Practical Rheology Electronic Handbook

Written by:

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Edited, Revised and Updated by:

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DrD Polymer Consulting Services

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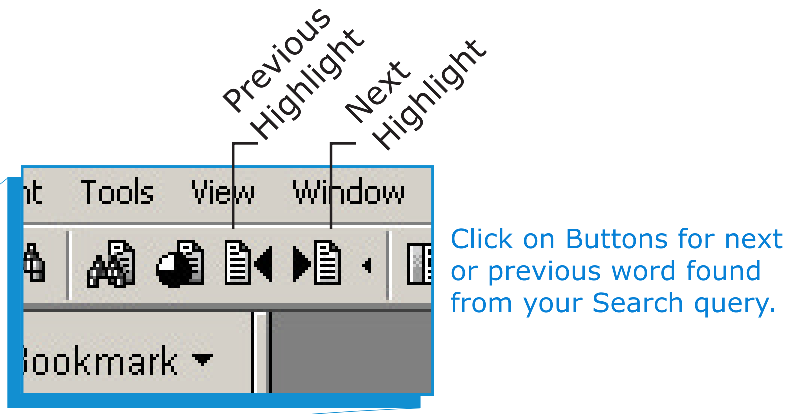

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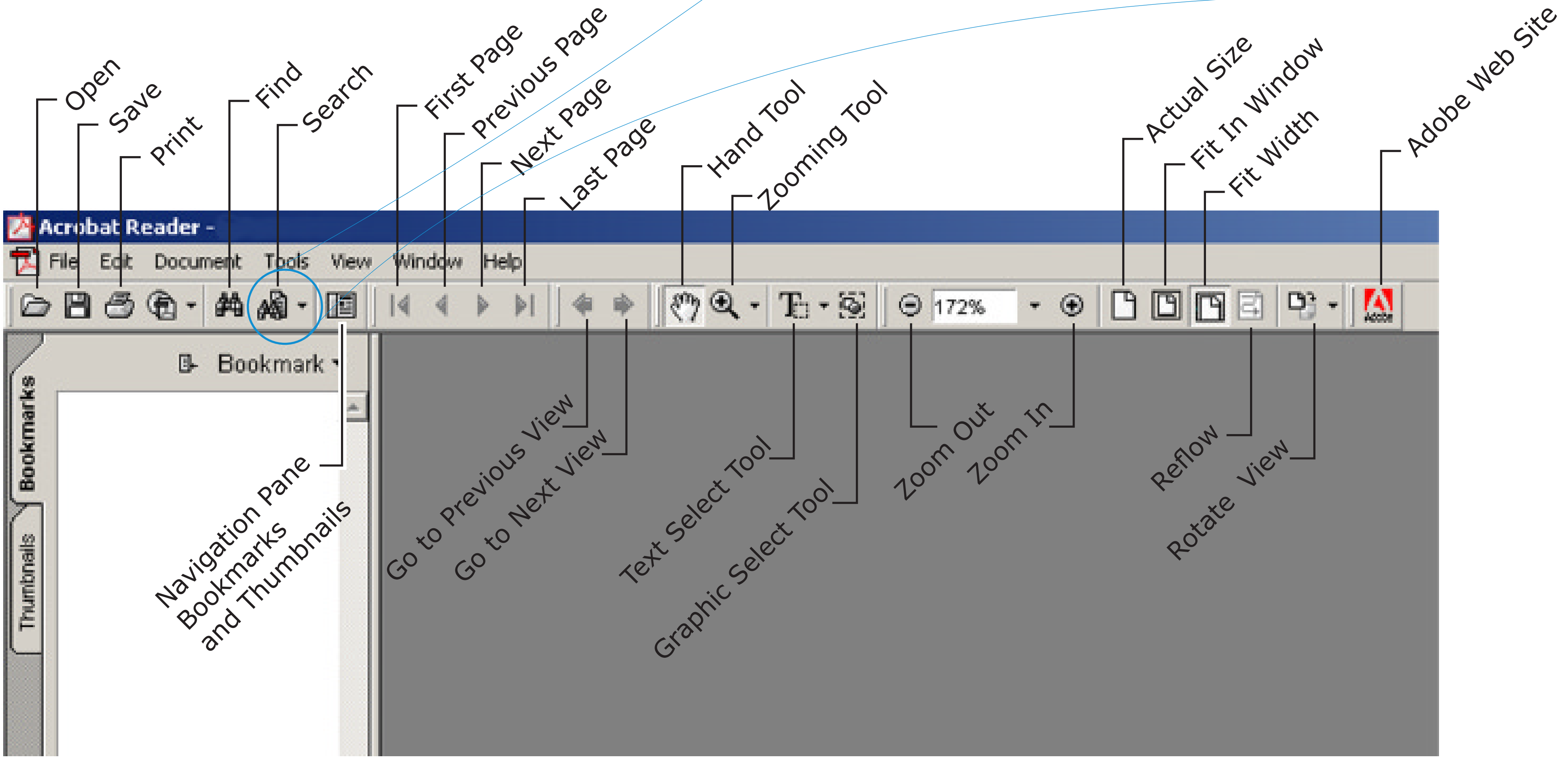

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Section 1

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Dynisco
Polymer Test

Practical Rheology Handbook

TABLE OF CONTENTS

Title **Page**

FIGURES

Title **Page**

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1. PLASTICS AND POLYMERS

Over the past 50 years the use of plastics materials throughout the world has increased dramatically and now stands at approximately 100 billion pounds.

Polymers.

Most commercial plastics, also known as resins in North America, are composed of polymers, with which modifying or stabilizing additives have been compounded. Polymer molecules are generally based on the element carbon and are manufactured from simple, oil-based raw materials. Small molecules, which are the starting materials for polymers, are called monomers. These small molecules are combined, by a process known as polymerization, to form very large molecules or polymers. The term polymer arises from the fact that the final product consists of many, identical, repeating molecule units. Because the final size (or length) of these molecules and thus their molecular weight, or mass, is generally very large, the polymer may also be referred to as a 'high polymer' or, as a 'macromolecule'. All plastics are polymers, but not all polymers are plastics. Many natural products, such as cellulose, are polymers, but they cannot be processed like a commercial plastic material unless they are modified from their natural form.

Types Of Plastics Material

A plastic material is defined as a compound of polymer plus additives, which is capable of being shaped or molded, into a useful product, under conditions of moderate temperature and pressure. Generally, plastics are distinguished from rubbers or elastomers, by their higher stiffness/modulus and a lack of reversible elasticity. There are two main categories of plastic, thermoplastics and thermosetting plastics (thermosets). Thermoplastic products, for example injection molding or extrusion resins, may be repeatedly softened, melted, and reshaped (or recycled), whereas thermoset products cannot. In terms of tonnage, thermoplastics are by far the more important. When the polymer in the plastic is based on one monomer it is known as a 'homopolymer'. When the polymer used is based on two or more monomers it is known as a 'copolymer.'

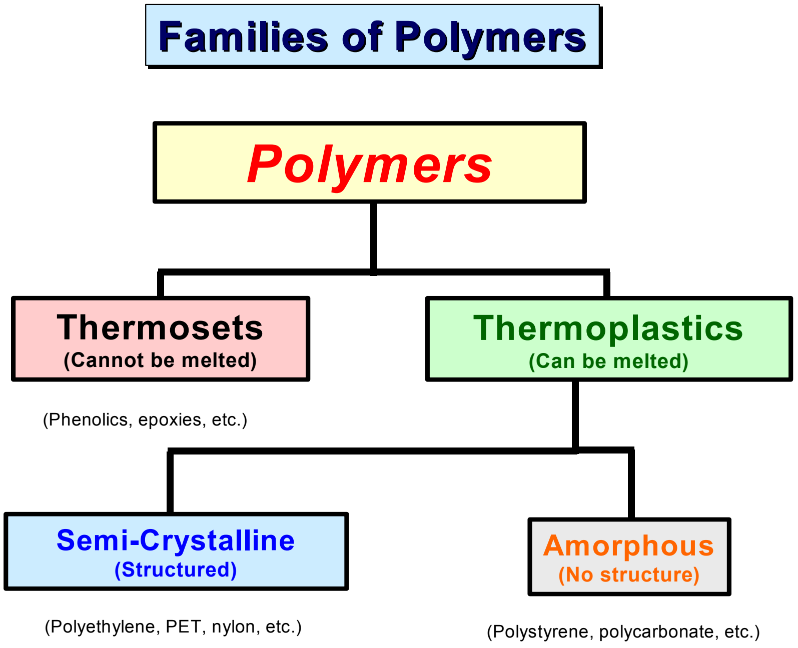


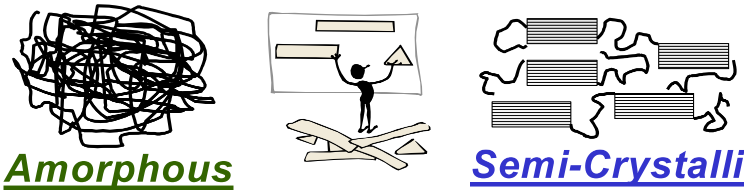
Figure 1.

Amorphous And Crystalline.

Thermoplastic materials may be further divided into two main categories, amorphous and semi-crystalline. An amorphous thermoplastic material has no uniform molecular structure and is usually a hard, clear, rigid material with low shrinkage, such as polystyrene. A crystalline polymer has an organized ("crystal-like") structure, but also contains amorphous material and is generally referred to as a semi-crystalline thermoplastic material. Such plastics are usually tougher and less brittle than amorphous thermoplastics and may have a higher heat distortion temperature. Such plastics are also translucent, or opaque, have a high shrinkage and a high specific heat. The best-known example of a semi-crystalline, thermoplastic material is polyethylene. (Note: Clear polystyrene is sometimes called as "crystal polystyrene". Polystyrene is an amorphous polymer, however, so this name refers to the fact that it is "crystal clear" and not a crystalline thermoplastic.) Both amorphous and semi-crystalline thermoplastics are commonly tested by rheometry and are widely used in rheological studies.

2. NAMES AND ABBREVIATIONS FOR THERMOPLASTICS

Of the two major types of plastics, thermoplastics and thermosets, thermoplastics are by far the ones most studied in rheology, therefore, this section will focus only on the major types of thermoplastic material.



Polymer Structure

Solid State Structure of *Thermoplastics*

Amorphous

No polymer structure.

Examples: Polystyrene
Polycarbonate
PMMA

Semi-Crystalline

Contains both crystalline (ordered)and amorphous polymer.

Examples: Polyethylene
Polypropylene
PET
Polyamides (nylon)

Figure 2.

Common Names.

Most thermoplastics begin with ‘poly’, which means ‘many’ followed by the name for the monomer from which the plastic is derived. (i.e., the name is source-based.) As the result of this practice we get names such as polystyrene and polyethylene for homopolymers. When the plastic material has more than one word in the name, parentheses (or brackets) may be put around the words so that we get poly (vinyl chloride). This practice is, however, not universal and one may also see the same term without the brackets i.e. polyvinyl chloride. Since source-based nomenclature is not universally used, so names such as ‘acetals’ and ‘cellulosics’ also may be encountered. To add to the confusion, many plastics are known by more than one name. For example, acetals may be known as polyformaldehyde or polyoxy-methylene. When this is so, then the alternative name(s) should be listed. Some common names and alternative names of thermoplastics are given in **Table 2**.

Abbreviations

Because of the complex, chemical names used to describe polymers, they are frequently referred to by abbreviations. Such abbreviations take the form of a short string of capital letters, where each capital letter refers to a part of the common name. If the plastic material begins with ‘poly’ then the first letter is P and the other letter(s) are derived from the monomer unit. Names such as polystyrene and polyethylene are thus shortened to PS and PE respectively (See **Table 2**.). Copolymers are often referred to by means of initials, which represent the monomers used i.e. without a “P” for “poly”. For example, the copolymer made from styrene and acrylonitrile is referred to as styrene acrylonitrile copolymer or as SAN. When mixtures are made from two or more polymers (blends or alloys), they are commonly represented by the abbreviations used for the individual materials, but each abbreviation is separated by an oblique stroke, for example, SAN/EVA.

Some Relevant Standards

Many standards organizations {for example, the American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO)} issue standards that specify what letters shall be used in naming plastics. See ASTM standard D1600-86 (that is standard number D1600 revised/published in 1986) and called ‘Standard abbreviations of terms related to plastics’.

Standard And Non Standard Abbreviations

It must be appreciated that both standard and non-standard abbreviations are used. Often materials appear and a name becomes used before a standards committee has issued its suggestion. By this time a ‘non standard’ abbreviation may become established or more than one abbreviation may ‘appear’ for the same material. For example, the thermoplastic elastomer known as polyether ester elastomer may be referred to as PEEL or, as COPE (from copolyester) or, as TEEE (thermoplastic elastomer ether ester) or, as YBPO (an American suggestion). Some abbreviations are shown in **Table 3**.

3. THERMOPLASTIC MATERIALS

A thermoplastic material is one, which softens (or melts) on heating and hardens (or freezes) on cooling. This heating and cooling process can be repeated many times. Approximately 80% of all plastics used throughout the world are thermoplastics. This important group of materials can be divided into four groups (each of which may contain amorphous or crystalline materials):

1. Commodity thermoplastics
2. Engineering thermoplastics
3. Thermoplastic elastomers or rubbers
4. Blends or alloys

Commodity Materials.

