/min. The cooling time to produce 50% crystallinity in the rod was measured. At 30,000 psi it occurred after 6 min. At 1000 psi the time more than doubled, requiring 15 min (20). The effects of the cycle time can be to increase or decrease crystallization. This will depend on the interaction of the mold temperature, subsequent temperature treatment of the piece, and the injection pressure.

For a given material the amount of shrinkage should depend on the crystallinity. The crystalline structure has the molecules closer together than the amorphous structure. Consider a cube completely filled initially with amorphous material. As the material crystallizes it requires less volume, decreasing the size of the original cube (shrinkage). It is easily seen, therefore, the more crystallinity the smaller the cube (higher shrinkage). This is shown in Figure 3-4 where by raising the mold temperature from 100 to 175°F the shrinkage of polypropylene in the direction of flow increased from 0.014 to 0.024 in./in. Following the same reasoning it is evident that the more crystals in the material, the higher its
Shrinkage
in./in.
mm/mm
0.030 37.8 52 66 80 107
In the direction of flow.

0.020

0.010

Perpendicular to the direction of flow

0.000  
75 100 125 150 175 200 225
Mold temperature (°F)

Figure 3-4 Shrinkage of polypropylene as related to mold temperature, both in the direction of flow and perpendicular to the direction of flow (Avisun Corporation).

density.

The Effect of Crystallinity on Properties

We shall briefly discuss the effect of crystallinity on physical properties.

There are many references in the literature relating processing conditions to properties of crystalline polymers. References 16 and 21 refer to high density polyethylene, Ref. 22 to polypropylene, and Ref. 23 to nylon.

1. Density. Since crystallinity gives a more compact structure, the density increases with crystallinity. A compression molded sample ofpolypropylene with 70% crystallinity had a density of 0.896. Increasing the crystallinity to 95% gave a density of 0.903 (24). As expected increasing the mold temperature increases the crystallinity and density. Nylon-6 measured immediately after molding showed a density of 1.094 with a 68°F mold temperature and 1.122 with the mold temperature at 212°F (23). High density polyethylene at a mold temperature of 75°F gave a density of 0.944. Raising the mold temperature to 250°F increased the density to 0.950 (16).

2. Stiffness. The flexibility of a plastic depends on the ability of its segments to rotate. Crystalline structures hinder such rotations; therefore, a crystalline material is significantly stiffer than the equivalent plastic in its amorphous condition. The tensile modulus (stiffness) of a 70% crystallized
polypropylene is 65,000 psi and at 95% crystallization it is 150,000 psi (24).* Amorphous polymers lose their stiffness about 50°F above the glass transition point. The effect of crystallization is to extend the upper temperature limit for a usable modulus. For example, high density polyethylene maintains a fairly high modulus to within approximately 20°F of its melting point (275°F). Additionally, because the crystalline structure is stiffer there will be less tendency to creep.

3. **Tensile strength.** The tensile strength increases significantly with increasing crystallization. One would expect to need more force to break the closer bonds of a compact crystalline structure than that of an amorphous material. The tensile yield strength (force required to start the polymer flowing) of a 70% crystalline polypropylene is 4000 psi. Increasing the crystallinity to 95% gives a tensile yield strength of 6100 psi (24). Since the flow is primarily in the amorphous section, it would be expected that the percent elongation at break would be higher when there is more amorphous material, that is lower crystallinity. A typical slowly cooled polypropylene will have a yield strength of 3750 psi and a 50% elongation at break. Cooling the same part rapidly will decrease its crystallinity lowering its yield strength to 3000 psi but increasing its percentage elongation at break to 800%.

4. **Impact strength.** From the strength of the crystalline structure one would expect the impact strength to increase with increasing crystallinity. This is not the case. Crystalline structures in all materials tend to rapidly propagate impact energy along the faces of the crystals where they break. This is used to advantage in some industries such as diamond cutting, but is a distinct disadvantage in molding. Seventy percent crystalline polypropylene has a notched Izod impact strength of 2.8 ft-lb/in. notch. Increasing the crystallinity to 95% reduces the impact strength to 0.9 (24).

5. **Shrinkage.** As mentioned previously, increasing crystallinity decreases the volume, thus increasing shrinkage.

6. **Hardness and Abrasion Resistance.** Hardness, which is a measure of depth of penetration, increases with crystallinity. The increase is relatively negligible until the crystallinity is over 80%. The wear and abrasion resistance are enhanced by crystallinity (23). For practical purposes, the changes in hardness and abrasion resistance caused by molding conditions is very small.

7. **Heat properties.** Increasing crystallinity has an important effect in raising the softening and heat distortion temperatures. Seventy percent crystalline polypropylene has a deformation temperature under load (ASTM D648) of 257°F, while at 95% it is 304°F (24). The higher softening point or heat distortion temperature causes the polymer to remain stiffer at higher temperatures. Since stiffness is the criteria for ejection from the mold, higher

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*The tensile modulus is the slope of the initial portion of the stress-strain curve. It is a good measure of stiffness. See page 339.
crystallinity reduces cycle time. Since higher crystallinity is caused by higher mold temperatures one would expect that cold mold temperatures would increase the cycle, particularly for thin walled objects (23). Crystallinity will increase the brittleness at low temperatures. The brittle temperatures of 55%, 83%, and 95% isotactic polypropylene (isotacticity being a measure of crystallinity) are 32°, 50°, and 68°F, respectively.

8. Permeability. Because of the closeness of the crystalline structure it is more difficult for a gas or liquid molecule to find its way through the plastic. For this reason increased crystallinity increases the resistance to permeability to gases and vapors.

9. Stress Cracking Resistance. The higher the crystallinity, the lower the resistance to stress cracking. This is probably due to a mechanism similar to the lowering of the impact strength with increasing crystallinity. Therefore, higher mold temperatures (which promote higher crystallinity) increase the effect of stress cracking. A polyethylene dishpan molded with mold temperatures of 118°, 135°, 150°, and 175°F had the following percent failures after 24 hr when subjected to a stress crack resistance test – 30%, 60%, 80%, and 100%.

10. Optical Properties. There is no simple explanation of the effect of crystallinity on optical properties. Higher crystallinity will give a higher surface gloss. A distinction is made between transparency or light transmittance and freedom from haze. Usually higher crystallinity will cause less transparency and more haze. However, higher crystallinity in nylon usually increases transparency. Nucleation of polypropylene has been reported to increase transparency. A good review of the optical properties of crystalline materials can be found in Ref. 25.

11. Warpage. Crystalline materials exhibit more warpage than the amorphous ones. It is probably related to the effect of temperature on crystallinity. When an amorphous material cools, the difference in density throughout the piece is primarily a function of how much material is forced into the cavity after the mold is initially filled. To this, a crystalline material adds the effect of varying amounts of crystallinity caused by differences in polymer temperature in the mold. (The amount of crystallinity is dependent on the polymer temperature.) The resulting differences in density causes differential shrinkage which sets up high internal stresses. When they exceed the strength of the polymer, strain or warpage occurs.

How Annealing Affects Properties

There is a great deal of uncertainty concerning the details of the effects of annealing crystalline polymers. Theoretical discussions not directly applicable to molding practices can be found in Chapter 5 of Ref. 10, and Ref. 26 and 27.

As one might expect annealing a crystalline material should increase its crystallinity. A 0.952 density PE annealed at 149° for 1 hr increased its density
to 0.953. Annealing the same material at $212^\circ$ increased its density to 0.955. Increasing the annealing time to 1 1/2 hr did not change the density when the annealing temperature was $149^\circ$. At $212^\circ$ it increased the density to 0.956 (21). For practical purposes the main advantage of annealing is to relieve internal stresses which is true for both crystalline and amorphous polymers and is discussed subsequently.

Orientation Also Affects Properties

Orientation strongly affects the properties of polymers. This is fully discussed later on in this chapter. The mechanism of orientation of a crystalline polymer involves at least three steps. There is an instantaneous deformation of the spherulitic structure. There is a slower slipping of the lamellae within the spherulite. Finally there is a still slower viscoelastic flow of molecules within the crystal (28).

Molding Crystalline Plastics

The processing of thermoplastic materials essentially involves applying heat to melt the material in the cylinder and removing this heat while the plastic part is in the mold and after removal of the part from the mold. The rate of heat transfer, which is important in determining the cycle time, will also affect the degree of crystallinity with its profound effect on physical properties. In molding, the size of the gate is also important; it affects rate of fill, as well as length of time to freeze.

Mathematical and graphical formulations of freezing time are of great value to the molder. Reference 29 shows such calculations with polyethylene, polypropylene, and polycetal. Figure 3-5a, taken therefrom, shows the freeze-off time for 0.945 PE starting at a cylinder stock temperature of 450°F. The curve shows the time to reach a freeze-off temperature of 266°F at the center of the part. For example, a 2-in. slab molded with cooling water at 70°F would require about 52 min for the last material in the center of the slab to reach 266°F. A 1/16 diameter (1/32 radius) gate under the same conditions would have a center freeze-off in 1.2 sec. While the 2-in. slab need not be kept the full 52 min in the mold for ejection, such information permits the molder to correlate his practice and the graph. It will then enable him to make accurate predictions. Such graphs are very useful in computing gate freeze-off times. Figure 3-5b gives the same information for polypropylene. Reference 30 shows the calculations for heating, cooling, and gate freeze-off temperatures for acetics. Reference 29a describes the effects of crystal size, orientation, and density on the thermal conductivity of polyethylene. Reference 31 is concerned with 66 nylon. Reference 20 has information on polyethylene though in less useful form. Reference 32 gives a general numerical procedure for calculating temperature
Figure 3-5 Freeze-off time of rods and slabs of polyethylene and polypropylene (Ref. 29).
(a) Freeze-off time of polyethylene (0.945 density) melt at 450°F (232.2°C): coolant as shown. (b) Freeze-off times of polypropylene melt at 500°F (260°C): coolant as shown.
profiles during the cooling of molded parts. Good agreement is obtained between theoretical and actual results for a 10 MI, 0.935 PE. Temperature, pressure, and cooling rate curves for different conditions are shown. References 32a and 32b describe, mathematically, heat transfer to molten polymers.

If a crystalline polymer is cooled rapidly, its crystal structure is fine with many small spherulites. If it is crystallized slowly, the crystal structure is coarse and the spherulites are fewer but considerably larger. Crystalline texture has a significant effect on the properties of the molded part so that the rate of cooling is an important variable in molding.

CROSS-LINKED PLASTICS

The properties of plastics that are associated with crystallinity are derived from the closeness of the crystalline structure. A similar result is obtained by cross-linking the carbon atoms in polymer systems. To date cross-linking in thermoplastics has been mostly performed on polyolefins used in wire and cable applications.

After cross-linking the material loses its thermoplastic characteristics and becomes thermostetting.

Cross-linking significantly improves the heat resistance, tensile strength, tensile elongation, and the stiffness. The tensile creep behavior of cross-linked polyethylene is similar to that of acetal, which is one of the most creep resistant thermoplastics. It is considerably better than nylon.

Cross-linking also improves the resistance to environmental stress cracking. Solvent resistance is strongly improved. For example, uncross-linked polyethylene in toluene for seven days at 155°C broke into pieces. The cross-linked material only increased its weight by 45%.

The two methods used are irradiation and chemical cross-linking. Irradiation techniques use high-speed electrons and neutrons, gamma rays, X-rays, and ultraviolet radiation. The properties of most commercial plastics (except cellulosics) are improved by radiation (32c, 32d).

Chemical cross linking systems use organic peroxides which decompose when heated, to yield highly reactive free radicals. These catalyze the chemical cross linking. A filler which may be a silica, carbon, calcium carbonate, clay, or alumina is generally required with these compounds.

Cross-linked polyolefin materials are molded with oil heated injection cylinders. The material is injected below the temperature required for the decomposition of the peroxide. Mold temperatures of 370 to 450°F catalyze the cross-linking. Cycle times are similar to those for molding regular polyolefins (33 to 36).
MOLECULAR WEIGHT: AFFECTS PROCESSING AND PROPERTIES

The distinguishing characteristic of polymers is their high molecular weight. Polymeric behavior is a function of molecular weight (MW). At room temperature ethylene, with a molecular weight of 30, is a gas. When ethylene is polymerized to a molecular weight of 170 it becomes a liquid. At 1000 it is a grease, at 4000 a wax, and at 12,000 a plastic.

It is not possible to polymerize ethylene (or any polymer) so that every polyethylene molecule will have the same molecular weight and configuration. The molecular weight distribution may be controlled within relatively large limits. However, the range can be extremely broad, such as in polystyrene, which may have molecules with MW's of 5000 and 2,000,000 in the same resin.

To determine the molecular weight distribution (MWD) it is necessary to fractionate, or separate the polymer into fractions of similar molecular weights. This is accomplished by ultracentrifuging the polymer or using its solubility characteristics. A high molecular weight material is less soluble than a low molecular weight. The fractionation is done either by precipitation or solution methods. None of these procedures are particularly precise, but they yield useful information which has been correlated with processing and properties.

The molder controls the molecular weight and the molecular weight distribution of a material only in that he is involved in its specifications.

This can be done in consultation with the material supplier (37, 37a, 38). Since they do affect his processing the product a general statement about them is desirable. More detailed information will be found in Chapter 4 of Ref. 39, Chapters 1 and 2 of Ref. 12, and Chapter 3 of Ref. 11.

The concept in measurement of molecular weight and molecular weight averages in polymers presents some difficulties. It is distinctly different than in a monodisperse system which consists of identical molecules. In ice, for example, all the molecules are identical. Therefore the molecular weight and any average molecular weight will be the same, that is, 18. Polymers have different chain lengths, different branches, and different molecular arrangements. In polydisperse systems the term average molecular weight alone has no meaning. Consider the case of a fatal disease striking people of the average age of 46 without discrimination regarding sex. The significance of this average lessens when one finds out there are only two cases reported, a girl 1 year old and a man 91 years old. In this instance averages are totally misleading. Therefore, in polymer science average molecular weights are only used when related to a specific property whose functions are directly related in some manner to the change in that molecular weight average.
Molecular Weight Determinations

There are two major molecular weight determinations. One is based on the number of polymer molecules \( M_n \) and the other on the molecular weight of the polymer molecules \( M_w \).

The number average molecular weight \( M_n \) is determined by taking the sum of this average for each fraction. Obviously the more fractions taken the more accurate the determination. The extreme difficulty and costliness of these determinations, as well as their relative inaccuracy, usually keep the number of fractions at a minimum.

Number average molecular weight \( M_n \) is the sum of

\[
\text{number of polymer molecules in fraction (A)} \times \frac{\text{total number of polymer molecules in all fractions}}{\text{in fraction (A)}}, \quad (3-1)
\]

(Similarly for fractions B, C, etc.)

The weight average molecular weight \( M_w \) is

\[
\text{number of monomer units in one of polymer molecule in fraction (A)} \times \frac{\text{molecular weight of polymer molecules in fraction (A)}}{\text{total molecular weight of all fractions}}, \quad (3-2)
\]

(Similarly for fractions B, C, etc.)

Two examples will clarify this concept. Consider a polymer of two polymer molecules, one with 10,000 monomer units and a molecular weight of 10,000 and the other with 100,000 monomer units and a molecular weight of 100,000. Let us mix an equal number of each polymer molecule. For simplicity let us use a two molecule plastic with fraction A have the one molecule with \( M_w \) equal 10,000 and fraction B one molecule with \( M_W \) equal 100,000. Therefore,

1 polymer molecule \( M_w \) (molecular weight) \( = 10,000 \)
1 polymer molecule \( M_w \) (molecular weight) \( = 100,000 \)
2 total polymer molecules \( M_w \) \( = 110,000 \)

The \( M_n \) from (3-1) is

\[
10,000 \times \frac{1}{2} = 5,000
\]
\[
100,000 \times \frac{1}{2} = \frac{50,000}{55,000} = M_n
\]
The $M_w$ from (3-2) is
\[
10,000 \times \frac{10,000}{110,000} = 909
\]
\[
100,000 \times \frac{100,000}{110,000} = \frac{90,909}{91,818} = 92,000 = M_w
\]

Let us now construct a polymer with the same molecules but using equal molecular weights instead of equal molecular numbers. Therefore,
\[
10 \text{ polymer molecules of } M_w (10,000) = 100,000 M_w
\]
\[
1 \text{ polymer molecule of } M_w (100,000) = 100,000 M_w
\]
\[
11 \text{ Total number of total } M_w = 200,000
\]

The $M_n$ from (3-1) is
\[
10,000 \times \frac{10}{11} = 9,090
\]
\[
100,000 \times \frac{1}{11} = \frac{9,090}{18,180} = 18,000 = M_n
\]

The $M_w$ from (3-2) is
\[
10,000 \times \frac{100,000}{200,000} = 5,000
\]
\[
100,000 \times \frac{100,000}{200,000} = \frac{50,000}{55,000} = M_w
\]

It should be noted that $M_w$ is always greater than $M_n$. $M_w$ is more sensitive to high molecular weight molecules while $M_n$ is affected more by the lower molecular weight fractions.

The ratio of the weight average ($M_w$) over the number average ($M_n$) molecular weight is usually used as a measure of the broadness of a particular polymer.

\[
\text{Degree of heterogeneity or polydispersity} = \frac{M_w}{M_n} \tag{3-3}
\]

Using our examples with equal number of polymer molecules
\[
\frac{M_w}{M_n} = \frac{92,000}{55,000} = 1.7
\]
With equal weight of polymer molecules

\[
\frac{M_W}{M_n} = \frac{55,000}{18,000} = 3
\]

This ratio does not show the distribution curve and is particularly sensitive to errors in the number average molecular weight. It is useful as a comparative value of the dispersity of a polymer rather than its absolute value.

**Molecular Weight Measurements**

Molecular weights are measured indirectly by such methods as osmotic pressure, light scattering, and sedimentation equilibrium. A second way is to measure properties which are connected to the molecular weight by a known function, such as viscosity. The number average molecular weight for polymers with weights below 20,000 are usually determined from freezing point, boiling point, and vapor pressure measurements. Above 20,000 and up to a 1,000,000 it is measured by the osmotic pressure of solutions of the polymer. When molecular weights are very high, over a million, an electron microscope is used for analysis of molecular weight and molecular weight distribution. Under certain conditions low molecular weight polymers are weighed by analyzing the end groups. Tagging end groups radioactively is also used.

The number average molecular weight is used in glass transition calculations, diffusion coefficients, sedimentation coefficients and analysis of polymerization kinetics.

The weight average is determined by light scattering techniques and ultracentrifuging. The weight average is used for viscosities at low shear rates, tensile impact strength, and turbidity. Some properties are best described by a molecular weight between \( M_n \) and \( M_W \). This is occasionally called \( M_Z \) and is used for viscosity at high shear rates, percentage elongation at failure, and tensile strength.

**Melt Index Viscosity and Molecular Weight**

All the preceding techniques are difficult and time consuming. A relationship has been found between the viscosity and the molecular weight. In dilute solutions the empirical relationship is

\[
\eta = K M_W^a
\]

(3-4)

where \( K \) and \( a \) are constants depending on the nature of the polymer, the solvent, and the temperature but independent of molecular weight.

Flory found an empirical relationship for molten polymers,

\[
\log \eta = A + B M_W^{1/2}
\]

(3-5)
where the constants $A$ and $B$ depend on the nature of the polymer and the temperature. The relationship holds for a number of linear condensation polymers over wide ranges of molecular weights. Although Eq. 3-5 has subsequently been modified, its form is intact and it is the basis for using the melt index (MI). The MI measures the viscosity of a polymer at low (Newtonian) shear rates, which, in effect, is a measure of the molecular weight. The viscosity of polymers are strongly influenced by the $M_w$. (39a).

**Melt Index (MI) and Molecular Weight.** Since MI is a measure of molecular weight, the change in properties with changing MI is best described in terms of molecular weight. High molecular weight materials would be expected to entangle more than lower molecular weight ones. Therefore they should be more resistant to flow and extrude less material (weight) under equal conditions, that is, a lower MI.

In general the physical properties of a polymer increase with increasing molecular weight. Above a certain molecular weight, specific for each polymer, the rate of increase rapidly diminishes. The processability (viscosity) of a polymer decreases exponentially with increasing molecular weight (Eq. 3-5). A point will be reached where the polymer is so viscous that it cannot be processed without degradation. A commercial polymer is a compromise between physical properties and processability.

**MI Measurement** The melt index is measured with an extrusion rheometer as described in the ASTM Test D-1238 (Figure 3-6). It consists of an insulated, heated chamber 3/8 in. in diameter with an orifice of 0.0825 in. The polymer is put into a cylinder under a plunger on which is a weight of 2160 g (equal to 43¾ psi on the polymer). The material extrudes from the orifice. When equilibrium conditions have been reached the extrudate is cut off and the weight, in grams, extruded in 10 min is the melt index.

The MI is primarily used for olefins. For polyethylene the chamber is heated to 374°F. The melt index of polyethylene normally used for injection molding varies from 0.2 to 30. The melt indexing of polypropylene and an analysis of some of the problems is given in Ref. 40. The MI is occasionally used in evaluating polystyrene, ABS, acrylics, nylon, and acetals. The MI measures the flowability or viscosity of the polymer at very slow flow rates. This is not necessarily characteristic of the flowability during injection molding, which is at much higher shear rates (41 – 46). Other methods have been developed for studying the flow rates during molding. They include plots of the shear stress against the shear rate, the apparent viscosity versus the shear rate, and the length of flow under specified conditions in spiral molds.
Figure 3-6 Melt indexer used for olefins. The melt index number (MI) is the amount of plastic extruded in 10 min reported as grams.