This group of plastics covers materials such as polypropylene, polyvinyl chloride, polystyrene and polyethylene (PP, PVC, PS and PE). Each of these materials includes a number of sub-divisions, for example PP includes homopolymers and copolymers, PVC covers rigid and plasticized, PS refers to general purpose PS and toughened PS (TPS, or IPS, or HIPS) and PE includes LDPE, LLDPE and HDPE. The importance of commodity thermoplastics cannot be over-emphasized as approximately 80% of all plastics used fall into this category.

Engineering Thermoplastics.

Engineering plastics are a group of polymers that offer a combination of properties including superior strength, stiffness, toughness and resistance to wear, resistance to chemical attack and heat resistance. The major materials in this group include the polyamides (nylons), acetals, polycarbonates, thermoplastic polyesters and modified polyphenylene oxide (also known as modified polyphenylene ether or PPE).

Thermoplastic Elastomers.

Materials referred to as ‘thermoplastic elastomers’ (TPE) or, as ‘thermoplastic rubbers’ (TPR) are a comparatively new group of materials that have become significant in terms of both tonnage and value. This is because they are creating new markets as well as replacing both plastics and traditional rubbers in some of their applications. They exhibit some of the properties associated with traditional or “vulcanized” rubbers, but they also can be processed with the speed and ease of thermoplastics and can be re-processed.

Blends.

Because of their ease of production, using twin-screw compounding extruders, there are many blends of plastics or blends of plastics with elastomers. Any of these materials may also be modified with fillers or glass fiber. Reasons for blending materials include the generation of “unusual” plastics materials, extending the performance of existing plastics quickly and cheaply and the recycling of plastic materials.

Property Guidelines.

Because of the large number of grades of plastics available, properties quoted in the literature should only be used as a general guideline. The final properties of any plastic material may be dramatically changed by the processing conditions employed and/or by the use of additives. With many materials, variations of basic formulas are available using additives to provide, improved heat resistance, or weatherability. Some formulations offer improved impact strength while others, which contain fillers, are used where, for example, moldings are required to possess tensile strength and/or a high heat distortion temperature. Processing and performance modifiers may also be added. These include lubricants, antistatic additives, and nucleating agents. Such additives may be included as part of a color masterbatch.

Choice Of Grade

Once a type of plastic material has been selected for a particular application, then the melt viscosity or melt flow rate (MFR or MFI) may be used to further define the grade to be used. If, for example, the components are to be subjected to severe mechanical stresses, a high viscosity grade may be the best choice. This is because the high viscosity grades usually have the highest molecular weight and frequently exhibit superior mechanical properties. (See the section on High Shear Rate Rheometers.) In some cases, however, this advice should not be followed. For example, the case where unacceptable levels of frozen-in strains in the molded part may result. An easy flow grade would then be preferred. An example of this would be when filling thin injection molded wall sections or where very smooth surfaces are specified.

Feed Forms.

Most processing equipment, for example, injection molding machines or extruders, can be fed with plastic resins or compounds in various forms. The feed may be fine powder, regranulated material or pellets. In general, higher output rates are obtained if uniformly sized pellets are used. It should be emphasized that to obtain a consistent output a consistent feed must be used.

4. POLYOLEFINS

Probably the best-known example of a semi-crystalline, thermoplastic material is polyethylene. We will provide a short discussion of this material here. This type of material is commonly tested by rheometry and is also widely used in rheology studies.

Polyolefin Materials.

Polyethylene (PE) is a member of the family of plastics called polyolefins (PO). Both homopolymer and copolymer polyolefins are available. Members of the polyolefin family include:

- Very low density polyethylene or VLDPE
- Low density polyethylene or LDPE
- Linear low density polyethylene or LLDPE
- High density polyethylene or HDPE
- Metallocene catalyzed polyethylenes MCPE
- Polypropylene or PP.

Polyethylene.

Polyethylene is made from a hydrocarbon gas called ethylene by the process of polymerization. Ethylene is a simple, low molecular weight (mass) material, which has a molecular weight of 28. When the gaseous ethylene (sometimes called ethene) molecules join together (polymerize) to produce a long chain structure, the molecular size and weight increase dramatically. If ten thousand ethylene molecules are joined together, to make (for example) a film grade of PE, the average molecular weight will be 280,000 atomic units (au). As a result of the random nature of the polymerization reaction, some of the chains will be a different size. Some will be larger than the average value and some will be smaller. Some, for example, may only contain 20 ethylene units, while others may contain a hundred thousand ethylene units. This results in a statistical distribution of weights (sizes) of the molecules, which is called the molecular weight distribution. (MWD) Just how the ethylene units are joined together is also important. For example, when two ethylene units add onto another growing chain at the same point a branching in the chain will be the result. This means that polyethylene is not necessarily a simple long chain material, but one that may also contain a large number of short and long side branches. These branches affect how the material flows and how the molecules will pack together (crystallize) on cooling.

Material Properties.

Each of the many polyethylene plastic materials available is really a family of materials that may differ in molecular weight, molecular weight distribution and chain branching. Changing anyone of these factors can dramatically change the properties of the material. What this means is that it is possible to get a wide range of properties for any material group. The following table shows how changes in melt flow rate (MFR – a measure of molecular weight), density (a measure of molecular packing), and molecular weight distribution (MWD) affect the properties of HDPE.

Effect Of Structural Changes For HDPE

The effects of changes in molecular weight, density and molecular weight distribution (MWD) are shown in the table below.

Types Of Polyethylene

When the density of PE is low (0.910 to 0.925g/cm^3) it is sometimes referred to as Type I. When the density is medium (0.926 to 0.94g/cm^3) the material is sometimes called Type II. HDPE with a density of 0.940 to 0.959g/cm^3 is sometimes known as Type III. If the density is very high (>0.959g/cm^3) then the material is known as Type IV. The grades of HDPE that have a density below 0.96, are produced by using a second monomer at low levels (<1%). Strictly speaking they are, therefore, copolymers of PE with another olefin. (For example, with butene –1 or, with hexene –1.) The use of the second monomer reduces the density by introducing short side chain branches that interrupt the crystalline structure. Such materials may be called MDPE. HDPE/MDPE copolymers account for approximately 55% of all plastics used in blow molding.

Property	Effect of Increasing:		
	MFR	Density	Breadth of MWD
Pseudoplasticity			Increases
Tensile strength at yield		Increases	
Tensile strength at break.	Decreases	Increases	
Elongation at break	Decreases	Decreases	
Impact strength	Decreases	Slight decrease	Decreases
Modulus		Increases	
Transparency		Decreases	
Long term load bearing		Increases	
ESC resistance	Decreases	Decreases	
Softening temperature		Increases	
Melt strength	Decreases		Increases
Melt elasticity	Decreases		Increases
Melt fracture tendency	Decreases		Decreases
Gloss			Decreases

PROPERTY DIFFERENCES FOR POLYETHYLENES

(Compared to the one left blank.)

Property	Polymer Density in g/cm^3		
	Low (Type I)	Medium (Type II)	High (Type III)
Tensile strength at rupture	Highest	Higher	
Elongation at break	Highest	Higher	
Impact strength	Highest	Higher	
Modulus	Highest	Higher	
Transparancy	Highest	Higher	
Long term load bearing		Higher	Highest
ESC resistance	Highest	Higher	
Softening temperature		Higher	Highest
Melt strength		Higher	Highest
Gloss	Highest	Higher	
Resistance to shrinkage	Highest	Higher	
Resistance to warpage	Highest	Higher	
Resistance to brittleness at low temperature	Highest	Higher	
Resistance to grease and oil absorption		Higher	Highest
Impermiability to gases and liquids		Higher	Highest
Freedom from film haze		Highest	Higher
Molding cycle times		Higher	Highest

5. ADDITIVES USED WITH PLASTICS.

All plastics consist of one or more polymers plus additives. Essentially no polymers are sold without some form of additive compounded into them. It is generally understood in the thermoplastics industry that the materials used contain small amounts of additives. Most thermoplastic materials cannot be commercially used without the addition of additives such as heat stabilizers and lubricants. The properties of the polymers used in plastic products may be dramatically changed by the processing conditions employed and by the use of additives. Variations of basic material formulas are available with additives to provide, for example, improved heat resistance or weatherability. Some formulations offer improved impact strength. Others, which contain fillers, are used where the products require greater modulus, flexural strength and heat distortion temperature. Processing and performance modifiers, such as antistatic and nucleating agents, may also be added. Frequently the additives form part of a color masterbatch.

Masterbatches

Processing equipment, such as injection molding machines, are often fed with a mixture of a plastic material and a masterbatch. A masterbatch is a mixture of one or more additives in a base polymer material. The use of such a mixture often produces significant cost savings, as a compounding step may be eliminated. Most commonly, masterbatches are only used to color a finished product, however, they may also contain other additives as well. The use of a masterbatch can sometimes cause problems. The most frequent problem is one of color shade differences between different machines. Another is separation of the masterbatch components from the plastic in the hopper, which may lead to variable properties in the molded parts.

Materials Modifications.

The use of the term ‘materials modification’ usually means the addition of larger amounts of additives. Such additives may include elastomers, flame-retardants and fillers.

Fillers And Reinforcements

Materials modification, such as with fibers or with fillers, is extensively used with engineering thermoplastics to obtain a desirable combination of properties. For example, the use of fibrous fillers, such as glass fiber, usually improves the modulus. These modifications are seldom produced in order to save money, since a molding made from a filled compound, is often the same price as one made from the unfilled plastic material. This arises from the high density of most fillers and high compounding costs. By the use of such fillers it is possible to lift a plastics material from one category to another. In the case of the commodity resin polypropylene, it can be changed into an engineering plastic by materials enhancement.

Impact Modification (Elastomer Addition)

Strictly speaking an elastomer or rubber that imparts added toughness when used with a thermoplastic material is called an impact modifier. These additives are extensively used in engineering thermoplastics for applications where high impact strength is required (for example, automotive bumpers). The impact strength of commodity resins may also be upgraded by the addition of impact modifiers. When rubber is added to styrene, and the mixture polymerized, a thermoplastic material called high impact polystyrene (HIPS or, TPS, or, IPS) is produced. Rubbers are added to other materials, such as polypropylene (PP), in order to improve the low temperature impact strength. What is required for these applications is a material, which can be processed like a thermoplastic and yet, has many of the properties of a cross-linked material. This is one reason for the current interest in polymer alloying and thermoplastic elastomers. One approach to making such thermoplastic materials is to disperse cross-linked rubber particles in a thermoplastic matrix. An example of this is Acrylonitrile Butadiene Styrene (ABS) copolymer, where butadiene rubber us used to improve the impact properties to SAN copolymer and produce a widely used plastic material. The impact strength of such UPVC bottles is improved by the use of methacrylate-butadiene-styrene polymers (MBS). These thermoplastic rubber materials, when used at approximately 10% addition, still give transparent bottles. However, because they are comparatively expensive, alternative cheaper solutions are now commonly used.

Flame Retardants.

Since they are based on carbon, most will polymers burn. It is natural for a carbon-based material to react (burn) with atmospheric oxygen to form carbon monoxide and carbon dioxide. Halogen atoms such as chlorine and bromine, however, form compounds that are naturally fire or flame retarding. In the case of PVC, the halogen atom is “built-in” the plastic material molecular structure. With other plastics, however, the halogen must be added in the form of compounds such as tribromotoluene. The efficiency of these compounds is often improved by the use of antimony trioxide. Unfortunately, the use of halogens can produce toxic smoke and fumes, so other flame-retardants may be preferred. One such material is aluminum trihydrate. The large amounts of this material required, however, can change the properties of the plastic material (for example, the flow properties). It may also introduce processing problems, because of aluminum trihydrate decomposition at processing temperatures. Phosphorous based compounds and some silicones are becoming more popular for use as flame-retardants.

Plasticizers.

Plasticizers, which are usually liquids, were first added to plastic materials, such as cellulosics and PVC, in order to allow them to be processed at temperatures below that at which they thermally degrade. Most commercial plasticizers are phthalate compound that include dioctyl phthalate (DOP) and di-iso-octyl phthalate (DIOP). By adding such materials to PVC, plasticized PVC (PPVC) is produced. This material flows much more easily than the unplasticized material (UPVC) and is softer and more flexible. The term "primary plasticizer" indicates that a compound is more compatible with the basic plastic material than a "secondary plasticizer".

Softeners And Extenders

The term "softener" is used by the rubber industry for products such as hydrocarbon oils, which are used as additives for hydrocarbon rubbers/elastomers. They produce soft compounds, which are relatively easy flowing. Extenders, sometimes referred to as "liquid fillers", are commonly associated with PPVC, where their use reduces compound costs. The chlorinated waxes used in this application also act as flame-retardants.

Anti-Aging Additives. (Anti-Oxidants, UV- Stabilizers, Etc.)

These additives are widely used with polymeric materials since heat and light will often cause their properties to change in normal use or during processing. Heat and light cause chemical reactions, including oxidation, ozone attack, dehydrochlorination and ultra-violet (UV) attack, to occur within the material, or on its surface. Which type of chemical attack occurs depends, on the type of polymer and the particular circumstances. As polyolefins (PO) readily degrade by oxidation, antioxidants are widely used in polyethylene (PE) and polypropylene (PP). PVC degrades more readily by dehydrochlorination and additives, which restrict this type of attack, are more widely used in PVC compounds. Ultra-violet (UV) attack is common with most polymeric materials. Thus UV stabilizers are usually found in products that are to be exposed to sunlight or used outdoors. Aging by ozone is peculiar to the rubbery class of materials and is combated and controlled by the use of anti-ozonants.

Lubricants.