**Molecular Weight versus Density**

The material becomes less dense as the molecular weight increases (MI decrease). It can be shown, for example, that polypropylenes of equivalent isostactic content (a measure of the maximum amount of crystallinity) processed under identical conditions will yield lower crystallinity as the molecular weight increases (MI decreases). It would seem that the smaller molecules have a greater number of chain ends per volume and can move more freely to positions favoring crystallization. The lower crystallinity explains some of the property changes caused by the molecular weight.
Molecular Weight versus Notched Izod Impact Strength

The notched Izod impact strength increases materially with increasing MW (lower MI). For example, a 5 MI polyethylene has an Izod notched impact strength of 3-ft-lb/in. notch. Decreasing the MI to 0.5 (increasing MW) raises the Izod to 21. A 1.7 MI polypropylene has a notched impact strength of 1.2. Reducing the MI to 0.3 raises the Izod to 3.8. In polypropylene an MI of 0.3 corresponds roughly to a molecular weight of 250,000, while an MI of 1.7 corresponds to 120,000. One would suspect that the increasing resistance to failure by impact, with increased molecular weight, is due both to the lowered crystallinity and the increased strength of molecular entanglements.

Tensile Yield versus Molecular Weight

Tensile yield strength increases slightly with increasing MW (decreasing MI). A 15 MI, 0.96 density PE has a tensile yield strength of 4300 psi. A 0.42 MI has a tensile yield of 4600 psi. The increasing tensile yield strength reflects the longer molecules and the increased degree of entanglements.

Tensile Strength versus Molecular Weight

For the same reason tensile strength increases with increasing MW (lowering MI). A 0.95 density polyethylene has a 3200-psi tensile strength at a MI of 8 and a 4000-psi tensile strength at a MI of 2.

Stiffness versus Molecular Weight

As the molecular weight increases (MI decreases) the stiffness decreases. This is probably the net result of the effects of crystallinity and chain length. A 0.4 MI polypropylene has a stiffness in flexure of 160,000 psi, while a 4 MI is at 220,000 psi.

Percentage Elongation to Failure versus Molecular Weight

The percent elongation to failure increases sharply with increasing MW (decreasing MI). The larger molecules have more entwining and more C-C linkages to stretch. A 2 MI polypropylene has a 40% elongation as compared 0.3 MI with a 600% elongation.

Brittleness Temperatures and Impact Strength versus Molecular Weight

The brittleness temperature decreases with increasing MW (decreasing MI). A linear polyethylene with a 5 MI has a brittleness temperature of -100°F. At 1.5
MI it is -180°F. Since brittleness temperature is a measure of the cohesive strength of the molecule, one would expect the higher molecular weight material to behave better at lower temperatures. For the same reason the impact strength at a given temperature is higher with increased MW (lower MI). At 120°F a 3 MI polypropylene has an Izod impact strength of 3, while a 0.3 melt is 11.

Environmental Stress Cracking versus Molecular Weight

The higher the MW (lower MI) the greater resistance to stress cracking. The greater entanglement of the polymer makes it stronger and probably leaves less molecular space for the "invading" molecules. For example, the time for a 0.96 density molded PE part to show stress cracking in a chemical environment was 15 hr. for a 1 MI and 270 hr for a 0.1 MI.

Shrinkage and Warpage versus Molecular Weight

The lower molecular weight (higher MI) materials flow much more rapidly into the mold. They also have lower melting points, requiring less time for cooling. Both these factors reduce the internal stress which is the main cause for warping and shrinking.

Creep versus Molecular Weight

Creep decreases with increasing molecular weight (lower MI). It is the permanent deformation resulting from a prolonged application of stress below the elastic limit. At room temperature creep is sometimes called cold flow. Below the glass transition temperature, molecular weight has little effect on creep. At these temperatures the molecular movement is basically that of segments or chains rather than the whole molecule. Therefore the total molecular motion will be fairly constant for a given amount of the polymer, regardless of the molecular weight.

Above \( T_g \) the polymer acts as a viscous liquid, with the whole molecule moving. The rate of creep is almost entirely dependent upon the viscosity which is directly related to the molecular weight (Eq. 3-5). (See Table 3-3).

MOLECULAR WEIGHT DISTRIBUTION AND PROPERTIES

There are properties of plastic which cannot be fully described by the density, weight average, or number average molecular weight of the polymer. They can be correlated to the molecular weight distribution (MWD) \((47)\). The MWD of a given grade of polymer is determined by the process of manufacture and is not altered by normal processing. The polymer consists of short, medium, and long
Table 3-3  Effect of molecular weight (MI) on polymer properties — increasing MW (lowering MI) causes a change in the property listed in column A

<table>
<thead>
<tr>
<th>A</th>
<th>Increase</th>
<th>Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Notched impact strength</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Stiffness</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Percentage elongation to failure</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Britteness temperature</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Shrinkage and warpage</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Creep</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Environmental stress cracking</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Chain molecules. The percentage of each determines the molecular weight distribution. If it is made up mostly of chains of the same length it is called a narrow molecular weight distributions (NMWD). If the distribution contains a relatively broad range of molecular weights it is called a broad molecular weight distribution (BMWD). This is approximately what is measured in the ratio of the molecular weight average and molecular number average (Eq. 3-3). A more accurate presentation is a graph showing the molecular weight distribution. Two high density polyethylenes with the same $M_W/M_n$ distribution but with different distribution curves produced polymers having separate flow, mechanical, and morphological properties (48). This method can be used to construct polymers with a combination of properties which might otherwise be unavailable.

Increasing the breadth of the molecular weight distribution makes the polymer more sensitive to the rate of flow (shear rate). Adding lower molecular weight fractions causes a rapid increase in flow (decrease in viscosity) at high shear rates. The reasons are discussed more fully in the sections on rheology and orientation. In effect, the small chains separate the large chains from each other. This reduces the Van der Waal’s forces. Additionally they are acting as lubricants for the larger molecules. Because of this, flow at very low shear rates (the melt index range) is not necessarily comparable to those at very high shear rates. A broader MWD will flow more readily. It is therefore possible to have a higher MI material flow more slowly under molding conditions than a lower MI material.

In general the broad MWD materials are more sensitive to molding conditions. A modified spiral flow mold was used to measure the flow length of a 20.5-MI 0.95-density PE at a cylinder temperature of 425°F, a cylinder pressure of 10,000 psi, and a mold temperature of 32°F. The same material with a narrow molecular weight distribution flowed 21 in. and a broad molecular weight distribution flowed 27 in. (44). Increasing the mold temperature increased the
flow length linearly. This relationship did not change with the MWD.

The increased pressure sensitivity was shown with the same material, using the same cylinder temperature and mold temperature, but varying the injection pressure.

<table>
<thead>
<tr>
<th>Cylinder Pressure</th>
<th>5000 psi; 352 kg/cm²</th>
<th>15,000 psi; 1,055 kg/cm²</th>
<th>Increase in Flow Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narrow MWD</td>
<td>in. 15</td>
<td>27</td>
<td>12</td>
</tr>
<tr>
<td>Flow length</td>
<td>mm 381</td>
<td>686</td>
<td>305</td>
</tr>
<tr>
<td>Wide MWD</td>
<td>in. 19</td>
<td>35</td>
<td>16</td>
</tr>
<tr>
<td>Flow length</td>
<td>mm 483</td>
<td>889</td>
<td>406</td>
</tr>
</tbody>
</table>

Increasing the pressure 10,000 psi increased the flow length of a narrow MWD 12 in. while that of the broad MWD 16 in.

The use of \( M_W/M_n \) ratios and MI for describing the effects of different MWD is discussed in Ref. 45.

The effects of broad MWD on the viscosity and shear rate are shown in Refs. 43 to 46.

The effects of MWD on some polymer properties are shown in Table 3-4.

**Table 3-4  Effects of molecular weight distribution on properties and processing characteristics**

<table>
<thead>
<tr>
<th>To obtain</th>
<th>Make the MDW narrower</th>
<th>Make the MDW broader</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher impact strength</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lower shrinkage</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lower warpage</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Better dimensional stability</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Higher tensile strength</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Higher resistance to creep</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Better low temperature brittleness</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Improved flow</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Higher sensitivity to pressure</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Higher sensitivity to temperature</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

**RHEOLOGY AND WHAT IT MEANS TO THE MOLDER**

Rheology is a study of liquid flow and deformation properties in terms of stress, strain, and time. Obviously this is of major importance for the injection molder.
Figure 3-7 Osborne Reynolds' flow experiment: (a) laminar – to 2000; (b) transition – 2000 to 3000; and (c) turbulent – over 3000.

The principles of rheology are concerned with the flow of hydraulic fluids in the molding machine, the fluids in the heat transfer of the mold, and in the flow of polymers in the heating cylinder and mold.
Reynolds Number

In the eighteenth century, Osborne Reynolds discovered some of the basic principles of flow. He took a container (Figure 3-7) to which he attached a tube with an outlet valve which could control the amount and rate of flow in the tube. There was a source of inlet water to maintain the level in the container. Feeding externally, directly into the tube, was a pot of dye with a controllable flow rate. When the flow rate in the tube was low, the dye assumed a straight path parallel to the tube. This Reynolds called a laminar flow. As the flow increased there came a range where turbulence began to occur. When flow became very rapid there was complete mixing of the dye in the tube. He derived a formula to describe this phenomena for a circular tube using a dimensionless number known as the Reynolds number.

\[ N_R = \frac{\rho UD}{\mu} \]  

(3-6)

where \( N_R \) = Reynolds number  
\( \rho \) = mass density \([(lb) (sec^2)/ft^4]\)  
\( U \) = velocity \((ft/sec)\)  
\( D \) = diameter \((ft)\)  
\( \mu \) = viscosity \([(lb) (sec)/ft^2]\).

When the Reynolds number is below 2000, the flow is laminar. Between 2000 and 3000 there is a transition period and above 3000 there is turbulent flow. It is obvious that the laminar flow is the most efficient. Imagine a molecule flowing the length of the tube. In laminar flow it will be least likely to collide with any other molecules or deviate largely from the direct straight line path. In turbulent flow considerable energy is lost in collisions with other molecules and in the much longer distance the molecule has to travel from one end of the tube to the other. In an oil hydraulic system, turbulent flow generates more heat, which has to be removed. Inspecting Reynolds’ equation we know that the mass density and viscosity of the oil will not change significantly. The velocity and pipe diameter are the variables.

Reynolds’ formula was developed for Newtonian fluids (p. 223). Although thermoplastics are non-Newtonian, experience shows the parameters described by Reynolds can apply. An outstanding example of this is in the molding of variegated colors. When two colors are molded simultaneously through a large gate, poor mixing is obtained and the desired mottled patterns ensue. If the gate is restricted (pin pointed), it will be impossible to obtain the same patterns. The turbulence generated by decreasing the diameter (increasing the velocity) will give excellent mixing. This principle is used in dispersion disks inserted in nozzles for improving the mixing and homogeneity of plastics alone or with colorants.
Newtonian Flow Rates

Two men, Hagan and Poiseuille, independently derived the volumetric flow rate for a Newtonian liquid.

\[ Q = \frac{\pi}{8} \frac{R^4}{L} \Delta P \frac{1}{\mu} \]  

(3-7)

where 
- \( Q \) = volumetric flow rate
- \( R \) = radius of tube
- \( L \) = length of tube
- \( \Delta P \) = pressure drop
- \( \mu \) = viscosity.

This formula, for a cylindrical tube, shows that the volumetric flow rate depends on three parameters. The first is the physical constants of the tube, \( R^4/L \). A Newtonian liquid is extremely sensitive to the radius. This is less so with plastics since, as we shall shortly see, viscosity varies with the shear rate (velocity). Increasing \( R \) will increase \( Q \), but also will decrease the velocity. This will increase the viscosity because of the polymer's sensitivity to shear rate and partially reduce the full flow effects of the increase of \( R \). As we would expect the more pressure (\( \Delta P \)) the higher flow rate. Finally, the more viscous (\( \mu \)) the material, the less the flow rate. The flow rate is influenced by the length of the tube (\( L \)). This corresponds to the land length of a gate. When we wish maximum flow into a cavity, which is the usual situation, we keep the land length to a minimum. The land length can be used to help balance the flow of material into multicavity molds.

In rheology the word stress is not used in the sense of a force acting on a body. It is the internal resistance of a body to an applied force. This resistance consists of the attraction of molecular bonds and forces. Thus when we say that we increase the shear stress to increase the shear rate, we really mean that we have to overcome increasing molecular resistance to achieve a faster flow rate.

Shearing stress is the measure of the resistance to flow of sliding layers of molecules. It is reported in pounds per square inch. Force is measured in the same units but is different in two respects. Force acts perpendicular to the body while shear stress acts parallel to the containing surface. Pressure is force per unit area while shearing stress is a resistance to force. Newton developed the concept of this doctrine by using concentric cylinders. He stated that the shear stress caused by the viscosity of the liquid is proportional to the shear rate. We can understand this concept by imagining a stationary plate (Figure 3-8) with a movable plate of area \( A \), moving at a velocity \( U \), with a force \( F \), stationed at a distance \( X \), above the stationary plate. Neglecting "slip" we assume the velocity of the liquid at the stationary plate as zero, and the maximum velocity \( U \) at the moving plate. The rate of change of velocity across the liquid is the slope of the
Figure 3-8  Concept of viscosity.

\( F \) is proportional to \( A \) and \( U \) (velocity).

\[ f = \mu (\text{Newtonian viscosity}) \text{ or } \eta (\text{non-Newtonian viscosity}) \]

\[
F = (f) \ A \ \frac{du}{dx} \\
\frac{F}{A} = \text{shear force} \quad \frac{lb.}{in.^2} = \frac{\text{dynes}}{\text{cm}^2} = \tau \\
\frac{du}{dx} = \text{shear rate} \quad \left( \frac{\text{in.}}{\text{sec.}} \right) \quad \left( \frac{1}{\text{in.}} \right) = \text{sec}^{-1} = \gamma \\
\mu = \frac{\tau}{\gamma} = \frac{(lb) \ (sec)}{in^2} = 68,948 \ \frac{(\text{dyne}) \ (sec)}{cm^2} \text{ (poise)}
\]

The line connecting the velocity vectors or \( du/dx \).

The force is proportional to the area and velocity.

\[ F = (f) \ (A) \ \frac{du}{dx} \]
The proportionality constant \( f \) is called the viscosity and designated \( \mu \) for Newtonian liquids or \( \eta \) for non-Newtonian liquids. Shear force or stress is represented by the Greek letter \( \tau \), and shear rate by \( \gamma \).

Rearranging the terms we have the following:

\[
\mu = \frac{F}{A} \frac{(\text{shear stress})}{(\text{shear rate})} = \frac{\tau}{\gamma}
\]  

(3-8)

In a Newtonian liquid, therefore, the shear force is directly proportional to the shear rate; double the unit force and you double the unit rate. In thermoplastic material this does not turn out to be the case. In the processing range a unit increase in the shear force may quadruple the shear rate. The viscosity is dependent on the shear rate and drops exponentially with increasing shear rate.

**Rheometers**

Rheometers were developed to measure the shear stress and shear rate during polymer flow. Viscosity is then calculated from Eq. 3-8.

Let us consider flow in a tube (Figure 3-9). Imagine the tube to be constructed by bending the flat plate of Figure 3-8 so that it becomes a cylinder. At the cylinder wall the velocity is zero (assuming that there is no slip of the polymer along the wall). Since one end of the polymer is anchored to the wall the shearing stress will be maximum at the wall. The shear rate \( \frac{du}{dx} \) is given by the slope of the velocity profile at any point. This would vary from zero at the center of the tube to its maximum at the wall. In the center of the tube the velocity will be maximum and the shear stress and shear rate will be minimum. To characterize the viscosity we must compare shear rate and shear stress at the same point. They are both maximum at the wall and rheometric calculations refer to this point.

The wave front of the fluid in a tube is a parabola. The volume under a parabola is

\[
\text{Volume} = \frac{\pi}{2} r^2 h \quad h = \frac{1}{2} r \quad \text{(Figure 3-9)}
\]

\[
\text{Volume} = \frac{\pi r^3}{4}
\]

shear rate \( \gamma \) = \frac{\text{Volumetric flow rate}}{\text{Volume}} = \frac{Q}{\frac{\pi r^3}{4}} = \frac{4Q}{\pi r^3}
\]

(3-9)
Figure 3-9 Flow in a capillary tube

At the wall of the tube
Velocity = 0
Shear rate = maximum (slope $du/dr$)
Shear stress = maximum

At the center of the tube
Velocity = maximum
Shear rate = minimum
Shear stress = minimum

**Shear Rate**

**Volume of parabola** = $\frac{1}{2} \pi r^2 h = \frac{1}{2} \pi r^2 \frac{r^2}{4} = \frac{\pi r^3}{4}$

**Shear rate** $(\gamma)$ = \frac{\text{Volumetric flow rate} (Q)}{\text{Volume}} = \frac{Q}{mr^3} = \frac{4Q}{mr^3}$

**Shear Stress**

$F = P \times A$

Force ($F$) acting parallel to tube = $P \pi r^2$
Stress opposing ($F$) = shearing stress ($\tau$) x shearing area $|2 \pi r L|$
The two forces are equal, thus:
$P \pi r^2 = \tau \times 2 \pi r L$
Shearing stress $\tau = \frac{P \pi r^2}{2L}$

Analyzing this equation dimensionally yields.

Shear rate $= \left( \frac{\text{in.}^3}{\text{sec}} \right) \left( \frac{1}{\text{in.}^3} \right) = \text{sec}^{-1}$

Therefore, shear rates in rheometry are reported in units of reciprocal seconds. The shearing stress ($\tau$) can be computed by considering what happens to a
plug of liquid \( L \) inches long. The force (perpendicular to it) is equal to the pressure times the area \( (P\pi r^2) \). The force opposing it would be the shearing stresses at the wall multiplied by the area of the wall (circumference \( \times \) length = \( 2\pi rL \) or \( \pi (2\pi rL) \)). Since the force required to move the plug is that required to overcome the shearing stress we can equate the two and solve for \( \tau \)

\[
P\pi r^2 = \tau (2\pi rL)
\]

\[
\tau = \frac{Pr}{2L}
\]

(3-10)

Analyzing this equation dimensionally yields

Shear stress \( = \left( \frac{lb}{in.} \right) \left( \frac{in.}{in.} \right) = \frac{lb}{in.^2} \)

Therefore shear stress in rheometry are reported as lb/in.\(^2\).

The viscosity is the shear force over the shear rate. Substituting dimensions

\[
\text{Viscosity} = \frac{lb}{in.^2} \frac{(lb)}{(sec)} \frac{(sec)}{in.} \]

The metric system uses dyne-sec/cm\(^2\) which is called a poise named after Poiseuille. The relationship is

\[
1 \frac{(lb)(sec)}{in.^2} = 68,948 \frac{\text{dyne-sec}}{\text{cm}^2} \text{ (poise)}
\]

The proceeding discussion suggests that shear rate and shear stress could be measured by constructing an instrument which would extrude the polymer through a capillary while measuring the force and speed of the plunger. The viscosity would then be a simple calculation. This has been done and the instrument is called a capillary rheometer (Figure 3-10).

It is also possible to calculate viscosity using a rotational viscometer. The plastic is sheared between a rotating cylinder and a fixed wall at a constant speed. Upon equilibrium the torque and velocity of the rotating body are measured. A second type of rotational rheometer often used in the plastics industry is called a Brabender rheometer. It consists of two irregularly shaped rollers in a heated chamber. The data consist of values of the torque and plastic temperatures at constant rotational speed versus time. Analyses of this rheometer and conversion of its data to that obtained by capillary rheometry is found in Ref. 49 to 52.

The most widely used instrument is the capillary rheometer (53, 247) (Figure 3-10). It consists of a 14¼-in.-long barrel in which a 0.375 hole is bored. A plunger is closely fitted into the bored barrel. The bore is attached to a capillary whose diameter can be varied between 1/32 and 1/16 in. The length of the
Figure 3-10 Calculations for a specific Instron® capillary rheometer.

Shear stress \( (\tau) = \frac{FD}{\pi LD^2} = \frac{lb}{in.} \)

Shear rate \( (\gamma) = \left( \frac{215}{15} \right) \left( \frac{UD^2}{D^3} \right) = \frac{1}{sec} = sec^{-1} \)

Apparent viscosity \( (\eta) = \frac{\tau}{\gamma} = \frac{(lb)}{in.} \) (sec)

Calculation \( \eta = \left( \frac{15}{2\pi} \right) \left( \frac{FD^4}{LUD^4} \right) \)
capillary is varied so that the $L/D$ ratios can be selected from 3.5 to 188. So that the capillary geometry does not affect the results, minimum $L/D$s of 60 are required for polystyrene and 30 for polyethylene.

The $L/D$ of a melt indexer is 3.8. This is another reason why MI does not always correlate with comparative flow properties. The barrel and capillary sections are kept at a constant temperature and controlled by thermocouples. The head of the plunger is attached to an Instron® testing machine. Speeds start at 0.02 in./min and the maximum load is rarely more than 2000 lb.

The method of calculating shear stress, shear rate, and viscosity are show in Figure 3-10. The only two variables are the force and the velocity. All others are the physical constants of the rheometer.

**Rheometer Corrections.** There are a number of corrections that have to be made to the raw data obtained in a rheometer. Since these corrections are only occasionally referred to in the literature on rheology and since, more importantly these corrections illustrate some of the properties of viscous elastic flow, a brief discussion on these corrections is warranted.