Lubricants are usually added to polymers in order to prevent the polymer from adhering to processing equipment or to ease the flow of the polymer compound. Stearic acid is an example of a lubricant that is added to PVC in order to prevent the compound sticking to the processing equipment. Such a lubricant is called an "external lubricant" as it comes to the surface of the molten polymer. An "internal lubricant" is one that is primarily used to increase flow. An example is glyceryl monostearate, which is used with UPVC. With some plastics materials, lubricants are added in order to reduce friction in use. For example, the addition of 2% graphite will reduce the friction between two molded gears. Silicone oils may be used for the same purpose.

Colorants.

Most plastic components are colored by techniques in which the coloring system is dispersed throughout the polymer. (It is possible, however, to color only the skin in order to save on colorant and compounding costs. This may be done, for example, by sandwich molding and extrusion.) Generally speaking, colorants are divided into two major types: dyes and pigments. Dyes are soluble, generally organic, coloring systems that produce transparent colors. Pigments are dispersed insoluble solids that produce opaque colors. Pigments are the most widely used. The most widely used colors are white (TiO_2) and black (carbon black).

Blowing Agents.

A great many polymeric products are cellular materials filled with gas cells. Either a gas (usually nitrogen) is added during processing or a chemical compound (a blowing agent) is used to generate the gas when required. A widely used class of blowing agents is the azo compounds. These organic materials can be structured so they decompose over a fairly narrow temperature range at the melt processing temperatures.

Cross-Linking Additives.

Many polymers can be cross-linked (cured, vulcanized or set) after shaping (usually during processing), so that either a vulcanized rubber (an elastomer) or a thermosetting plastic material results. Two well-known cross-linking systems are sulfur (used with diene rubbers) and peroxides (used with some rubbers and polyolefins). Accelerators and activators are often associated with cross-linking systems. Accelerators, as the name implies, speed up the cross-linking reaction and may, in turn, only function efficiently in the presence of an activator.

Degradants.

Once a plastic part has fulfilled the function required, it often becomes a nuisance and the once valuable component becomes classed as litter. This problem is most serious for plastic materials used in packaging. One way of overcoming this problem is make the plastic material subject to decomposition, or degradation. This may be done by incorporating a filler, such as starch, into the plastic material. Another route is to use a biodegradable plastic material such as polyhydroxybutyrate (PHB), either on its own, or in combination with other plastics. PHB is produced by bacterial action on glucose and is a semi-crystalline, thermoplastic material similar, in some ways, to polypropylene (PP).

Reclaimed Material.

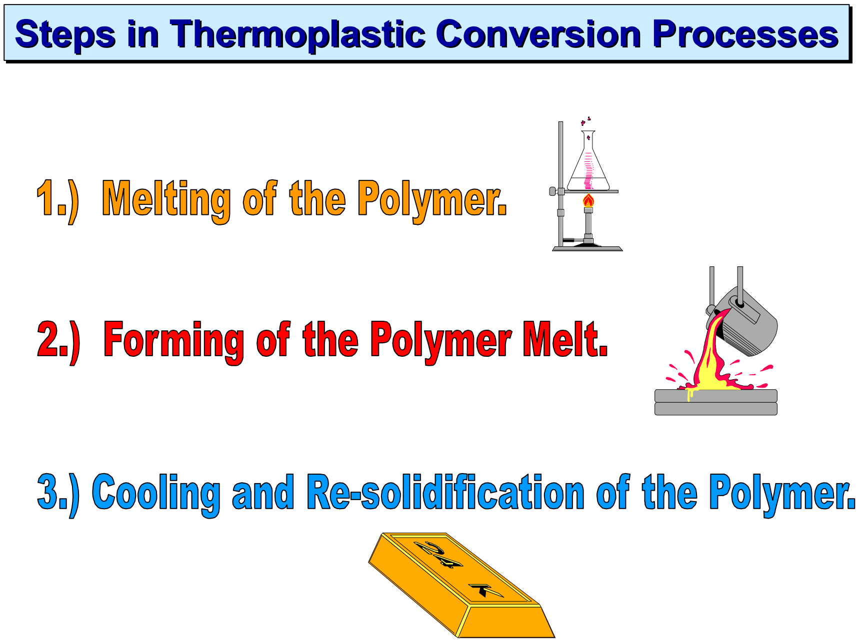
The most common additive used with thermoplastic materials, is reclaimed (or recycled) material. This is usually added to reduce component costs. It is most important that this additive (as with any additive) is added at a consistent, pre-selected ratio so that the flow properties of the resultant blend, for example, remain constant. It is also important to ensure that the reclaimed material is clean, dry and of regular particle size.

Good Dispersion.

To get the best results from additives they must be very well dispersed within the basic polymeric material. This is why melt mixing is very important to the polymer industry. Such melt mixing is done at relatively low temperatures in order to keep the polymer viscosity at a high value and so increase the shear input, which improves dispersion.

6. MELT PROCESSES AND THERMOPLASTIC BEHAVIOR.

Most processes used to shape thermoplastics are melt processes. That is, the plastic material is heated until it becomes molten; next it is shaped and then cooled to set the shape. There are several ways of obtaining a desired shape and these are summarized in the following section. It must always be remembered that plastic processing equipment can be very dangerous, unless used correctly, and must therefore only be used by people who know what they are doing.



Steps in Thermoplastic Conversion Processes

1.) Melting of the Polymer.

2.) Forming of the Polymer Melt.

3.) Cooling and Re-solidification of the Polymer.

Figure 3.

SUMMARY OF SHAPING METHODS

1. Deformation of a polymer melt – either a thermoplastic or a thermosetting melt. Processes using this approach include blow molding, calendaring, extrusion and injection molding.
2. Deformation of a polymer in the rubbery state. This approach is used in sheet shaping techniques such as thermoforming and the shaping of acrylic sheet.
3. Deformation of a polymer solution either by spreading or by extrusion to make films and fibers.
4. Deformation of a polymer suspension. This approach is used in rubber latex technology and in PVC plastisol technology.
5. Deformation of a low molecular weight polymer. This approach is used in the manufacture of acrylic sheet and in the preparation of glass reinforced product.
6. Machining operations.

In terms of tonnage, those processes involving the deformation of a thermoplastic polymer melt are by far the most important. These include extrusion and injection molding, which are the most common.

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Section 2

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TABLE OF CONTENTS

FIGURES

7. MELT PROCESSING OF THERMOPLASTICS.

The most important conversion methods used by the thermoplastics processing industry are extrusion and injection molding. Whether extrusion or injection molding is being used, there are certain factors that should be considered before a thermoplastics material is processed. These factors include the hygroscopic behavior of the material (whether it picks up water), the granule characteristics, the thermal properties (such as heat transfer and the thermal stability), the flow properties, crystallization behavior, shrinkage, and molecular orientation.

Hygroscopic Behavior.

If a polymer compound contains water, or another material with a low boiling point, then the heat needed for processing can raise its temperature above the boiling point. Visible bubbles will then form within the thermoplastic material when the pressure falls, such as when it emerges from the die of an extruder. Generally speaking, the higher the processing temperatures, the lower is the amount of water that can be tolerated. This is because the higher temperatures will generate a larger volume of steam from the same quantity of water. Usually commodity thermoplastics do not suffer from water-related problems to the same extent as the engineering thermoplastics. Some of these materials, for example PET and Nylon absorb water i.e. they are hygroscopic and must be carefully dried before processing. Water may also be introduced into the system by additives, which contain excessive water.

Granule Characteristics.

Processes such as extrusion, blow molding and injection molding often use, as the feed, material in granular form. If the material is available in more than one feed form, then feeding problems will probably be encountered if a mixture of feed forms is used. In terms of feeding efficiency, spherical granules (of approximately 3mm(0.125in) diameter) are the most efficient and fine powder is usually the worst. Regranulated material, because it may contain a range of particle sizes, can be almost as bad. Cube cut granules are better and lace cut granules are better still (lace cut granules are made by chopping strands with a circular cross-section). Because of the feeding differences of the various granulates, the machines must be fed with a consistent raw material mix. This particularly applies to masterbatch mixes (see the section on Additives used with plastics).

Thermal Properties And Heat Input.

Thermoplastic materials require large heat inputs to raise their temperatures to those required for melt processing. They also differ enormously in the amount of heat energy that is needed to bring them up to processing temperatures. These differences are not simply due to the different processing temperatures required, but also to the fact that different plastics materials have different specific heats. (The amount of heat required to raise the temperature of a specific weight of a material by 1^{o} C or F.) Different materials require different amounts of heat to raise their temperature a fixed number of degrees. For example, when melt processing a semi-crystalline, thermoplastic material heat must be supplied to melt the crystal structures. This extra heat input is not needed in the case of an amorphous resin. Both types of material will, however, require a large amount of heat to be put into the material quickly. This causes problems since plastics are poor conductors of heat and can have limited thermal stability at the processing temperatures employed. As plastic materials are poor thermal conductors, the removal of the large amount of heat required to solidify a part also poses severe problems, if high-speed production is to be maintained. Table 3 shows heat removal figures for several different thermoplastic materials.

Thermal Stability.

Thermoplastic materials differ widely in their thermal stability. For example, UPVC is very unstable even when stabilized and can only be held at processing temperatures (175ºC/347ºF) for a few minutes. (Unstabilized PVC will show some degradation in boiling water!) On the other hand, polysulfones require melt temperatures in the region of 400ºC/752ºF, where they are stable. The thermal stability of a material is governed not only by the temperature, but the residence time at that temperature, the atmosphere surrounding the material (oxygen or inert) and the materials in contact with the plastics material. For example, copper causes rapid decomposition, or degradation, of polypropylene (PP). Copper cleaning pads should, therefore, not be used to clean rheological equipment used to test this material. In general, the decomposition products from plastics should be regarded as being potentially harmful and any gases evolved should be properly vented.

Flow Properties.

Because of thermal stability problems, the processing temperatures employed for thermoplastics are frequently limited to relatively low values. This means, in turn, that melt viscosities are generally high. Process melt viscosities are not uniform and differ from one material to another and from one grade of the same material to another grade. While these differences may be due to intrinsic differences in the nature of the polymers, they may also be affected by temperature and by molecular weight. In general, viscosity decreases with an increase in temperature and as the molecular weight is reduced. Small variations of temperature, molecular weight, and molecular weight distribution can cause large differences to arise in melt viscosity. This, in turn, affects output and quality in both extrusion and injection molding. For this reason, strict control over both the processing conditions, and the material fed to the machine, must be employed. This is why there is such an interest in flow testing of thermoplastic materials. (It is also worth noting that since the viscosity goes down with an increase in output rate, through a given die, the energy used per unit output, tends to go down as the extrusion rate is increased.)

Thermal Properties And Cooling.

Thermoplastic materials require large heat inputs to raise their temperatures to those required for melt processing. As these materials are good thermal insulators, the removal of the large amounts of heat poses severe problems for high-speed production. Table 3 shows some heat removal data for different thermoplastic materials. Variations in the cooling rate may have a pronounced effect on the crystalline morphology of the product and on factors such as molecular orientation and shrinkage.

Crystallization And Shrinkage

Generally all polymeric products shrink on being cooled from processing temperatures. The shrinkage of an amorphous thermoplastic material, such as polystyrene (PS), is much less than that for a semi-crystalline thermoplastic such as high-density polyethylene (HDPE). (For PS the amount of shrinkage may be 0.6%, whereas for HDPE it may reach 4%.) This is because when polymer molecules crystallize they tend to pack more efficiently than they do in the disorganized amorphous state. With thick-sectioned moldings and extrusions, the cooling rates will differ from the outside edges to the center. This results in differences in the degree of crystallinity throughout the part. This, in turn, explains why a shrinkage range is always quoted for each material. This range is always higher for a semi-crystalline thermoplastic material than for an amorphous one. For example, the shrinkage of PS is listed as 0.02 to 0.08%, while that of HDPE is 1.5 to 4%.

Molecular Orientation.

Polymer melts are extensively deformed during melt processing. The hot material is then cooled extremely fast to achieve the high output rates demanded. The shearing processes result in the molecules taking up a deformed, or oriented, shape and the rapid cooling results in this deformed shape being frozen-in the product. This orientation, which results in the product having different properties in different directions, is known as anisotropy. In many cases such orientation is undesirable, however, in some cases, orientation in introduced or enhanced, to improve the properties of product. The process of deliberately orienting extrudates is used in the manufacture of fibrillated tape, many types of fibers, and in the extrusion blow molding of bottles.

8. FLOW TESTS

Because most methods of shaping plastics are melt processes, such as injection molding and extrusion, the measurement of melt flow properties is extremely important. A large number of tests have been devised to measure such properties, but, in general, they may be grouped into low shear rate tests and high shear rate tests.

Flow Rate.

The most commonly used test is usually referred to as the melt flow rate (MFR) or melt flow index (MFI). This test is popular, particularly for polyolefins, since it is easy to do and understand and the instrumentation is inexpensive. A heated plastic material (for example, PE) is forced through a circular die of a certain size, at a specified temperature, by a specified force, produced by an accurate weight. The amount of PE extruded in 10 minutes is called the MFR and the results are reported as, for example, MFR (190, 2.16) = 2.3. This means that the temperature was 190ºC and a force-producing load of 2.16 kg was used. Under these conditions, 2.3 g of the plastics material was extruded in 10 minutes. MFR is general a low shear rate test where, the shear rate may be as low as 1 sec^{-1}. Weights greater than 2.16 kg may be used as well as different temperatures. These will depend upon the material and the grade of material being tested (see Table 4). For example, with UPVC a weight of 20 kg may be employed and the temperature suggested in ASTM D 3364 is 175ºC (347ºF). (See the section on Flow Rate Testing.)

Extrusion Testing.

In some companies checks are made on the incoming raw material by using a small single-screw extruder as a rheometer. Usually a rod die is used and the machine is set at specified temperatures. The extrusion behavior is measured over a range of screw speeds and graphs of the output, temperature, and die swell against screw speed are plotted. A major problem is in this test is maintaining the melt temperatures, since any alteration in screw speed may cause it to change due to shear heating. At the higher screw speeds the shear rates in this test can become quite high, so this type of equipment can be regarded as a high shear device.

Flow Path: Wall Thickness Ratio.

This test, which is another way of indicating the ease of flow of a plastic material, is performed on an injection molding machine under specified conditions and using ‘typical’ molds. The result is expressed as a ratio. If the ratio is quoted as being 150:1 then this means that when the wall thickness of the molding is 1mm the maximum length of flow possible will be approximately 150mm. Because the amount of flow possible is dependent upon wall thickness, the flow ratios may be quoted for a range of wall thicknesses. [For example, 1,2 and 3mm (0.04, 0.08 and 0.12 inches)] As a range of gates is employed, the shear rates can be quite high, so this type of equipment is regarded as a high shear device.

Spiral Flow Length

This is not a standard test, although it is widely known in the injection molding industry. The test is performed on an injection-molding machine under specified conditions of temperature and machine conditions. The mold cavity consists of an Archimedean spiral that is fed from the center via the sprue. As material is forced into the cavity, flow continues until the material sets or cools. After ejection, either the weight or the length of the spiral is recorded. The result is expressed, for example, as a certain length produced under specified conditions. When this test is being performed, it is important to hold the screw cushion constant while changing another machine setting such as the temperature or injection rate. The test is not a straightforward rheological test as hot material is flowing into a cooler mold. As an injection-molding machine is employed, the shear rates employed can be quite high and this type of equipment is regarded as a high shear device.

Flowtab Length.

This is not a standard test, although it is widely known in the injection molding industry. It is performed on an injection molding machine under production conditions and using a production mold. Somewhere within the system, for example at the end of a runner, a graduated tab is added. As material is forced into the cavity, this flow tab is partially filled at the same time. After ejection, with the component, the length of the flow tab is measured. The result is expressed as a certain length produced under the specified production conditions and is entered on the production records. The test is not a straightforward rheological test as hot material is flowing into a cooler mold. Since an injection-molding machine is used the shear rates employed can be quite high and this type of equipment is regarded as a high shear device.

Minimum Molding Pressure

This is not a standard test, but was fairly popular when injection-molding machines were only fitted with an injection pressure control. This valve controlled the injection line pressure and, therefore, indirectly, the speed of injection. The test is performed on an injection molding machine under the production conditions and using the production mold. At a specified time, component production is stopped, but the machine continues molding components using the set cycle. The injection line pressure is then progressively reduced until the cavity, or one of the cavities, begins to short. The result, expressed as a pressure (psi or bar) used under the specified production conditions, is entered on the production records. As an injection-molding machine is employed, the shear rates employed can be quite high and this type of equipment is regarded as a high shear device.

The Injection Molding Machine As A Rheometer

The job of a laboratory capillary rheometer (LCR), a high shear rate rheometer, can be performed by an injection molding machine, when the machine is equipped with a suitable nozzle pressure transducer and the injection speed can be set and held at a specified value. The barrel is charged with the plastic material using a slow screw rotational speed and a low backpressure. This charge of material is then allowed to stand in the barrel for, say, 2 minutes. (This will promote temperature uniformity and should simulate the residence times found in a LCR.) The melt is then purged from the barrel, into the air, and the pressure, speed, and melt temperature recorded. If a melt temperature cannot be measured directly then the temperature of the purged material may be measured using a probe. The conditions are then changed and the measurements repeated. The data obtained can be used to produce a shear stress (or viscosity) verses shear rate curve for the material at the test temperature. This is generally considered a high shear rate test.

High Shear Rate Rheometry

In high shear rate flow testing a heat-softened, plastic material is forced through a specified die, using a piston (ram), at a known speed and material temperature. The pressure opposing flow, or the force needed to maintain a specified flow rate, is measured. (Most modern capillary rheometers operate by measuring either pressure or force at a constant shear rate.) The piston speed is then changed and the new force, or pressure, needed to maintain this speed is measured and recorded. From the barrel dimensions and the piston speed, the volumetric flow rate through the die is calculated. The shear stress is calculated from the force measured on the piston or pressure drop across the capillary. The shear stress and the shear rate are then used to construct flow curves. Since the viscosity, or resistance to flow, is defined as the shear stress divided by the shear rate, viscosity verses shear rate or shear stress curves may also be constructed. This procedure may be repeated at different barrel temperatures to characterize a material’s shear flow properties over a range of temperature and imposed rates.

Constant Shear Rate And Shear Stress Testing.

While most high shear rate rheometers are of the constant shear rate type (i.e. constant ram speed) machines are also available in which the force is controlled. The force, or pressure, is set at a constant level and the ram rate is measured during the test. The volume extruded per unit time is determined, and from this the shear rate is calculated. When the melt density is known the weight extruded per unit time can be calculated. Both this type of machine and the melt flow rate instrument, may be referred to as a constant pressure, force, or shear stress type rheometer.

Moisture Content.

With many plastic materials, the level of moisture in the material used by the processing equipment must be kept at very low values. For example, a typical resin fed to an injection-molding machine must have a moisture level of below 0.2%. This is usually to prevent the production of parts with a poor surface finish; however, water can also act as a plasticizer or cause degradation. This means that if the flow properties of a production material are being assessed for processing information, the sample used for flow testing must have the same water content as the production material.

9. ELASTIC EFFECTS IN POLYMER MELTS

Polymers consist of long chain molecules that become distorted when they are subjected to shear during processing operations. Such shearing tends to straighten out (orient) the molecules. When the shearing process ceases, however, the molecules, providing they are still molten, will tend to coil up again. If cooling occurs rapidly after the shearing, this re-coiling (sometimes called relaxation) may not be complete. Such uncoiling/recoiling processes can give rise to a number of phenomena that are often referred to as elastic effects. The most important elastic effects are extrudate swell, melt fracture, sharkskin, frozen-in orientation and draw down.

Extrudate ("Die") Swell

When polymer melt emerges from a die the extrudate may swell so that its cross-section, after it leaves the die, is greater than that of the die orifice.

Terms used. For a capillary die, the ratio of the extrudate diameter to the die diameter is known variously as the die swell ratio, extrudate swell, swelling ratio or as the puff-up ratio. For a slit die, the relevant ratio is of the thickness of the extrudate height of the slit.

Chain distortion. The swell occurs because, as the melt passes through the die, the molecules become extended (with the greatest extension occurring near the die wall). On emergence from the die, the molecules tend to coil up (re-coil), contracting in the flow direction and expanding in directions perpendicular to the flow. If an extrudate is cut at the die face the leading edge of the extrudate is convex, indicating that the greatest contraction in the flow direction is near the wall where the shear has been greatest.

Factors affecting Extrudate Swell

Experimental work has shown that:

1. Swell increases with an increase in extrusion rate (shear rate) up to a critical shear rate.

The Source of Extrudate Swell

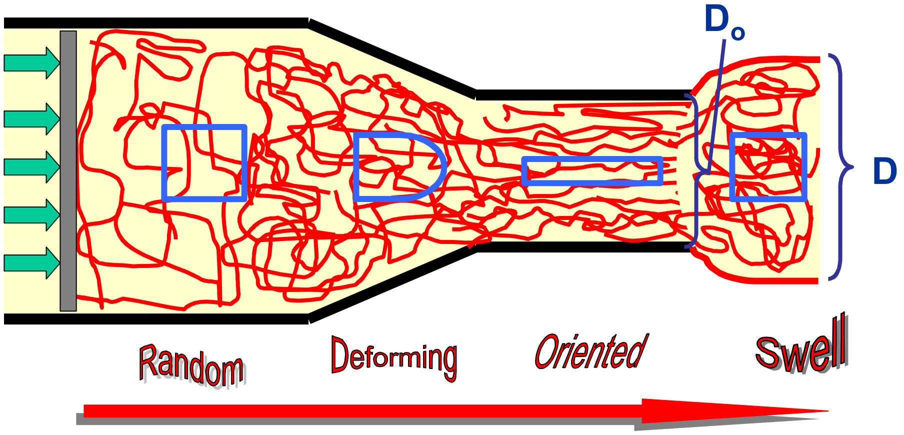


Figure 4.

2. Swell decreases with an increase in temperature at a given shear rate or extrusion rate.
3. At a fixed shear stress, die swell is little affected by temperature.
4. At a fixed shear rate, die swell decreases with an increasing length of the die.
5. Extrudate swell through a slit die is somewhat greater than through a capillary die and increases more rapidly with increasing shear rate.
6. Extrudate swell increases with an increase in the ratio reservoir diameter / capillary diameter (although little affected at ratios above 10:1).

Methods for the measurement of extrudate swell are given in the section entitled “Measurement of Extrudate Swell”.

Compensation for die swell by drawing down. It is common practice to compensate solid extrudates for die swell by stretching, or drawing down, the extrudate, so it can just pass through a sizing die. Using this technique, it is not necessary that the two be exactly balanced. It should, however, be noted that drawing down will cause molecular orientation. This results in increased strength in the flow direction and decreased strength in directions transverse to the flow, which may or may not be desirable. Drawing down is also somewhat limited where the solid extrudate has varying section thicknesses. This is because shear rates, and hence die swell, will be higher at the thinner sections. These thinner sections may also have a shorter die length, to ensure that extrusion rates are constant through the cross-section. This will increase the extrudate swell even further.

Compensation for extrudate swell with pipe and tubing. In the extrusion of pipe and tubing, the situation is further complicated by the fact that the extrudate is usually inflated to the dimensions of a sizing die. In this case, it may be assumed that on emergence from the extruder die that, the wall thickness will expand to the die swell appropriate to the shear rated used. The wall thickness, however, will be reduced in proportion to the amount of inflation, which is given by the ratio of the diameter of the sizing die to the external diameter of the extrusion die.

Melt Fracture.

When extrusion is carried out at high rates it is frequently observed that distortion of the extrudate occurs.

***Terms used*.** The observed distortion may be due, either to the phenomenon known as melt fracture or elastic turbulence (and in some cases bambooing) or it may be due to what is know as sharkskin formation. These phenomena, which appear to have different origins, are not fully understood.

***Critical shear rate*.** Melt fracture occurs when the shear rate exceeds a critical value (the critical shear rate) for a particular polymer melt at a defined temperature. There is a corresponding critical shear stress. The point these define on the shear rate-shear stress diagram (flow curve) is known as the critical point. Melt fracture is believed to originate in the die entry region where material is being funneled from the die reservoir into the capillary. In an extruder, this corresponds to the point where melt moves into the die parallel portion of the die. Some further complicating effects may occur at the wall of the die.

***Form of distortion*.** The form of distortion varies from one polymer type to another, but is generally helical in nature. With materials such as polyethylene and polypropylene a distortion like a screw thread may appear. With polystyrene the extrudate may form a spiral, while with other melts, ripples, or bamboo-like repetitive kinks may appear. With all melts, at rates well above the critical point, the helical nature becomes obscured by severe distortion that appears quite random.

Occurrence. Melt fracture is most likely to occur where small diameter extrudates are being extruded at high rates. The most notable examples occur in wire coating.

***Factors affecting melt fracture*.** Since it is easily observed in the laboratory, melt fracture has been widely studied. Experiments have shown that:

1. The critical shear rate for melt fracture increases with an increase in temperature.
2. The product $\tau_C M_W$ is a constant. (τ_C= Critical shear stress, and M_W= weight average molecular weight) Melt fracture will start at lower shear stresses, and rates, with high molecular weight resins than with low molecular weight polymers.
3. Two polymers differing in their levels of branching, but with similar melt viscosities tend to have similar critical points.
4. Extrudate quality may be markedly improved by tapering the die entry. This allows externally undistorted extrudates to be obtained at rates well above the critical point. (There is some evidence that internally there may still be some distortion.) There is also some evidence that tapering the so-

called die parallel (by up to 10º) may also substantially increase the critical point.
5. There is some evidence that increasing the L/D ratio of the die also increases the critical shear rate.

The above factors affecting melt fracture have been well known and applied for many years. As a result, high speed wire coating and other operations involving high shear rates, are operated without undue trouble from melt fracture effects.

Melt Fracture

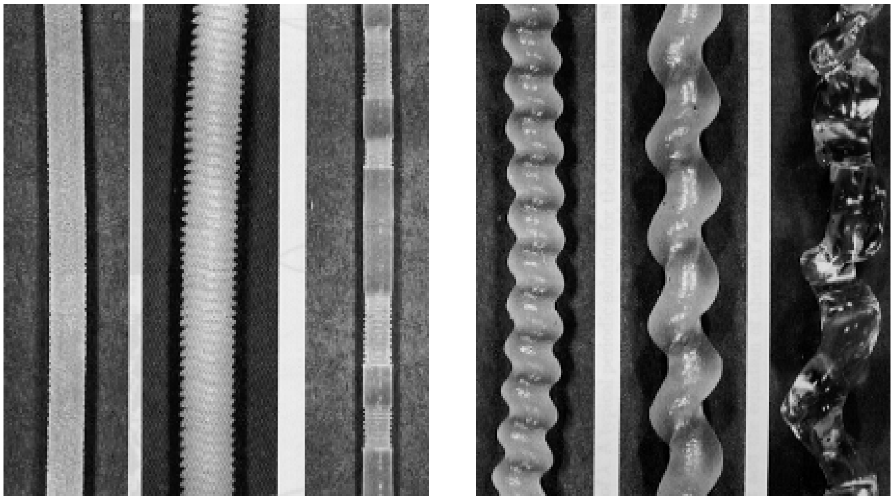


Figure 5.