1. An important error which must be corrected is in the effect of forcing the polymer from the large diameter piston chamber into the much smaller capillary. The energy lost should only come from viscous flow, rather than any elastic effects of this compression. This error can be corrected by using capillaries of varying $L/D$ dimensions and suitable graphic treatment. Also since polymers are sensitive to the shear rate, these determinations are made at different shear rate values. There are other elastic absorbences of energy in the system. These are usually negligible when large $L/D$ capillaries are used.

2. Energy is required to accelerate the fluid velocity to obtain the average flow rate. This energy is lost after the plastic has been extruded. The effect of this is small enough to be ignored for most calculations.

3. When a plastic flows, the "friction" of the molecule is appreciable and can raise the temperature of the material. Because of the low thermal conductivity of the plastic the heat cannot be dissipated quickly enough. Consequently, the temperature of the material will increase and the viscosity will decrease. Under most circumstances this temperature rise is ignored.

4. The material is compressed significantly when it enters the capillary. As the pressure drops it expands and becomes a lower density material. This changes the volumetric flow rate which can be corrected from the equation of state of the polymer.

5. Since the apparent viscosity varies with the fourth power of the capillary diameter, accurate measurements are needed. The difficulties of accurately measuring a capillary tube have not been completely overcome. While this error can be of considerable magnitude, it does not appreciably effect the use of flow curves.
6. There is one other important correction. The shear rate equation has been
derived for a Newtonian fluid but plastics are generally non-Newtonian.
Calculated values obtained with data using this equation are called the apparent
Newtonian wall shear rates. Rabinowitch derived a correction for converting the
Newtonian wall shear rate to what is called the "true wall shear rate."

**Plotting Rheological Results.** The results of rheological measurements—shear
rate, shear stress, and viscosity—are usually shown graphically. The curves of
each type material assume characteristic shapes which are used for their
classification (Figure 3-11). The arithmetic plot of shear rate versus shear stress
for a Newtonian material is a straight line whose slope is related to its viscosity.

**Dilatant Material.** A dilatant material requires more than a unit increase in
shear stress for a unit increase in shear rate. These materials are found in some
plastisols and highly filled plastics. One explanation for this type flow assumes
that at low flow rates the particles can glide over each other. At higher rates
eddy currents causes one phase to ball up and require the other phase to jump
over it. This causes the expansion or "dilatant" effect. As expected this is a
reversible phenomena. Dilatant behavior does not normally occur in injection
molding.

**Bingham Materials.** A Bingham material is one that will not flow until a
certain shear stress is applied. Once these materials flow their flow characteristics
are usually between Newtonian and plastic. Examples of Bingham materials are
concentrated polymer solutions which may form a gel structure, catsup, mustard,
and toothpaste. Bingham materials are not normally met in injection
molding.

**Plastic Flow.** This flow (sometimes called pseudoplastic) is characteristic of
molten polymers above their glass transition point. At low shear rate the flow is
Newtonian (straight line). At shear rates in the processing range, a unit increase
in shear stress will result in several unit increases of shear rate (curved line). At
very high shear rates the flow is again Newtonian (straight line).

An arithmetic plot of the viscosity versus shear rate Figure 3-11 shows the
Newtonian curve—a straight line parallel to the shear rate axis. This shows that
the shear rate has no effect on the viscosity. The Dilatant curve shows that as the
shear rate increases the viscosity increases. In a plastic material the viscosity
drops exponentially with the shear rate, so that there is a different viscosity
value for each shear rate.

Since viscosity is the measure of flowability, it is readily apparent that a
plastic may be too viscous to fill a mold at low shear rates but perfectly suitable
if the shear rates are increased. The flow can be approximated by a power law

\[ \tau = K (\gamma)^n \]  

(3-11)

which describes flow curves very well for large intervals of shear rate up to 4
magnitudes. The $K$ and $n$ are constants. When $n$ is 1 the flow is Newtonian and $K$ is the viscosity. The exponent $n$ is called the flow index and its numerical value is a measure of the deviation from Newtonian flow. The greater the difference from 1 the less Newtonian is the system.

When $n$ is less than 1 the material is plastic with the slope of the flow curves getting smaller with increasing shear rate. The viscosity decreases with increasing shear rate.

When $n$ is greater than 1 the material is dilatant. The slope of the flow curve increases with increasing shear rate as does the viscosity.

It is evident that for reasons of accuracy and convenience these curves can best be plotted on log-log paper. In that instance the shear stress/shear rate curve shows a Newtonian material at an angle of $45^\circ$ (slope of 1). A plastic will have a slope of less than 1 at every point on the curve and a dilatant material will have a slope more than 1 at every point of the curve.

Similarly log-log plots of viscosity/shear rate show that a Newtonian material will have a slope of 0 and be a straight line parallel to the shear rate axis. A plastic material will have a decreasing curve as the shear rate increases and a dilatant material will have an increasing curve as the shear rate increases.

Figure 3-12 shows a log-log plot for the shear stress/shear rate curve for four different plastic materials. The shear rate for compression molding ranges from 1 to 10 sec$^{-1}$, for calendering 10 to 100 sec$^{-1}$, extrusion 100 to 1000 sec$^{-1}$ and injection molding 1000 to 10,000 sec$^{-1}$. It is impossible to characterize completely plastic flow over large shear rates by measuring it only at one shear rate point. The melt index is taken at very low shear rates. In some instances the
flow curves cross at higher shear rates, giving erroneous results (the higher MI having poorer flow properties in the molding range). Therefore, in selecting a specific resin for a critical application, or in changing suppliers for the same material (particularly in the olefins), shear stress/shear rate curves of each material should be inspected.

**Melt Fracture**

It must be noted here that we are only discussing the viscous flow component of the plastic. There is an elastic component which is reversibly stored kinetic energy. When the shear stress exceeds the shear strength of the melt, melt fracture occurs. It is most likely to occur where there is a sudden increase in shear rate, such as at a restricted gate. Since it is reversible, it will usually disappear in the molded part. In some instances, particularly with a cold mold, it will result in surface blemishes which are overcome by lowering the shear rate. It is a significant problem in extrusion and there is considerable literature on melt elasticity and fracture (54–59).

The assumption was made that there is zero velocity at the wall of the capillary. Experience tells us this is not so, otherwise it would be impossible to change color. By using small irregularly shaped carborundum particles about
0.002 in. in size as tracers, velocity profiles for polyethylene melts were determined (60). Analysis showed only about 25% of the particles at the wall have 0 velocity. About 15% move with a moderate velocity and the balance at relatively slow velocities. The proposed mechanism suggests that the melt elasticity causes the slipping. The polymer just away from the wall deforms elastically and the polymer along the wall slips to reduce the elasticity. The flow in the center region of the tube had little shear and a uniform velocity. Slippage increases with molecular weight so that ultrahigh molecular weight polyethylenes become difficult to extrude (61). These considerations do not affect the practical use of rheometric data for injection molding.

Applications of Rheological Data

Before discussing experimental results and the applications of rheological data let us consider, conceptually, how polymer molecules flow. A plastic differs from a Newtonian material in that it contains long molecules. Its segments and chains are flexible. They intermingle and are held together by Van der Waal’s type of forces.

All molecules have heat energy which result in vibration or movement within the bounds of molecular attraction. This Brownian movement, named after its postulator, tends to locate the polymer sections in a random position, this being the lowest energy level. This might be shown schematically in Figure 3-13. The plastic molecule is too large to move as a unit. Motion occurs in segmental units of the polymer.

If a force is applied in one direction to a polymer above its glass transition point, segments will begin to move in the direction away from the force, to relieve the stress. The net result is a movement of the viscous mass. As the polymer moves, it tends to untangle and orient itself parallel to the direction of flow. If the force is applied very slowly, so that the Brownian movement can cancel the orienting force caused by the flow, the mass of the polymer will move with a rate proportional to the applied stress. This is Newtonian flow (62).

As the plastic begins to move more rapidly the molecular segments and chains tend to orient in the direction of flow, as they did before. At this faster flow rate the Brownian movement is no longer able to return all of them to the random position. The orientation results in untangling the polymer and separating the molecules from each other, reducing the Van der Waal’s forces (Figure 3-14). Obviously the untangled molecules will slide over each other more easily than the tangled ones, that is, lowering the viscosity. When the polymer is in the configuration of Figure 3-13, a unit increase of shear stress will give a unit increase of shear rate. Compare this with the situation in Figure 3-14. The polymer molecules are now further apart and the resistance to shearing is much less because of the decreased Van der Waal’s forces. Therefore the same unit
increase of shear stress will give a greater increase in the shear rate by at least several units. This is the plastic flow section of the curve in Figure 3-11. This process will continue until the polymer has reached its maximum state of orientation. At that time there is no further untangling and a unit increase in shear stress will again give a unit increase in shear rate, that is, Newtonian flow. This range is rarely met in injection molding. These shear rates are so high that they usually start to degrade the plastic.

Figure 3-15 shows an arithmetic plot of apparent viscosity and shear rate which illustrates plastic flow. At all temperatures, the viscosity decreases rapidly with increasing shear rate. Raising the temperature of the 0.7 MI-PE increases the separation of the molecules so that orientation (lower viscosity) starts more quickly. This effect of heating is shown by an almost identical curve displaced toward the left. As the shear rate increases the apparent viscosity of the materials at both temperatures tend to approach each other. This is saying, in effect, that the point has been reached where the overwhelming percentage of orientation has taken place and that additional shear rate will have relatively little effect on viscosity. This is true of most plastics in the processing range. It is interesting to note that most polymers have similar apparent viscosities,
Figure 3-14 Schematic representation of Figure 3-13 when the polymer is flowing at rapid speed and is oriented in the direction of flow.

10^{-1} to 10^{-2} \text{ lb sec/in.}^2, \text{ at the shear rates (}10^{-3} \text{ to } 10^{-4} \text{ sec}^{-1}\text{)}\text{ used in injection molding.}

**How Rheological Properties Relate to Molding Conditions**

As the shear rate increases beyond the area of rapid change, the dependency of viscosity on shear rate decreases. For example, increasing the shear rate of the 0.7 MI-PE (428°F) from 200 to 400 sec^{-1}, decreases the viscosity by 4500 P. The same increase in shear rate from 900 to 1100 sec^{-1} decreases the viscosity by 350 P. Large variations in the viscosity caused by small changes in the shear rate will lead to molding difficulties. Surface imperfections, uneven filling, unequal densities, high stress levels, warpage, and differences in linear shrinkage may result. It is therefore important to mold at the part of the curve where the effect of shear rate is minimal.