Sharkskin.

The phenomenon of sharkskin has been less widely studied than melt fracture, but it is probably a greater problem in industrial extrusion.

Melt tearing. In this case the distortion consists of transverse ridges rather than helical distortions. It is believed to occur as a result of the melt tearing as the polymer exudes from the die. This takes place because, within the die, the melt close to the wall moves very slowly (in the case of the layer next to the wall this movement is zero). As the melt emerges, the whole extrudate moves away from the die face at a constant speed, so that the outer layers are suddenly stretched and may tear.

Incidence of sharkskin. Experimental studies have indicated that the critical shear rate for onset of sharkskin (γ_C) is inversely proportional to the die radius ®. (i.e.γ_C R=constant). Thus the critical shear rate is much lower with larger diameter dies. One result of this is that, although with small dies (such as those used in typical laboratory rheometers) melt fracture may occur at shear rates below those for the onset of sharkskin, the reverse may be observed with full-scale industrial dies.

Critical linear extrusion rate. It can be shown, as a consequence of the above relationship, that sharkskin is likely to occur above a critical linear extrusion rate irrespective of the die size. That is, for a particular polymer melt, it may occur at a certain extrusion rate no matter what the size of the die.

***Conditions favoring sharkskin*.** Sharkskin appears to be most severe when the melt is partially elastic and has the consistency of a friable cheese. Improved results may sometimes be obtained by reducing melt temperatures, so the melt is more strongly elastic as it emerges from the die. Alternatively, improved results have been obtained by heating the die at the point of exit to make the surface layers of melt more fluid and tearing less likely. The severity of sharkskin may vary enormously. At one extreme, the distance between ridge and adjacent trough may be one-third of the extrudate cross-section. At the other extreme, the effect may be barely detectable to the naked eye, but may show up as a matt finish or may be felt by running a fingernail over the surface. In blow molding, a rough surface on the inside of a bottle is indicative of sharkskin as the outside is usually flattened against the wall of the blow mold.

***Molecular factors*.** The only molecular property, within a polymer type, that appears to greatly influence sharkskin is molecular weight distribution (MWD). A broad distribution generally greatly reduces any tendency to produce sharkskin effects.

Frozen-In Orientation.

In the molten state, polymer molecules tend to coil up when they are not subjected to external stresses. They prefer to exist in a random coil configuration.

***External stress application*.** When external stresses are applied (as occurs during extrusion, molding and other shaping operations) the molecules are distorted from their randomly coiled state and become oriented. In most processing operations it is desirable to freeze (or “set”) the polymer as soon as possible after it has been shaped. (For example, by cooling in a water bath after extrusion through a die.) In such circumstances, the polymer molecules may not have time to re-coil (relax) completely before the melt freezes. This results in frozen-in orientation.

***Anisotropy*.** Because of frozen-in orientation, plastic products may be anisotropic in their behavior; their properties differ when measured in different directions. For example, the tensile strength will be greater in the direction of orientation than across it. Impact strength is also affected by frozen-in orientation. An Izod impact test sample, injection molded with the gate at one end, will have the molecules roughly aligned along the axis of the sample. Thus to break the sample in a standard Izod test will require fracture across the elongated molecules. This results in higher impact strength than would be measured on unoriented samples. On the other hand, if impact strength is being measured by dropping a weight onto a flat plate, lower impact strength will be recorded with a more oriented molding. This is because fracture can occur more easily parallel to the direction or orientation, which largely requires fracture between, rather than across, the molecules.

Types Of Orientation

Increased orientation may be introduced into a product by stretching the polymer melt just before it freezes. Uni-axial orientation, i.e. stretching in one direction, is important in the manufacture of fibers. Biaxial orientation, a simultaneous stretching in two directions, is important in film manufacture. It may also be desirable to build biaxial orientation into piping, bottles, and other hollow containers, to enhance the hoop strength and fracture resistance of the product.

Desirability or undesirability Frozen-in orientation may thus be either desirable or undesirable according to circumstances. Frozen-in orientation is greatest when the melt has been subjected to high stresses and the interval between shearing and setting of the melt is reduced. Such conditions occur when low melt temperatures and low cooling temperatures (e.g. low injection mold temperatures or low extrusion cooling bath temperatures) are present.

Draw Down.

In a number of extrusion processes, such as in the manufacture of film, the extrudate may be subjected to extensive stretching after leaving the die. In other processes, such as the chill-roll casting of film, it is important that the extruded web does not tear on stretching.

***Viscous behavior*.** In processes where stretching of the melt occurs, viscous behavior rather than elastic behavior is the more important factor. Although it is desirable that the melt has some strength and elasticity, the main requirement is that the molecules of the melt can flow past each other.

***Neck-in*.** One phenomenon associated with chill roll casting is that of “neck-in”. The edge of the extruded web tends to shrink inwards towards the center of the web. At the same time, this edge tends to become thicker than the bulk of the film. More elastic melts, which can maintain a tension in the extrusion direction, are less liable to neck-in.

***Parison sag*.** Elastic effects may also influence parison sag, which occurs during blow molding. Parison sag is the thinning of the parison caused by the effect of its own weight as it leaves the die. Part of the sag may be due to an elastic effect (chain uncoiling) and part due to viscous flow as the molecules slide past each other. It is reasonable to assume that the elastic component resisting sag increases as a proportion of the total as the:

1. Molecular weight, and hence viscosity, increases.
2. Melt temperature decreases (increasing viscosity).
3. The length of parison per unit weight increases. This is because an elastic deformation under a standard load depends on the length of the part being stretched, while the viscous flow does not (as long as the weight of the parison is constant).

10. MELT FLOW RATE TESTING

Of all the tests used by the plastics industry, melt flow rate testing (or melt flow index) is most widely used. It has been traditionally associated with the testing of polyethylene materials to determine lot-to-lot consistency of resin lots or batches for quality control purposes. It is, however, also used for other purposes such as testing new materials, determination of material stability verses residence time within plastics processing equipment, or the assessment of regrind content within materials or moldings. It is generally a low shear rate test, however, using larger weights can increase the shear rate.

Basic Description.

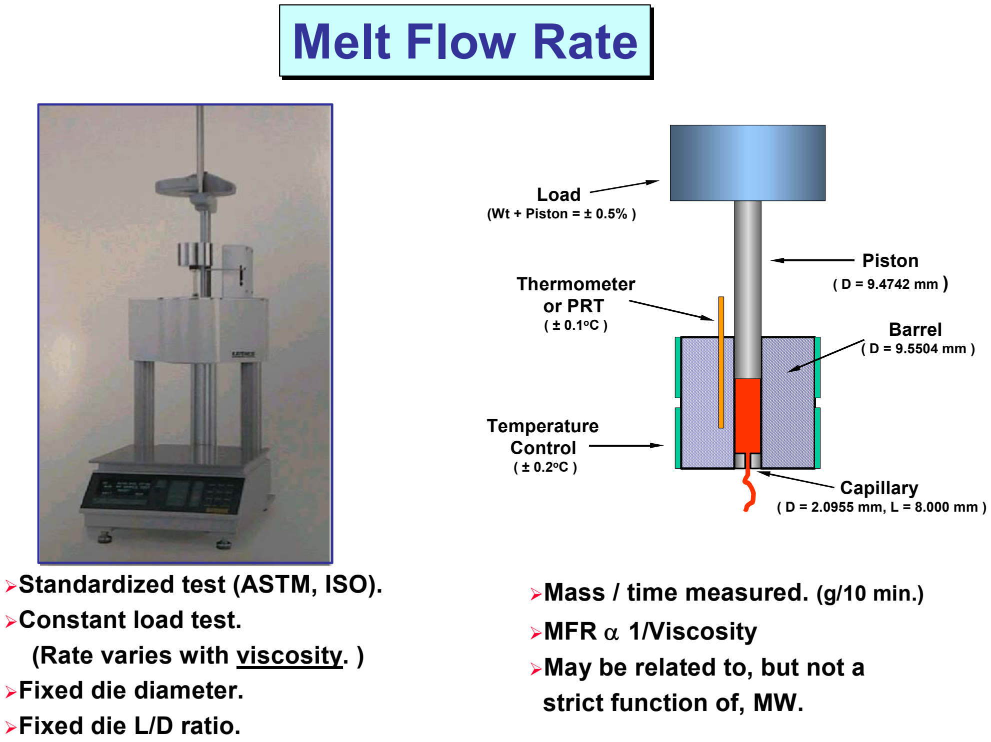
Melt flow rate (MFR) testing is widely used since it is easy to do and to understand. A melted plastic material (See Table 4.) is forced through a die of a specified diameter and length under prescribed conditions of temperature, load and piston position in the barrel. The amount of plastic extruded in 10 minutes is weighed and reported as the melt flow rate (MFR). The results may be reported as FR-190/2.16 = 2.3, if the test is done according to ASTM D 1238. This means that the temperature was 190ºC and a load of 2.16 kg was used. Under these conditions, 2.3 g of the plastic material was extruded in 10 minutes. If more plastic extrudes in the 10-minute period, then the material is a more easily flowing material. If less plastic material is extruded in the 10-minute period, then it is a less easily flowing (stiffer) material.

Test Report.

The melt flow rate (MFR) is reported, (ASTM D 1238) as the rate of extrusion expressed as grams per 10 minutes. The results are sometimes shown as MFR (190, 2.16)=2.3. They could also be shown as, MFR (190, 21.2)=2.3. This means that the temperature was 190ºC and a load of 21.2 kg was used. It is important to specify, in any report or table, the test procedure used for testing, the nature and physical form of the material tested, the temperature, the load used, details of any material conditioning (for example, drying), the procedure used (for example, Method A or B), and any unusual behavior of the plastic material seen during the test

MFR, MFI and MI.

The terms “melt flow rate” (MFR), “melt flow index” (MFI) and “melt index” (MI) refer to the same test. MFR was introduced to replace MFI. The term MFI is used to refer to the flow rate of PE obtained under Condition 190/2.16 (formerly known as Condition E). The use of such terms is not encouraged for other materials. It is suggested, by ASTM D 1238 that the term melt flow rate (MFR) be used for other plastic materials.



Melt Flow Rate

- **Standardized test (ASTM, ISO).**
- **Constant load test.**
  (Rate varies with viscosity.)
- **Fixed die diameter.**
- **Fixed die L/D ratio.**

- **Mass / time measured. (g/10 min.)**
- **MFR α 1/Viscosity**
- **May be related to, but not a strict function of, MW.**

Figure 6. Melt Flow Rate Tester

Alternative Settings.

MFR is a low shear rate test. The shear rate may be as low as 1 sec^{-1}. Weights larger than 2.16 kg as well as different temperatures may be used in the test. The conditions used depend upon the material and upon the grade of material (See Table 4). [For UPVC a weight of 20 kg (44.1 lb) may be used at a temperature of 175ºC (347ºF), in ASTM D 3364.] When the MFR test is run with a high load, (for example 21.6 kg or 47.62 lb), it is referred to as the high load melt index or the HLMI.

Standards And Methods

Flow rate testing is governed by various international standards including ASTM Method D 1238 and ISO R1133. Such standards specify orifices size, melt temperature, heat chamber size and piston tip diameter as well as the method of conducting the test. The object is to obtain consistent results from different melt indexers. Two basic methods have been developed for melt index testing, Method A and Method B. Method A is the traditional manual test method, whereas Method B uses electronic sensing of plunger displacement and calculates the flow data from such measurements. Once set up, Method B is simpler to run and more precise for routine testing.

Equipment Details.

The details quoted here are those specified by ASTM Method D 1238-86. For full details please consult the appropriate standard.

Barrel Size	L = 162 mm/6.375 in	D = 50.8 mm / 2 in
Barrel Bore		D = 9.5504 mm/0.376 in
Die	L = 8.0000 mm/0.315 in	D = 2.0955 mm/0.0825 in
Piston Land	L = 6.35 mm/0.250 in	D = 9.4742 mm/0.3730 in

The metal surfaces must be very well finished (12 rms or better in accordance with ANSI B 46.1). The set temperatures must be held to within +/-0.2ºC and the combined weight of the piston and load must be within +/- 0.5% of the specified load.

Method A.

Method A, also known as Procedure A, is a manual cutoff test used for materials having flow rates that fall within 0.15 to 50 g/10 minutes. The test specimen can be in any form that can be introduced into the cylinder. The piston tip position during the timed measurement, however, is required to be between 51 and 20 mm (2.0 and 0.8 in) above the die. The specific conditions of temperature and load can be selected by consulting the D-1238 standard. For example, when a PE with an expected MFR of 2 is tested, the temperature is set at 190ºC and a load of 2.16 kg is selected. After packing the PE (5 ± 0.1g) into the barrel, the sample is allowed to heat for 4 minutes with the piston in contact with the material. The weight (2.16 kg) is then placed on top of the piston. After a further 3 minutes (usually between 2 and 4 minutes) the lower reference mark, inscribed on the piston must be level with the top of the barrel. The material is then allowed to extrude for a specified time (for example, 2 minutes), after which the extrudate is carefully cut off and saved. This should be repeated three times if possible, before the upper inscribed reference mark reaches the top of the barrel. The three samples are then individually weighed, to the nearest milligram (0.001g), and the average mass in grams is found. The flow rate is reported as the weight of resin extruded, in grams, over 10 minutes (obtained in this case, by multiplying the average mass of polymer extruded (m) by 5). Thus

$$\mathbf{MFR = MFI = m \times 600/t.}$$

Where:

t = the cut-off interval expressed in seconds (s).
m = the mass of polymer extruded.

Method B.

Method B, also known as Procedure B, is an automatically timed melt flow rate measurement used for materials having flow rates that fall within the range of 0.50 to 1,200 g/10 minutes. To ensure reproducibility, it is required that the timing device used is accurate to within +/- 0.1 seconds and the position of the piston tip at the end of the test is 25.4 mm (1 in) above the die. During the measurement, the length of timed piston movement must be measured to within 0.025 mm (0.001 in) over a prescribed distance. This measurement accuracy is achieved by using an opaque flag, hung from the piston, which interferes with the passage of light to an electronic eye. Mechanical encoders are also used for this measurement. If the system is computerized, then the operator need only to select and enter the test conditions of temperature and load by consulting the standard, or the computer memory, and load the material. The test specimen can be in any form that can be introduced into the cylinder. The electronics will automatically control the temperatures and time measurement (and, sometimes, even change the weight during the test run if required). The apparent melt density of the polymer (See Method A to B conversion.), at the test temperature, is entered to allow the calculation of the weight of extrudate from the piston displacement. Once the test has been completed the electronics can calculate flow rate, flow rate ratios, viscosity, shear rate and shear stress. The computer also may contain statistical software for SPC/SQC analyses of the data for quality control purposes. (See Table 5.)

Flow Rate Ratio.

Since polymer melt viscosity may vary as a function of shear rate, the single point determination by a melt indexer does not fully characterize material flow. To obtain more useful information, flow rate testing may be done with more than one load. For example, in blow molding the sag behavior of the parison is best measured by the low shear flow while the flow through the die lips is best measured by the higher shear flow. Flow rate ratio is obtained by dividing the flow rate obtained when a large load is used by the flow rate obtained when a smaller load is used. The load ratio, which is general 10:1, may be measured automatically during a single test run on some machines.

Method A To B Conversion.

Method A to B conversion may be obtained on some machines with an appropriate computerized control system. The operator runs a Method A test while the machine conducts a Method B test. Upon test completion, a display of flow rate and apparent density is obtained. The apparent density is then used in subsequent method B tests. The apparent melt density is obtained by equating two equations and solving for melt density. By Method A, the flow rate (FR) is

$$\mathbf{FR_{(A)} = m \times 600/t_A}$$

Where m is the average mass extruded (m) within the cut-off interval t_A (expressed in seconds). By Method B the flow rate is calculated from

$$FR_{(B)} = \pi R^2 \times L \times A \times 600/t_B.$$

Where R is the piston radius in cm, L is the effective length of the flag in cm, A is the apparent melt density in gcm³ and t_B is the time taken for the test measurement (in seconds). If the two FRs are the same then, the equations may be solved for A. (See Table 5.)

$$A = (m / \pi R^2 L)(t_B/t_A)$$

The advantage of this system is that by using an apparent density obtained from any given machine, Method B will always equal Method A and it takes into account frictional and other variations.

Cleaning.

The cylinder and die should be thoroughly cleaned after each test. First run out any material left in the barrel, and then push the die out through the top of the barrel. The barrel may then be cleaned by repeatedly pushing cloth patches through it or by careful swabbing with a suitable small metal (preferably brass) brush. The die may also be cleaned using a suitable sized drill or by pyrolytic degradation in a nitrogen atmosphere at 550ºC/1022ºF.

11. HIGH SHEAR RATE RHEOMETERY

The information required to generate polymer flow curves may be obtained from a variety of different machines. These include the dynamic or rotational cone and plate viscometers, co-axial cylinder viscometers (drag flow) and capillary rheometers (pressure driven flow). The capillary rheometer is of greatest interest to the plastics technologist since it provides data in the shear rate ranges seen in injection molding and extrusion. The data so obtained, may in turn be used to size the dies or runner systems used in these processes. Capillary rheometers, when applied in the processing shear rate range, are called high shear rate rheometers.

Ease Of Flow

Plastic materials differ widely in their viscosity, or ease of flow. The problem of testing such materials is made more difficult by the fact that each material is available in a range of grades, each of which also may have a different flow behavior. The situation is made even more complicated by the fact that the flow of most plastics is non-Newtonian. In most cases, plastics are pseudoplastic materials. This means that they become less viscous (more easier flowing) when they are transported more rapidly. There is not a linear relationship between pressure and flow. Thus, the flow properties cannot be represented meaningfully by a single number. Flow testing over a range of conditions is required.

Flow Testing – Imposed Stress.

There are high shear rheometers available, in which melt is extruded using a gas at constant pressure and the extrusion rate noted. In this controlled stress type rheometer the gas pressure is varied to change the rate of extrusion. Such designs are usually more restrictive and less convenient to use than controlled rate instruments. Some motor driven controlled stress capillary rheometers are also available that control the force and then measure the rate.

Flow Testing – Imposed Rate.

High shear rate flow testing is commonly carried out by forcing the melted plastic material through a die of specified size, using piston (or ram), at a known piston speed and material temperature. The pressure, or force, required to maintain the specified flow rate is measured. (***Dynisco Polymer Test*** **LCR 7000 Series** of rheometers operate by measuring force, using a load cell, or pressure, using a pressure transducer located above the die.). The piston speed is then changed and the new force or pressure generated at this speed, is measured and recorded. For each piston speed a force or pressure is recorded. Knowing the barrel dimensions and the piston speed, the volumetric flow rate through the die can be calculated. In turn the shear stress and the shear rate are calculated and used to construct flow curves. This procedure can be repeated at different barrel temperatures.

Suggested Conditions.

One of the uses of this rheology equipment is for quality control. The user of a plastic material measures the flow properties of incoming resin to determine its lot-to-lot consistency. As the flow properties of plastics cannot be represented meaningfully by a single number, flow testing over a range of conditions, typical of those encountered during processing, is suggested. The temperatures listed in Table 6 are those recommended for testing injection-molding grades of those particular materials. The most useful data is obtained at temperatures actually used in production; so, Table 6 is given for guidance only. The shear stress and shear rate conditions used should closely approximate those seen at different points in the production process. Such characteristic shear rates should include the speed of shearing at various points within an injection molding system; such as a low shear point, a medium shear point and a high shear point.

Flow Tables.

When the shear stress is divided by the apparent wall shear rate the viscosity at that particular shear rate is obtained. This is called the apparent shear viscosity. In practice the word 'apparent' is sometimes omitted. As flow testing is generally performed over a range of conditions (temperatures and piston speeds), the variation of viscosity with temperature and rate of flow can be easily obtained by simple calculations. On some rheometers, these calculations are performed automatically by a built-in computer and displayed in tabular form. The information thus obtained may then be used to construct flow curves (See Calculating flow data and Figure 1.).

12. DYNISCO POLYMER TEST RHEOMETER DETAILS.

The barrel diameter for the Dynisco Polymer Test Capillary Rheometer (LCR 7000 Series) is 0.376", (9.550mm). In this case the formula used to obtain flow rate Q (See Calculating Flow Data) becomes

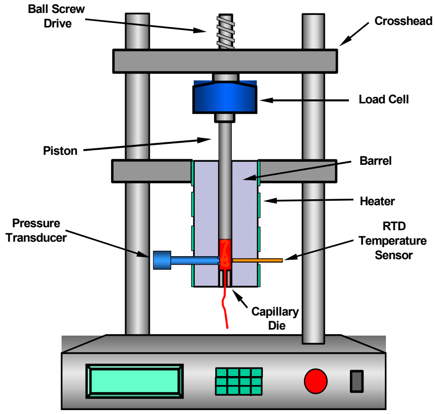
$$\mathbf{Q = 71.630\ (S)}$$

and the relationship for shear rate is

$$\dot{\gamma} = \mathbf{91.203S/R^3_c}$$

when the capillary radius (R_c) is in mm and the piston speed (S) is in mm/s.

The Capillary Rheometer



- **A driven piston provides a constant volume flow (Shear Rate) or pressure (Shear Stress).**
- **The force on the piston or pressure (Shear Stress) or rate (Shear Rate) is measured.**
- **The viscosity (resistance to flow) is calculated from η = Shear Stress/Shear Rate.**

Figure 7.

Since the shear stress at the capillary wall is given by the expression

$$\tau = PR_c/2L_c$$

where L_c is the capillary length. Then, for die with an L/D ratio of 20:1,

$$\tau = P/80$$

where P is the pressure at the entrance to the capillary (P=F/A).

In operation the required temperature is entered via a membrane touchpad or computer and is viewed on the rheometer LED display or computer screen. An adaptive PID control algorithm, controls barrel and orifice temperatures to better than ±0.1ºC. The operator then enters shear rate or shear stress points and other test parameters into the rheometer, again via the membrane touchpad or computer. Material (approximately 10 – 12 grams) is loaded into the barrel, packed down with a charging tool, and the piston assembly is inserted.

When the operator presses RUN, the piston descends into the barrel and applies a predetermined force on the material for a preset time called the “melt time”. The melt time, which is used to achieve a uniform melt temperature, is usually 360 seconds. This is followed by the polymer test, which is usually run starting with a high shear rate to compress the material.

A precision load cell or pressure transducer measures the forces or pressures being applied to the material. This signal, along with piston position, is sent back to the rheometer's computer. As the piston proceeds down the barrel, the computer monitors the forces or pressures. When using computer controlled steady state acquisition a preprogrammed volume of polymer is extruded and ten measurements are made and averaged. Then another ten points are measured and averaged for a second volume. This second value is compared to the first. This process is continued until the average of the averages is constant. Then a force or pressure measurement is made and saved by the computer. (The point at which the measurement is made can also be based on the position of the piston, the time in the test, or taken manually by the operator.) Usually the piston starts down at a high speed and then proceeds to the next speed at an ever-decreasing rate, so that decreasing shear rates are created. In this manner, the forces involved in extruding the material through the rheometer die are generated from high to low shear rate values. These data are used to produce the viscosity curve. (See Figure 1. and Table 7.).

Software present in the computer ("LabKARS") allows the operator to plot shear rate or shear stress versus viscosity curves or to produce viscosity verses time (thermal stability) plots. The data may be plotted and presented in numerical format. Multiple runs can be plotted together on the same chart, so material differences can be quickly observed.

Cleaning.

The barrel and die must be thoroughly cleaned after each test. First any material left in the cylinder, or barrel, is run out and then the die is removed by loosening the die retainer nut. The barrel is cleaned by repeatedly pushing cloth patches through it or by swabbing with a suitably sized metal brush. The die may also be cleaned by an appropriately sized drill, hot solvent immersion or by pyrolytic degradation in a nitrogen atmosphere at 550ºC/1022ºF.

Practical Rheology Electronic Handbook

Section 3

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Dynisco
Polymer Test

Practical Rheology Handbook

TABLE OF CONTENTS

FIGURES

Title **Page**

13. CALCULATING FLOW DATA

Some important assumptions are made in the analysis of flow in a capillary rheometer. Of these the most important are:

1. The flow is isothermal.
2. There is no slip at the capillary wall.
3. The melt is incompressible.
4. The flow pattern is constant through the die. (“Fully developed flow”.)
5. Dissipation of energy at the die entrance, or due to chain uncoiling, is negligible. (See the next chapter.)

13.1 Basic Equations.

The most common type of flow occurring in the processing of polymer melts is shear flow. In this type of flow, one may visualize that one layer of melt flows over another on application of a shearing force. The process is described by the relationship between two variables, the shear rate and the shear stress. The shear rate is usually designated by

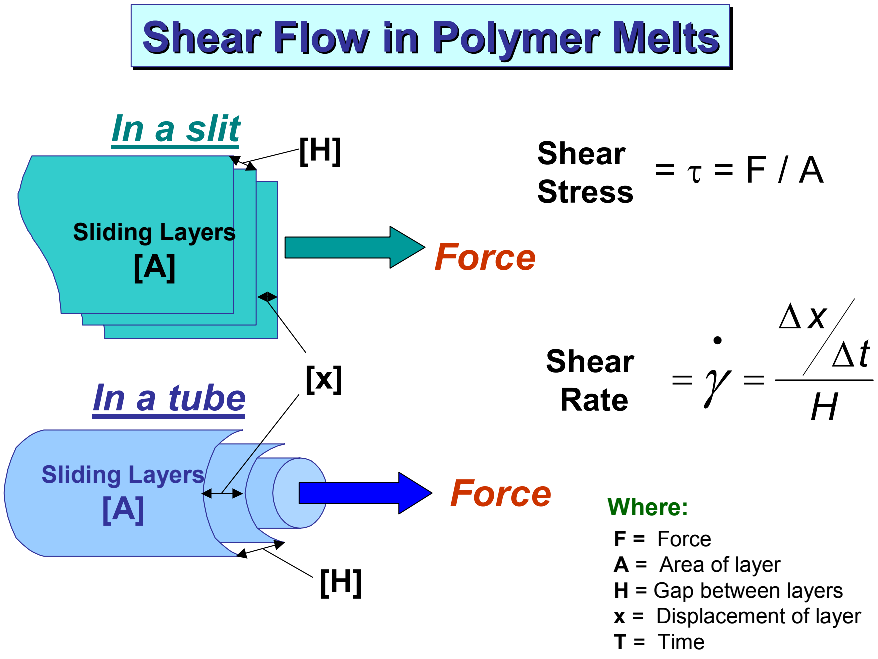


Figure 8.