When a mold does not fill it means that the viscosity is too low at the gate. This assumes the molding machine has enough injection speed to satisfy the flow
Figure 3-15 Arithmetic plot of viscosity/shear rate curves for (a) 0.7 MI polyethylene at two temperatures, and (b) MH cellulose acetate. (Ref. 63).
requirements \( Q \) and that the runner system is large enough to transmit this to the gate. One way of decreasing the viscosity is to raise the temperature (Figure 3-20). This is limited by the activation energy of viscous flow (which is discussed on p. 237) and the temperature at which the polymer degrades.

The second approach is to increase the shear rate. Figure 3-16 shows the effect of shear rate on viscosity for an acrylic. Assume a mold requires a viscosity of 0.07 lb-sec/in.\(^2\) to fill. When the shear rate is 100 sec\(^{-1}\), the material must be at 475\(^\circ\) for this viscosity. If the shear rate is increased to 1000 sec\(^{-1}\), the temperature is 400\(^\circ\)F or 75\(^\circ\)F lower. Consequently, the material will have to be cooled 75\(^\circ\) less when molded at 1000 sec\(^{-1}\). This is a major saving in molding time. Figure 3-17 shows the effects of shear rate on viscosity for some materials. Aside from the machine, the major limitation on increasing the shear rate is the possibility of polymer degradation. (As we have seen when discussing molding machines, high surface speeds rip the polymer apart.)

Shear rate can be increased by changing the geometry of the gating system and/or increasing the pressure (shear stress).

Both of these methods will lower the viscosity. If one substitutes for \( Q \) (Eq. 3-7) in the shear rate Eq. 3-9, one gets

\[
\gamma = \left( \frac{4}{\pi R^3} \frac{\pi}{8} \right) \left( \frac{R^4 \Delta P}{L \mu} \right)
\]

\[
\gamma = \left( \frac{R \Delta P}{2L} \right) \left( \frac{1}{\mu} \right)
\]

The first group on the right hand side \( R\Delta P/2L \) is, of course, the shear stress. Most materials are molded with short restricted gates to increase shear with diameters of about 1/16 in. diameter (0.003 in.\(^2\)) to 0.10 in. diameter (0.008 in.\(^2\)).

There are two other advantages to small gates. They break off easily requiring little if any cleaning, and they freeze off quickly so that the extra material packed into the cavity cannot flow back into the runner system. With large gates, however, injection forward pressure must be held for a considerably longer time to revent back flow, thus increasing cycle time. The shear stress also depends on the pressure drop between the runner and the cavity (\( \Delta P \)). However, if the gate, cross-section \( R \), is too large the machine system may not be able to deliver enough plastic to maintain a large pressure drop and in turn, shear stress would be significantly reduced. Beyond restricted gate sizes, gates must be
increased by many orders of magnitude to be moldable, so that $R$ is increased enough to overcome the lowering of the shear stress caused by the lowered pressure drop ($\Delta P$) of the larger gate.

Figure 3-16 Effect of shear rate on viscosity for polymethyl methacrylate (Lucite 129 E. I. duPont de Nemours & Company).
The effects of static pressure on viscosity have been investigated (64–66). The static pressure increase affects the flow much less than does $\Delta P$, the pressure drop. Increasing the pressure drop from 100 to 1000 psi increases the flow rate from 0.01 to 1 in.$^3$/sec.

Increasing the static pressure from 10,000 to 25,000 psi raises the viscosity from 1000 to 4100 P for polystyrene, and from 1000 to 1220 P for polyethylene. Apparently one might expect a decrease in flow with very high
pressures. An excellent analysis of these type data (67) shows that under normal conditions raising the injection pressure will always result in an increase in flow.

**Rheology and Production Control.** Rheological data are useful for production control in the manufacture of resins, raw material control for processors, and determining relationships between polymer structure (MWD, branching, etc.) and flow properties (68, 69). To be of further value to the molder, rheological data obtained from capillary flow rheometers must be correlated with actual performances of molding machines and their extruder plasticizers. This would permit the molder to improve the quality of the molded part, processing rate, and selection of proper conditions (69a).

For example, polyethylene was extruded at 400 and 504°F four times, successively, with no change in the apparent viscosity. This means that degradation did not occur. Raising the temperature to 525°F showed a 29% reduction in viscosity after ten extrusions. Raising it to 646°F showed a 53.6% reduction after 10 extrusions (70). Data from a capillary rheometer were used to estimate operational performance in terms of output and processability of rigid PVC. Shear rates where melt fracture occurred and conditions for maximum output were predicted (71, 71a).

A simplified analysis of mold filling and some of the flow properties in injection molding are given in Refs. 72 and 73. Some of the effects of mold design, molding conditions, and materials on thermoplastic flow are discussed.

Looking at the schematic diagram of the rheometer, one is impressed by its similarity to an injection cylinder. The plunger corresponds to the injection plunger, the plastic material to the plastic in the "cylinder, nozzle, and runner system", and the capillary to the gate. There are some major differences however. The flow rate in a rheometer is steady, compared to the large variations in the mold. The material in the rheometer is at a constant temperature, compared to the nonisothermal state of the mold. The rheometer's material is heated by conduction while, in a screw machine, the material is heated primarily by shearing. Notwithstanding, there is good qualitative correlation between the results of rheometry and the injection molding process (74–77). Westover (78) has compiled extremely useful rheological data for many plastic materials.

The filling of a cold cavity with a hot non-Newtonian fluid was studied (79). Evidence was presented to show that the flow process depended on the rheological properties as measured in an isothermal, steady-state rheometer. Rheological data obtained for polystyrene in a capillary rheometer were correlated with the length of spiral flow over a broad range of temperature, but with otherwise constant conditions in a specific molding machine (80).

**Spiral Flow Mold.** To evaluate better the moldability of material, a spiral mold was developed (81). These molds showed good correlation with rheological data (82), are an excellent method for comparing flow properties of different batches of the same material and of the same material from different sources.
Many types of molds using this principle have been developed for polymer evaluation. They have been used for studying the effect of gate size, cavity depths, flow rates, and evaluation of physical properties. A variation of this idea can be very useful in molding parts to tolerance. The shrinkage of a part is directly related to the amount of material molded in the cavity. A tab can be machined near the end of the gate. It should be long enough and thin enough so that it does not fill out even if the shot is flashed. Equally distant lines are machined and numbered successively. The length of the tab can be correlated with the critical dimensions. Control limits are set for the tab. If the moldings fall outside the specified limits an alert operator can call the foreman and prevent molding rejects.

When viscosities are taken at high shear rates approximating molding conditions (1500–2500 sec\(^{-1}\)) excellent correlation with spiral flow is obtained. Viscosities taken at low shear rates and constant shear stress (such as in the MI determination) did not show good correlation with spiral flow length.

*Average Viscosity*—The use of an expression for the “average” viscosity instead of the one point viscosities (MI) was developed. It correlated reasonably well with such practical molding tests as spiral mold length, minimum cycle temperatures, molding area diagram limits, and experiences in production runs on commercial parts (76).

Reference 83 states that for broad ranges of operating conditions in a wide variety of high pressure polyethylenes, the flow data obtained from a high shear rate viscometer and a commercial extruder were identical. Good correlation was obtained in using the data for predicting screw power consumption.

**GLASS TRANSITION TEMPERATURE**

Throughout this section we described plastic flow in terms of molecular properties. The differentiating characteristics of a polymer are the length of its molecules, the ability of its parts to rotate and be flexible, and the nature of the internal and external molecular forces. The ability of the C-C linkages to rotate freely permits the polymer molecule to move in segmental jumps. Mathematical models based on these assumptions are beginning to describe qualitatively these segmental motions.

There are two theoretical approaches to the flow of polymers. One approach treats viscous flow as a modified simple liquid. Here the viscosity of the system is caused by the frictional drag of molecular segments over each other when they move from position to position. This drag is due to exchanges of momentum between molecular segments.

The second approach, chosen by Eyring, examines the polymer as a disordered solid. Each polymer segment, containing approximately 20 to 40
monomer units, is assumed to move in a limited area bounded by the attractive and repulsive forces of its neighboring segments. Many defects or "holes" appear as a disorder in the disordered condition of the polymer. From time to time a segment will receive excessive kinetic energy and will be able to break the intermolecular forces and jump into a hole. Another segment will move into the hole just vacated. These are random movements. This approach is based on the assumption that there are unoccupied areas known as "free volume." The jump frequency of the segments depends on the energy level required to move them and the amount of free volume in the polymer. The free volume is distributed equally throughout. When an external stress is applied in one direction, the jumps will no longer be random but will move in such a manner as to relieve the stress. This causes the polymer to flow.

The Glass Transition Point

We are now in a better position to understand the glass transition point. If we take a molten polymer and cool it slowly, it gradually becomes elastic in nature, then it becomes leather-like, and, finally in a specific small temperature range, it abruptly changes into a solid. This point is called its glass transition point ($T_g$). At this point the polymer segments are no longer free to rotate. This applies to the longer molecular segments in the neighborhood of 20 to 40 monomer units long. Motions of shorter segments continue and other transition temperatures below $T_g$ are found which indicate the cessation of a particular type of motion.

Figure 3-18 graphically shows the effect of free volume. Each small figure represents the rotational area of a polymer segment approximately 20 to 40 monomer units long. Below the glass transitional point there is not enough free volume for a significant number of segmental jumps. The amount of heat energy (temperature) is not enough to break the intermolecular forces. The specific volume (a measure of the free volume) increases relatively slowly with the increase in temperature.

At $T_g$ the cohesive forces yield drastically and the polymer expands so that there is room for segmental rotation. Segment $A$ moves into area $A-1$, $B$ to $B-1$, $C$ to $C-1$, and so on. Other segments move into the vacated spaces. The polymer now starts to flow, its characteristics being determined by the temperature increase above $T_g$ and the crystalline structure, if any. Once this initial state ($T_g$) has been reached and the high energy barriers have been broken, a smaller amount of heat energy ($T$) will be required to expand a unit volume. This is in consonance with our understanding of the Van der Waal's forces which decrease as the sixth power of the distance.

There are a number of ways of determining $T_g$. The most common is to plot the specific volume against the temperature (Figure 3-19). At a particular point there is an abrupt change in the slope of the curve. This is the glass transition
Below $T_g$ there is little room for Brownian movement. Rotation area required for polymer segments to vibrate.

above $T_g$ segments are far enough apart so that "free volume" appears, leaving room for segmental migration in that direction which tends to relieve the applied stresses.

Free volume into which polymer segments may move.

Figure 3-18 Eyring "free volume" theory: (a) below $T_g$ there is little room for Brownian movement, and (b) above $T_g$ segments are far enough apart so that "free volume" appears, leaving room for segmental migration in that direction which tends to relieve the applied stresses.

temperature. As has been stated, below $T_g$ the heat energy is not enough to break the intermolecular forces so that a unit raise in temperature gives a small unit increase in volume. Above $T_g$ these barriers have been broken and the same unit increase in temperature will produce a much larger increase in volume. The second curve in Figure 3-19 shows a plot for a crystalline polymer. The amorphous section shows its own $T_g$. When the material reaches the melting point ($T_m$) the crystalline structure melts. Since crystals occupy the least volume, there is a very large increase in specific volume at that point.