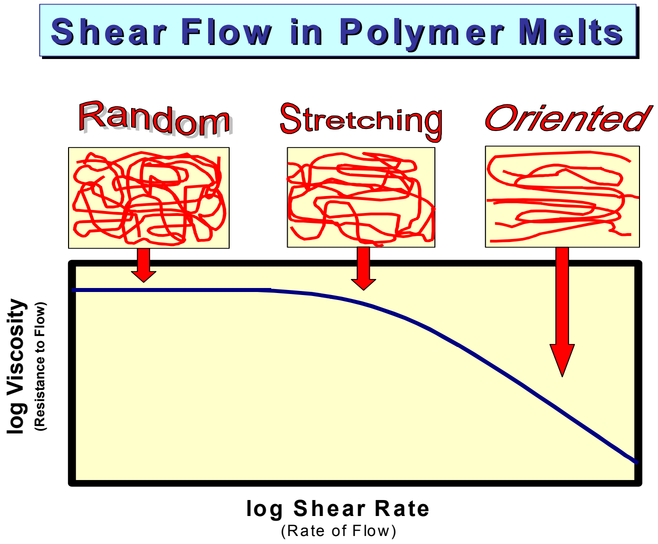


Figure 9.

the Greek letter gamma with a dot above the letter, that is, gamma dot or $\dot{\gamma}$. Shear rate is given in reciprocal seconds (that is, in 1/sec or sec^{-1}). The larger the number quoted the faster the material is being sheared or forced to flow. The shear stress, which is usually designated by the Greek letter τ, is the stress (i.e. the force per unit area) required to cause one layer to flow over another at the required rate. If the assumptions made above are considered to be valid then it may be shown that:

τ = The Shear Stress at the Wall of the Die = $PR_c/2L_c$,

$\dot{\gamma}_{a,w}$ = The Shear Rate = $[4Q\ (3n^*+1)] / [\pi R^3_c\ (4n^*)]$

Where:

$n^* = \Delta\log(R_cP/2L_c) / \Delta\log(4Q/BR^3_c)$
τ = the shear stress.
P = the measured pressure.
R_c = the die radius.
R_b = the barrel radius
L_c = the die length.

$\dot{\gamma}_w$ = the shear rate at the wall of the die.
Q = the volumetric flow rate.

Flow Curves.

The expression for the shear rate at the wall of the die is rather cumbersome, so in practice it is just as useful to use the expression

$$\dot{\gamma}_{a,w} = \ 4Q / \pi R^3_c$$

where, $\dot{\gamma}_{a,w}$ is known as the apparent shear rate at the wall.

It may be shown that, as with the true shear rate, there is a unique relationship (i.e. just one relationship) between shear stress and $\dot{\gamma}_{a,w}$ and this simplified expression may be used for scale up work. Hence the “flow curves” provided by most laboratories are generally obtained by plotting τ or η (viscosity) against $\dot{\gamma}_{a,w}$. The wall of the tube is, however, simply a place at which the shear stress and shear rate may be calculated from knowledge of flow rates and pressures. The relationship between τ and $\dot{\gamma}_{a,w}$ will, however, be independent of the position in the flow system and equally applicable to flow in other geometries such as slits. For this reason it is quite correct to plot τ against $\dot{\gamma}_{a,w}$ without printing the subscripts. Occasionally shear rate is denoted by γ without the dot above it. This should not be encouraged since this symbol is widely used to indicate elastic shear strain. By plotting shear stress (Pa) against shear rate (1/sec) flow curves may be obtained. Viscosity (Pa-sec) is obtained by dividing shear stress by shear rate.

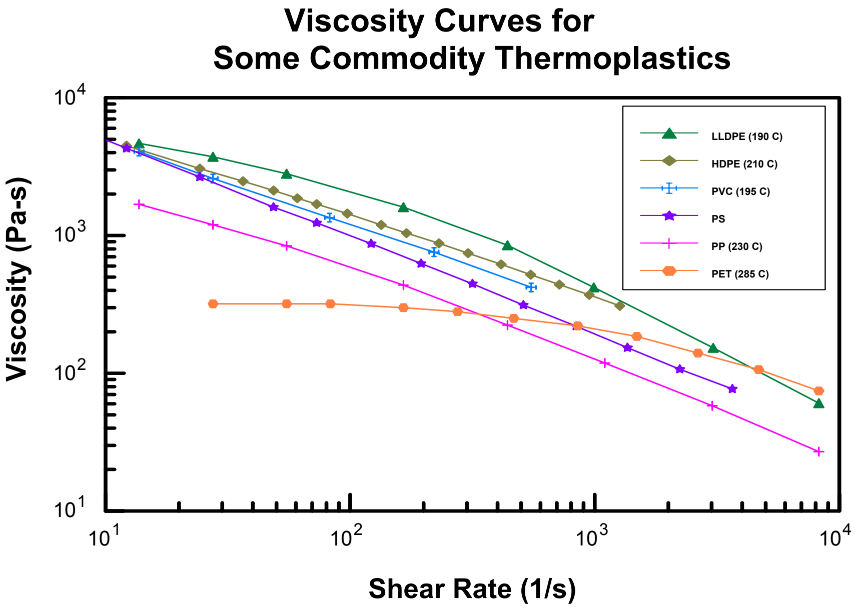


Figure 10.

Measuring $\dot{\gamma}_{A,W}$ and τ

Let the ram speed = S (measured in mm/s) and the barrel diameter = D (measured in mm). Then the volumetric flow rate

$$\mathbf{Q = S\,(\pi D^2_b/4)} \qquad \text{(Equation1).}$$

This is the same in both the barrel and the capillary.

Now the apparent shear rate at wall is

$$\dot{\gamma}_{a,w} = \mathbf{4Q/\pi R^3_c} \qquad \text{(Equation 2).}$$

Where R_c is the radius of the capillary in mm.

Substituting equation 1 into equation 2 and simplifying we obtain:

$$\dot{\gamma}_{a,w} = \mathbf{S\,D^2_b / R^3_c = 4\,S\,(R^2_b / R^3_c)}$$

(Equation 3).

The barrel diameter for the Kayeness capillary rheometer is 0.375”, i.e. 9.550 mm. In this case the formula becomes:

$$\dot{\gamma}_{a,w} = \mathbf{91.203\,S / R^3_c}$$

when the capillary radius is in mm and the ram speed is in mm/s.

Since the shear stress at the wall is given by

$$\tau = \mathbf{P\,R_c / 2L_c} \qquad \text{(Equation 4).}$$

Then, for a 20:1 L/D die, τ = P/80 (where P is the pressure at the entrance to the capillary.)

Apparent Viscosity.

By plotting shear stress (Pa) against shear rate (1/sec) flow curves may be obtained. Viscosity (Pa-sec) is obtained by dividing shear stress by shear rate. Dividing τ (the shear stress) by $\dot{\gamma}_{a,w}$ (the apparent wall shear rate) then, a viscosity at a particular shear rate may be obtained from the ***Dynisco Polymer Test*** LCR7000 capillary rheometer from the expression:

$$\eta_a = (\tau / \dot{\gamma}_{a,w}) = \mathbf{[(P\,R_c / 2L_c)] / [\,91.203\,(S / R^3_c)]}$$

$$= \mathbf{[P\,R^4_c\,] / [182.4\,S\,L_c\,]} \qquad \text{(Equation 5).}$$

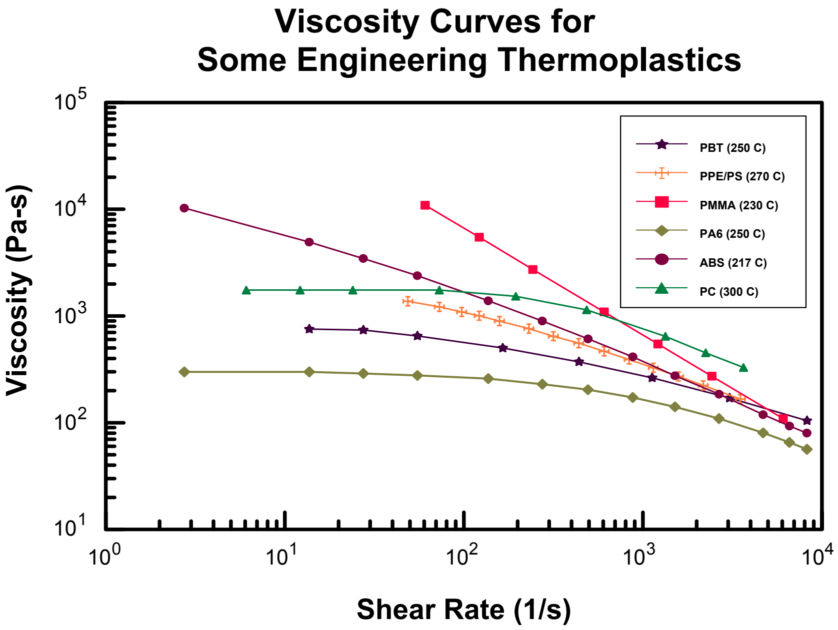


Figure 11.

This is an apparent viscosity. In practice the word 'apparent' is often omitted and the symbol η is used. As flow testing is performed over a range of conditions (temperatures and/or piston speeds), the variation of viscosity with temperature and rate of flow can be easily obtained by simple calculations. With the ***Dynisco Polymer Test*** rheometers, these calculations are performed automatically by a built-in microprocessor or connected computer and displayed in tabular or graphical form.

Mold Filling Data.

Shear flow data obtained from the capillary rheometer are available in material databases such as those maintained by Moldflow Ltd. The data is used in software designed predict how an injection mold will fill. For this purpose the effect of changing temperature at a constant shear rate is needed, together with values that show the effect of changing shear rate at a constant temperature.

Tabulated Results.

The figures in the following table were obtained when samples of nylon 6 (PA 6), produced by Akzo, were tested. (Such results are typically obtained using a die with high L/D ratio, for example, 20:1) These figures clearly show that the three, injection-molding grades tested, have very different viscosities, with the first grade having the lowest, that is, it is the easiest flowing grade. It would be used where mold filling is difficult, or where long flow lengths are involved. The viscosities of all three materials fall as the shear rate is increased. Thus mold filling becomes easier at higher rates. Raising the melt temperature, while keeping the shear rate constant, reduces the viscosity and thus the amount of injection pressure required to maintain a certain rate of flow.

MOLD FILLING DATA FOR AKZO ‘AKULON’ PA 6.

Viscosities (Pa-s) at 1,000 sec^{-1} at the following temperatures:

Grade	**ºC/ºF** (240/464)	**ºC/ºF** (260/500)	**ºC/ºF** (280/536)	**ºC/ºF.** (300/572)
Easy flow	98	78	63	50
Medium flow	149	115	89	69
Stiff flow	394	319	259	210

Viscosity (Pa-s) at 280ºC/536º F

Grade	**100sec^{-1}**	**1,000sec^{-1}**	**10,000sec^{-1}**	**100,000sec^{-1}**
Easy flow	197	63	20	6
Medium flow	323	89	25	7
Stiff flow	1220	259	55	12

The Power Law Equation

In practice the slope of the log-log flow curve is not a straight line, as n* varies slightly with shear rate. However, for many purposes it may be assumed to be linear and is equated with a single value of n, the flow behavior index, or the flow index. Using this assumption the Power Law equations for flow are developed:

$$\tau = K\dot{\gamma}^{n} \text{ or } \eta = K\dot{\gamma}^{n-1} \quad \text{(Where } n = n^*\text{)}$$

This equation works very well with PVC and is often used to describe its flow behavior.

The Power Law

$$\eta_{pl} = m \left| \dot{\gamma} \right|^{n-1}$$

Where: m = Constant
n = Flow index
n < 1 for shear thinning fluids.
n = 0 for Newtonian fluids.

- **Describes only the shear thinning portion of the curve.**
- **The value of n ranges from 0.2-0.6 depending upon the type of polymer, MW, and MWD.**

Figure 12.

The Cross/Carreau Equation

By combining the Newtonian and Power Law Equations with a function to describe the "break" in the viscosity curve (See Figure 13.) Cross and Carreau (Chiang, H., Hieber, C., and Wang, K., SPE ANTEC Technical Papers, Vol. XXXIV, pp.1099-1102 (1988).) have developed and equations that fit many experimental viscosity curves very well. A combined form of these equations is shown in Figure 14. In this equation η_o is the "zero shear rate" or Newtonian viscosity for the particular polymer, n is its Power Law exponent, and $\tau^{'}$ is the shear stress at the "break". These equations along with the Power Law and several others are resident in the LabKARS Rheology Software used with the Dynisco Polymer Test LCR Series of capillary rheometers.

13.2 Effect Of Temperature

As can be seen in the data shown above and Figure 13 temperature significantly affects the viscosity of polymers. In general, viscosity decreases as the temperature is increased. Behavior contrary to this observation can usually be attributed to further reaction or cross-linking taking place in the material.