Some of the other ways of determining $T_g$ are dynamic mechanical methods, nuclear magnetic resonance, dielectric loss in polar polymers, the onset of brittleness, and refractive index (84, 85).

The most comprehensive listing of glass transition temperatures and melting points is found in Ref. 86.

Most commercial amorphous polymers have $T_g$ from 115 to 300°F. Hence they act as solids at room temperatures. Most commercial crystalline polymers have glass $T_g$ from -150 to 27°F. Therefore, they are usually ductile at room
temperatures but maintain their rigidity because of the high modulus caused by crystallinity. Material such as nylon with low glass transition points and high crystalline melting points exhibit excellent mechanical properties.

From our conceptual model it would seem that as soon as the free volume is slightly larger than the moving segments, segmental displacement will occur (Figure 3-18). This in effect, is the glass transition temperature. From this we can infer how the $T_g$ depends on polymer structure.
Polymer Structure and $T_1$

The following observations are made relating $T_g$ to Polymer structure.

1. Polymers that have chains with stiff backbones or bulky side groups will have a high $T_g$. The moving segments will be large and a correspondingly large free volume would be required for $T_g$. This would require a correspondingly higher temperature than for a simpler polymer.

2. Polymers which have a high attractive force between the segments will require higher energy ($T$) to disassociate them, hence a higher $T_g$. The higher the molar cohesion energy, all other things being equal, the higher the $T_g$ (87). Cross-linking the polymer would increase the size of the moving segments and raise $T_g$.

3. Polymer structures which include chains and side groups tend to spread the polymer allowing for more free volume. These tend to lower $T_g$. Similarly the addition of plasticizers will accomplish the same purpose.

Melting Point and $T_g$

There is a relation between $T_g$ and the melting point ($T_m$). The ratio $T_g/T_m$ generally is between 0.50 and 0.75. Symmetrical polymers such as polyethylene are in the lower range and nonsymmetrical polymers such as polystyrene are in the upper range. Table 3-5 shows the $T_g$ and $T_m$ of some thermoplastic polymers.

Relationship of Viscosity to Flow

One would predict from this model of polymer flow that increasing pressure would decrease the free volume and reduce the number of segmental jumps. This pressure increase should increase the viscosity. This has been found to be so (65), and might explain why increasing pressure when molding through restricted gates does not always produce as much increase in flow rate as expected. The increased pressure will increase the viscosity and tend to reduce the added flow effect of the pressure increase.

As one would expect the viscosity or resistance to flow is temperature dependant. The higher the temperature, the further apart are the molecular segments. This increases the free volume and decreases the electrostatic or Van der Waal's forces. The relationship is expressed by the Arrhenius equation

$$\eta = Ae^{(E/RT)}$$  \hspace{1cm} (3-12)

where
\begin{align*}
\eta &= \text{viscosity} \\
A &= \text{constant depending upon the material} \\
R &= \text{Gas Constant} \\
T &= \text{°K} \\
E &= \text{activation energy for viscous flow.}
\end{align*}
<table>
<thead>
<tr>
<th>Material</th>
<th>Glass Transition Temperature ($T_g$)</th>
<th>Melting Point ($T_m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile-butadiene-styrene</td>
<td>$-$ $-$</td>
<td>374 190</td>
</tr>
<tr>
<td>Acetal</td>
<td>-121 -85</td>
<td>347 175</td>
</tr>
<tr>
<td>Acrylic</td>
<td>158, 221 70, 105</td>
<td>320 160</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>109 43</td>
<td>$-$ $-$</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>102 39</td>
<td>$-$ $-$</td>
</tr>
<tr>
<td>Cellulose tri-acetate</td>
<td>158 70</td>
<td>583 306</td>
</tr>
<tr>
<td>Cellulose acetate butyrate</td>
<td>122 50</td>
<td>$-$ $-$</td>
</tr>
<tr>
<td>PTFE (polytetrafluoroethylene)</td>
<td>-171, 68  -113, 20</td>
<td>626 330</td>
</tr>
<tr>
<td>Chlorinated polyether</td>
<td>$-$ $-$</td>
<td>358 181</td>
</tr>
<tr>
<td>CTFE (polychlorotrifluoroethylene)</td>
<td>95 to 113 35 to 45</td>
<td>428 220</td>
</tr>
<tr>
<td>FEP (fluorinated ethylene propylene)</td>
<td>52 11</td>
<td>$-$ $-$</td>
</tr>
<tr>
<td>PVF$_2$ (polyvinylidene fluoride)</td>
<td>-40 -39</td>
<td>340 - 410 171 - 210</td>
</tr>
<tr>
<td>Nylon 6/6</td>
<td>122 50</td>
<td>500 260</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>122 50</td>
<td>437 225</td>
</tr>
<tr>
<td>Nylon 6/10</td>
<td>104 40</td>
<td>415 428 213 - 220</td>
</tr>
<tr>
<td>Nylon 11</td>
<td>115 46</td>
<td>360 - 381 182 - 194</td>
</tr>
<tr>
<td>Nylon 12</td>
<td>99 37</td>
<td>354 179</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>306 152</td>
<td>437 225</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>-193, -4  -125, -20</td>
<td>230 - 286 110 - 141</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>23, 113  -5, 45</td>
<td>342 - 349 172 - 176</td>
</tr>
<tr>
<td>Polystyrene GP</td>
<td>178 to 212 81 to 100</td>
<td>455 235</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>158 to 176 70 to 80</td>
<td>392 200</td>
</tr>
<tr>
<td>4-Methyl pentene-1</td>
<td>104 40</td>
<td>464 240</td>
</tr>
<tr>
<td>Polyvinylidene chloride</td>
<td>$-$  17</td>
<td>410 210</td>
</tr>
</tbody>
</table>

From this equation one would expect that the plot of the log of the viscosity versus any linear function of the temperature would be a straight line over narrow temperature ranges and would describe flow fairly accurately. This holds true for a temperature range of approximately 100°F, Figure 3-20. In the plot of the log of viscosity against $1/T$ the slope of the line is the activation energy for viscous flow. It is related to the temperature coefficient of viscosity or the temperature dependency of the viscosity. The temperature coefficient of
viscosity per °F, for example, is $3.3 \times 10^{-3}$ for low density polyethylene and $1.9 \times 10^{-2}$ for cellulose acetate butyrate. The higher the temperature coefficient or the activation energy, the more dependant is the viscosity on the temperature.

It should be noted that activation energies or temperature coefficients must be calculated at a constant shear. The results will differ, depending on whether these energies or coefficients are determined at a constant shear stress or a constant shear rate.

A very useful plot is the log of the viscosity versus the temperature at a constant shear rate of 1000 sec$^{-1}$, which approximates injection molding conditions (Figure 3-20). The slope of these lines is related to the temperature coefficient of viscosity. The greater the slope, the more sensitive is the viscosity to temperature. This has practical value in molding. For example, if a part in cellulose acetate or nylon (which both have small slopes) was not filling out, raising the temperature would have a minimal effect. Increasing the injection pressure or increasing the gate size would be more helpful. On the contrary an
acrylic or butyrate part would be very sensitive to any increase in melt temperature.

In both instances attention must also be paid to the shear rate (Figure 3-17). Accurate cylinder temperature control is much more important in molding acrylic or butyrate than in molding nylon or acetate. Log viscosity/temperature plots at different shear rate are available from material manufacturers. A compilation of such graphs and other data for acrylics, cellulosics, nylon, polyethylenes, polystyrenes, and vinyls can be found in Ref. 78. It is interesting that the viscosity of most molding materials at shear rates approximating molding conditions are very similar. They range from 0.1 to 1 lb-sec/in.² (7 × 10³ to 7 × 10⁴ P). This is not unexpected, as molders try to mold at a minimum temperature (i.e., viscosity) to fill the mold. This viscosity (flowability) should depend on the mold, gate size, and machine rather than the particular polymer.

Viscosity and Free Volume

We now consider the polymer in terms of free volume. This is another way of describing intermolecular distance, which controls viscosity. A qualitative distinction is made between the volume occupied by the polymer segments and that unoccupied or free. Since the viscosities are very high below the glass transition temperature, it can be assumed that the free volume remains constant until that point is reached. The increase in volume with temperature below $T_g$ is caused by larger vibration of the segments. This increases the volume they occupy (thermal expansion) but does not increase the free volume.

Above $T_g$ Doolittle (88) defined the free volume as the free volume at $T_g$ plus the increase in temperature multiplied by the thermal coefficient of expansion.

$$ f = f_g + (T - T_g) \Delta \alpha \quad T > T_g $$

(3-13)

Where

- $f$ = total free volume
- $f_g$ = free volume at $T_g$
- $T$ = temperature within 100°C of $T_g$ (°K)
- $T_g$ = glass transition temperature (°K)
- $\Delta \alpha$ = thermal coefficient of expansion.

This implies that above the $T_g$, free volume will occur proportional to the increase in temperature and the size of the coefficient of thermal expansion.

Williams, Landel, and Ferry (89) found that above $T_g$, the log of the viscosity varies inversely with the free volume. Therefore, the relationship of the viscosity and free volume at $T_g$ and above can be written as
\[
\ln \left( \frac{\eta}{\eta_g} \right) = \frac{1}{f} - \frac{1}{f_g} \quad T > T_g
\]  
(3-14)

This relation also holds within approximately 100°F above \(T_g\).

Combining (3-13) and (3-14) gives the well-known WLF equation:

\[
\log \left( \frac{\eta}{\eta_g} \right) = 2.303 \frac{1}{f_g + (T - T_g) \Delta \alpha} - \frac{1}{f_g}
\]

\[
\log \left( \frac{\eta}{\eta_g} \right) = \frac{a(T - T_g)}{b + (T - T_g)} \quad T > T_g
\]  
(3-15)

where

\[
a = \frac{1}{2.303 f_g}
\]

\[
b = \frac{f_g}{\Delta \alpha}
\]

Empirically they found that when \(a\) is equal to 17.44 and \(b\) is equal to 51.6, not only the behavior of polymers was satisfied but also other organic and inorganic materials that exhibit a glassy transition point were satisfied. Equation 3-15 can now be written

\[
\log \left( \frac{\eta}{\eta_g} \right) = \frac{17.44 (T - T_g)}{51.6 + (T - T_g)}
\]  
(3-16)

Knowing \(a\) we can now substitute

\[
a = \frac{1}{2.303 f_g} = 17.44
\]

\[
f_g = 0.025 = 2\frac{1}{2}\
\%
\]

This states that the glass transition temperature occurs when the free volume reaches 2\(\frac{1}{2}\)% for all thermoplastics. If the percentage is the same for all plastics and is directly related to viscosity, one would expect that the viscosity of all thermoplastics would be the same at \(T_g\). This is the case with the viscosity (in
poises) being about \(10^{13}\) Pa.

We can now calculate the coefficient of thermal expansion at \(T_g\)

\[
b = \frac{f_g}{\Delta \alpha} = 51.6
\]

\[
\Delta \alpha = \frac{0.025}{51.6} = 4.8 \times 10^{-4} \text{°C}
\]

The observed coefficients of expansion are reasonably close and give support to the theory of free volume. Amorphous PE has a coefficient of \(1.6 \times 10^{-4}\), and PVA \(5 \times 10^{-4}\).

Substituting the viscosity of thermoplastics at \(T_g\) (\(10^{13}\) Pa) into (3-16) gives

\[
\log \eta = 13 - \frac{17.44}{51.6} \frac{(T - T_g)}{(T - T_g)}
\]

\[T_g < T < (T_g + 100\text{°C})\]  

(3-17)

which will permit us to estimate the viscosity at any temperature within 100° above \(T_g\). It can also be used to estimate molding temperatures if \(T_g\) and the viscosity at the shear rate required for molding is known.

Assume the viscosity of a particular polystyrene (\(T_g = 100\text{°C}\)) is \(10^2\) lb-sec/in.\(^2\) at the shear rate required for molding. What is the approximate material temperature required?

\[
10^2 \frac{\text{lb sec}}{\text{in}^2} = 7 \times 10^3 \text{ Pa}
\]

Substituting (3-17)

\[
3.85 = 13 - \frac{17.4}{51.6 + T - 373}
\]

\[T = 342\text{°K} = 319\text{°F}\]

It is therefore evident that knowing the \(T_g\) and the temperature of the material flowing into a mold it is possible to calculate its viscosity at the shear rate of injection. This is the theoretical justification for stating that at a given shear rate, the temperature is an accurate indication of the viscosity. It also forms the basis for feedback techniques in computer controlled equipment.

The WLF equation is an example of using experimental data determined at one temperature (\(T_g\)) for determining data at other temperatures. This is called a temperature superposition. A good example of viscosity — shear rate — temperature superposition is found in Ref. 90. Time is also a variable and time-temperature superpositions are extremely useful in determining engineering
properties of plastic material (91-93).

The WLF equation is remarkably accurate in describing amorphous polymers. From our concept of molecular structure we would expect that crystallinity would change the viscosity, because of the different, ordered, special relationship. This is the case, so that the WLF equation shows small deviations for crystalline polymers, depending on the amount of crystallinity.

CONTROL OF INJECTION MOLDING MACHINES—AUTOMATION

Injection machine control started with fixed logic systems based on limit switches and relays being tripped in a preset sequence. The next step can be termed variable logic where events were programmed to occur in sequence.

Most of the control systems today are based on the event type of control listed above. The latest systems, however, aim at controlling the process rather than the event. For example, rate of fill, pressure, and temperature can be controlled by some sort of analog or analog digital type system, reading either pressure, temperature, position and/or other variables. Cavity pressure is measured in many systems.

Computers may be used in either of these systems to store data or make calculations which alter the machine conditions which control the process and/or the events of one machine or many machines. (Process control must not be confused with production control which means control of downtime, counting parts, and relating production to accounting, inventory, and payroll).

Theoretical Basis for Automatic Control

The theoretical basis for the automatic control of injection molding machines has long been established. They have been discussed previously and are restated here for convenience. Hagan and Poiseuille independently developed the formula for the volumetric flow rate of a Newtonian liquid in a tube at a constant temperature.

\[ Q = \left(\frac{\pi}{8}\right) \left(\frac{R^4}{L}\right) \left(\frac{\Delta P}{\mu}\right) \]  

(3-7)

where  
\[ Q = \text{volumetric flow rate in tube} \]
\[ \mu = \text{viscosity} \]
\[ \Delta P = \text{pressure drop} \]
\[ R = \text{radius of tube} \]
\[ L = \text{length of tube}. \]

For a given mold \( R \) and \( L \) represent the geometry of the runner, gate, and mold and are constant (\( A \)) so that 3-7 can be rewritten
\[ Q = (A) \frac{\Delta P}{\mu} \]  \hspace{1cm} (3-7a)

A characteristic of Newtonian fluids is that the viscosity does not change with the flow rate. Thermoplastics do not exhibit Newtonian flow. Viscosity is dependent on shear rate \((4Q/\pi R^3)\), which is a function of the volumetric flow rate.

For example, a graph of the viscosity versus temperature at different shear rates for an acrylic resin is shown in (3-16). At 425°F, increasing the shear rate from 10 sec\(^{-1}\) to 10,000 sec\(^{-1}\) decreases the viscosity from 0.34 to 0.01 lb/sec/in.\(^2\). The viscosity at 375°F at 1000 sec\(^{-1}\) shear rate is the same as for 460°F at a 100 sec\(^{-1}\) shear rate.

Viscosity is a measure of the resistance to shearing stress. It depends on the composition of the polymer and the intermolecular distances. If a given volume of polymer is heated, its volume increases. Since the number of atoms and the internal atomic dimensions do not change, one must assume that the intermolecular spaces (distance between polymer segments) increase. The farther apart they are, the smaller are the Van der Waals' electrostatic forces. It is thus easier for the polymer segments to slide over each other.

This temperature dependence of viscosity is described by the Arrenhius equation

\[ \eta = A e^{(E/RT)} \] \hspace{1cm} (3-12)

where \( \eta \) = viscosity
\( A \) = constant depending on material
\( R \) = gas constant
\( T \) = °K
\( E \) = activation energy of viscous flow.

The glass transition temperature, \( T_g \), of a polymer, is that small temperature range which marks the change of its amorphous portion between the characteristics of a solid and viscous fluid. The viscosity of polymers at \( T_g \) is about \( 10^{13} \) P. Substituting this into the WLF equation

\[ \log/\eta = 13 - \frac{17.44(T - T_g)}{51.6 + (T - T_g)} \] \hspace{1cm} (3-17)

which describes the viscosity for temperatures up to 100°C above \( T_g \). It is interesting to note that the viscosities of most plastics at their molding temperatures fall into a narrow range of approximately 0.01 to 0.1 lb/sec/in.\(^2\).

Equation 3-7a implies that if the volumetric flow rate and the pressure drop are constant at a given temperature the viscosity will be constant. Equations 3-12 and 3-17 imply that the temperature must be constant to maintain a constant viscosity. Therefore if the polymer is processed with the same \( Q, \Delta P, \)
and \( T \) from shot to shot, it will flow with the same characteristics and produce parts with identical properties. This assumes that the molecular weight and molecular weight distribution do not change substantially. This may not be a valid assumption (94). If molecular weight and molecular weight distribution do not remain constant, the viscosity would have to be checked before molding. Then, automatic molding requires the monitoring of \( Q, \Delta P, \) and \( T \) by measuring the machine and mold conditions which affect them and automatically correcting any deviations from the preset standards.

It is only recently that instrumentation is available to monitor and record temperature, pressure, and speed during molding. Hydraulic servovalves and electrical control equipment are not new. The use of solid state controls has simplified computer control. It should be noted that a "computer" can also be a small relatively inexpensive unit developed just for controlling molding machines.

Instrumentation can now simultaneously record the nozzle pressure: two pressures in the mold; the screw position; the oil pressure behind the injection cylinder; and the oil pressure at the hydraulic motor turning the screw (95); and the screw position: plastic pressures in the cylinder, nozzle, runner, pregate, postgate, and the end of the cavity, and the plastic nozzle temperature (96); and the screw location: plastic cylinder pressure and nozzle pressure; two mold pressures; and the plastic temperature at the nozzle (97).

There is no suitable instrument to measure viscosity continually. The previous discussion shows that with \( Q \) and \( \Delta P \) constant viscosity depends on temperature. Therefore the measurement and control of temperature is substituted for the measurement and control of viscosity. This is the procedure in automatic control.

**Temperature Control**

Conventional temperature control uses a thermocouple to measure the temperature of the steel barrel of the injection cylinder. This is not necessarily or usually the same as the molten plastic.

Good approximations of the plastic temperature are obtained by extruding the plastic into the air and plunging a needle thermocouple into the molten mass. In addition to its inaccuracy, the inherent disruption of the cycle prevents continual repetitive measurements under equilibrium conditions during molding. With increasing need for better data and processing control, thermocouples were inserted in the moving stream of plastic, primarily in the nozzle. This presented a number of technical problems which have been successfully solved (98 to 100, 246). Nozzles with indicating pyrometers and recording charts are now commercially available.
Plastic Pressure During Injection Molding

On almost all machines the only injection pressure measurement of the material during the molding cycle is of the hydraulic oil behind the injection cylinder. In single stage plunger machines it is an extremely poor indication of the pressure on the plastic in the nozzle and mold. In two stage machines and the reciprocating screws the correlation is much better, although far from accurate.

Recently pressure transducers have been developed that can withstand the temperatures and pressures in the nozzle and the mold (101 to 102\textsuperscript{c}). Pressure transducers that fit behind knockout pins, and the appropriate amplification and recording charts, are commercially available. They measure the plastic pressure in the mold. In the event the transducer is not needed, a blank piece of steel can be rapidly interchanged with the sensing head. Thus the injection pressure on the material can be measured in the cylinder (nozzle) and the mold.

For a given machine under given conditions, the volume and the pressure of the oil delivered to the back of the injection ram controls the injection pressure in the cylinder and mold. A secondary factor is the plastic leakage past the injection plunger. This will be reasonably constant for a given material in a given temperature and pressure range. There are distinct pressure losses from the nozzle to the mold. For a given mold, the major parameters are (a) initial temperature of the material, (b) mold temperature, (c) resistance to flow, and (d) time.

A 4-oz plunger machine molded ABS in a 7\textfrac{1}{32} by 3\textfrac{1}{16} in. spiral mold. The material temperature was 445\textdegree{}F and the mold water temperature 150\textdegree{}F. The oil hydraulic pressure was 12,200 psi which corresponded to a pressure of 9000 psi on the plastic entering the mold (25\% pressure loss). Pressure measurements were made after 20 sec at varying distances from the gate (103).

<table>
<thead>
<tr>
<th>Distance from Gate</th>
<th>Pressure on the Plastic Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>in.</td>
<td>psi</td>
</tr>
<tr>
<td>0</td>
<td>9000</td>
</tr>
<tr>
<td>2\textfrac{1}{4}</td>
<td>7300</td>
</tr>
<tr>
<td>7</td>
<td>5000</td>
</tr>
</tbody>
</table>

As this discussion is directed toward controls, it is assumed that the condition of the hydraulic system and injection cylinder are within the machine design.

Mold Filling

It is relatively easy to describe qualitatively mold filling. The initial fill is at very low pressure. The rate of fill depends on the machine settings and the hydraulic oil flow rate. When the mold is filled there is a rapid build-up of pressure. The constant $A$ (Eq. 3-7a) represents the gate dimensions, $(\pi/8) (R^4/L)$. While the