The Ahhrenius Equation

$$\eta = k\ e^{(E/RT)}$$

where:
η = shear viscosity
k = constant
E = viscous energy of activation for the polymer (Kj / mole)
T = the absolute temperature (in ^{o}K)
R = gas constant (0.008314 J / ^{o}K mole)

The Viscosity Curve

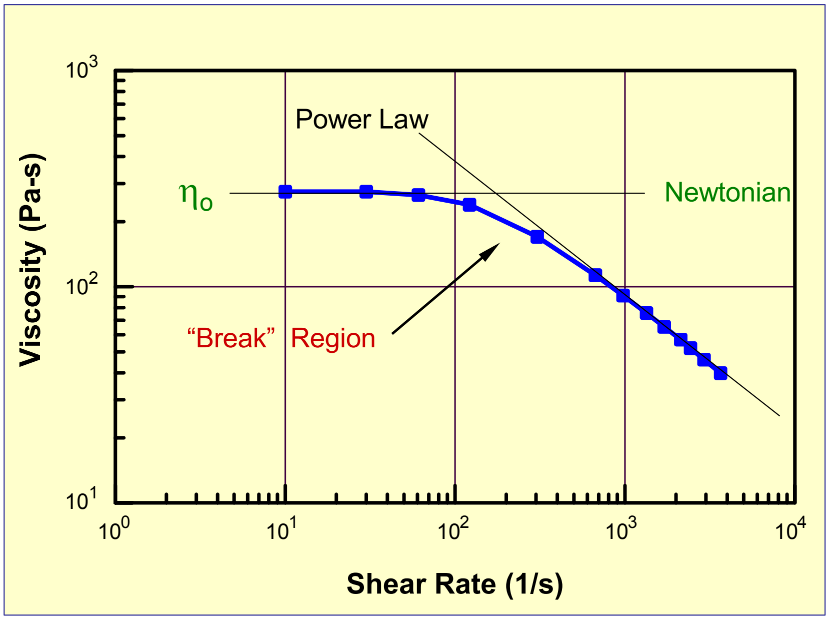


Figure 13.

The Generalized Cross-Carreau Equation

$$\eta = \frac{\eta_0}{\left[1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^a\right]^{\frac{1-n}{a}}}$$

- ➢**Combines the power-law and Newtonian regions of the complete flow curve.**
- ➢**Useful for numerical simulations that require a more complete description of the flow curve.**

n = Flow index
τ^* = Stress at the break in the curve.

a = 1 - n (Cross Model)
a = 2 (Carreau Model)

(Hieber & Chang, Cornell Univ.)

Figure 14.

is usually used to describe the temperature dependency of polymers at temperatures in excess of 100 °C above their glass transition temperatures (T_g). For most polymers a plot of ln η vs. 1/T yields a straight line over a temperature range of 50 – 150 °C. Thus if the viscosity of a polymer is known at temperature T_2 and we can calculate its viscosity at a temperature T_2 from the equation

$$\ln [\eta(T_1) / \eta(T_2)] = (E/R) [1/T_1 - 1/T_2]$$

using the activation energies shown in the table below.

EFFECT OF TEMPERATURE

Polymer	Activation Energy (Kj/mol)	% Change in η/°C	at Temp (°C)
PET	45	1.7	285
HDPE	25	1.4	190
LDPE	49	-	190
Nylon 6	36	1.7	230
PP	44	2.1	230
PC	85	3.1	300
PMMA	65	3.1	230
PVC	85	4.8	190

The table above also shows the percentage of change in the viscosity that occurs when the temperature, which is close to the temperature shown to the right, is increased by 1 °C. In general, the linear form of a polymer has the lower activation energy. As one increases the side chain lengths the activation energies tend to rise. (Note that PVC is very sensitive to temperature.)

The calculations shown above assume a constant shear rate. There are different activation energies if the measurements are made at constant shear stress. The relationship between the activation energies at constant rate and constant stress can be shown to be

$$E_\tau / E_\gamma = 1 - \gamma (\Delta\eta/\Delta\tau)_T$$

Where: E_τ = shear stress dependent energy of activation
E_γ = shear rate dependent energy of activation.

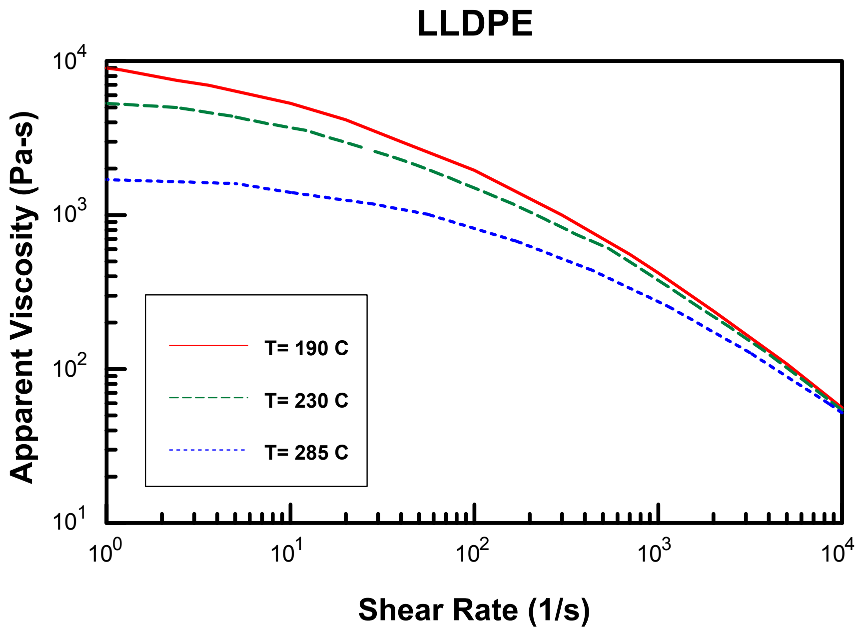


Figure 15. Effect of Temperature on Viscosity

The table below shows a comparison of the activation energies at constant shear rate and constant shear stress for a low-density polyethylene material in the range of 120 –230 °C.

Shear Rate ($\dot{\gamma}$)		**Shear Stress (τ)**	
(sec^{-1})	**E_γ (Kj/mole)**	**(Pa)**	**E_τ (Kj/mole)**
0	49	0	49
10^{-1}	43	10^3	57
10^0	39	10^4	68
10^1	32	10^5	72
10^2	27		
10^3	23		

13.3 Effect Of Pressure

Sometimes it is assumed that molten polymers are non-compressible fluids. It has been shown, however, that due to their molecular structures, they all have a certain amount of “free volume”. Under pressure this “free volume” is reduced resulting in a compression of the fluid, which causes an increase in the viscosity. It has been shown that the viscosity increases exponentially with increasing pressure and can be represented by the expression:

$$\eta\ (P) = \eta\ (P=0)\ e^{\beta P}$$

Where P is the pressure and β is the pressure dependence coefficient, which is characteristic of the polymer. Studies with polystyrene show that its viscosity doubles at a pressure of 10,000 psi (69 MPa). Some data for polyethylene are shown below

Polyethylene

($\beta = 0.0033\ \text{atm}^{-1}$)

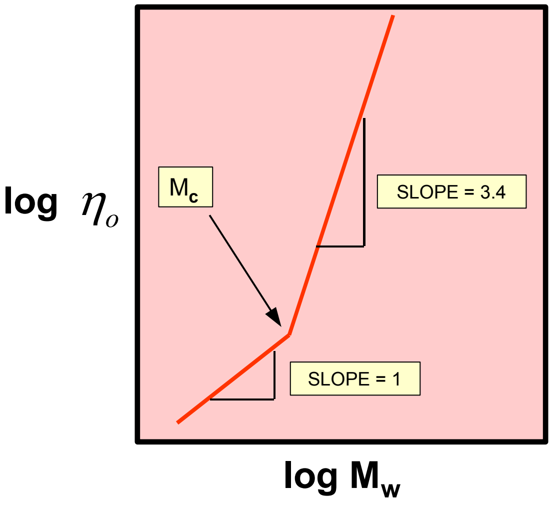
Pressure (atm)	η / η_o
30	1.11
100	1.39
300	2.70
500	5.29
1000	27.9
3000	22026

(1 atm = 14.5 psi ≅ 1 bar)

13.4 Effect Of Molecular Weight And Molecular Weight Distribution

Of all of the parameters that affect the melt rheology of a particular polymer, the molecular weight (which reflects the size of the molecules) is the most important. Below a critical molecular weight (M_C), where molecular entanglements begin to occur, there is a direct relationship between the melt viscosity and the weight average molecular weight (M_W). Above M_C the "zero shear rate" melt viscosity (where the viscosity becomes Newtonian) for a linear polymer depends on weight average molecular to the 3.4 power. (See Figure 16.) Above the Newtonian region the viscosity is still related to $M_{W,}$ however, the exponent decreases with increasing shear rate. For branched resins a relationship between viscosity and M_W exists that includes a constant branching parameter "g" and an exponent of 6.6 to 6.8. Thus as the average molecular weight increases we see an increase in the melt viscosity of a polymeric material. (See Figure 17.) It is interesting to note that while the shear sensitivity of most commercial polymers increases with increasing molecular weight, the temperature sensitivity and flow activation energy are not affected.

Relationship of the Molecular Weight to Melt Viscosity



$$\eta_0 = K_2 (M_w)^{3.4}$$

Where:

η_o= "Zero shear rate" melt viscosity.

K_2 = Constant

M_W = Wt. avg. molecular wt.

M_C = "Critical" molecular wt.

Figure 16.

Effect of Molecular Weight on Melt Viscosity

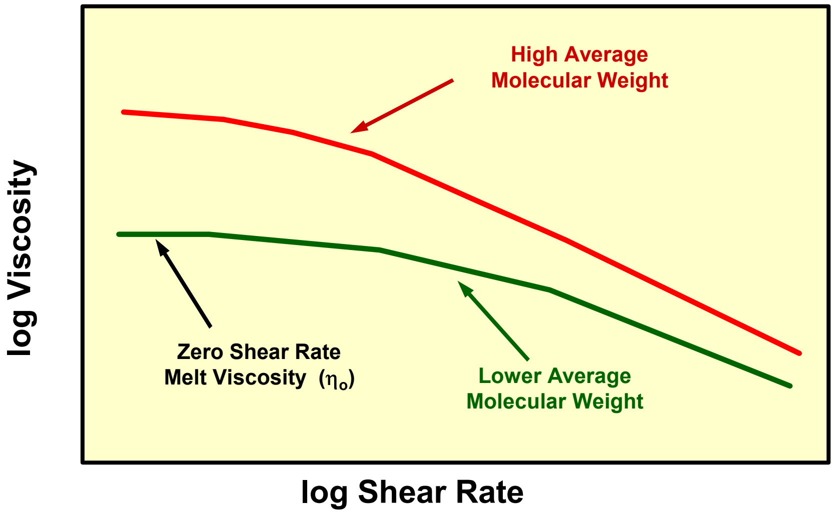


Figure 17.

The molecular weight distribution – MWD – (sometimes called the "polydispersity index) is usually defined as:

$$\mathbf{MWD = M_W / M_N}$$

Where: M_W = weight average molecular weight.
and M_N = number average molecular weight.

A MWD = 1 means that all of the molecules have the same size (or molecular weight) while a MWD > 1 means there is a range in the sizes of the molecules present. As the MWD becomes higher (broader MWD) more high and low molecular weight molecules are present in the polymer and this affects the shear thinning behavior of the melt. As shown in Figure 18 as the MWD broadens the shear thinning behavior begins at a lower shear rate. This often produces better processing conditions for a material, but may also cause a resultant deterioration in physical properties due to the presence of more low molecular weight molecules.

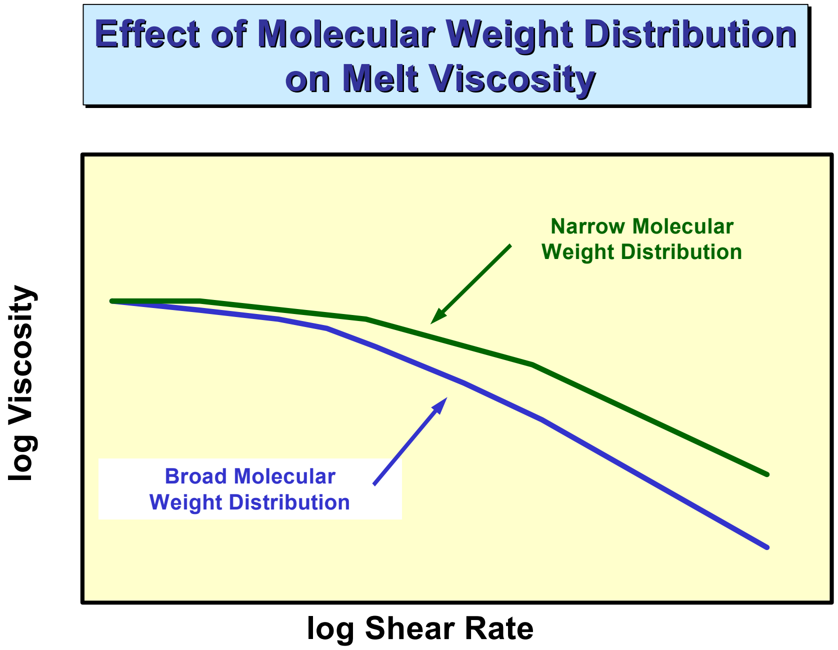


Figure 18.

13.5 Effect of Various Factors on the Viscocity Curve

Although we have discussed the effect of temperature, pressure, molecular weight and molecular weight distribution on the viscosity curve, there are many other factors that may change its behavior. Some these factors include the presence of other (compatable or incompatable) polymers, fillers, lubricants, or plasticizers. Since most plastics are composed of a blend of a polymer and one or more of these additives, their effect is important to the properties of the molten plastic. The specific effects of these additives can be found in many of the included references in the “For Further Reading” Section. Figure

19 provides a general guide to the effects of some additives, along with temperature, pressure and molecular weight, on the viscosity curve.

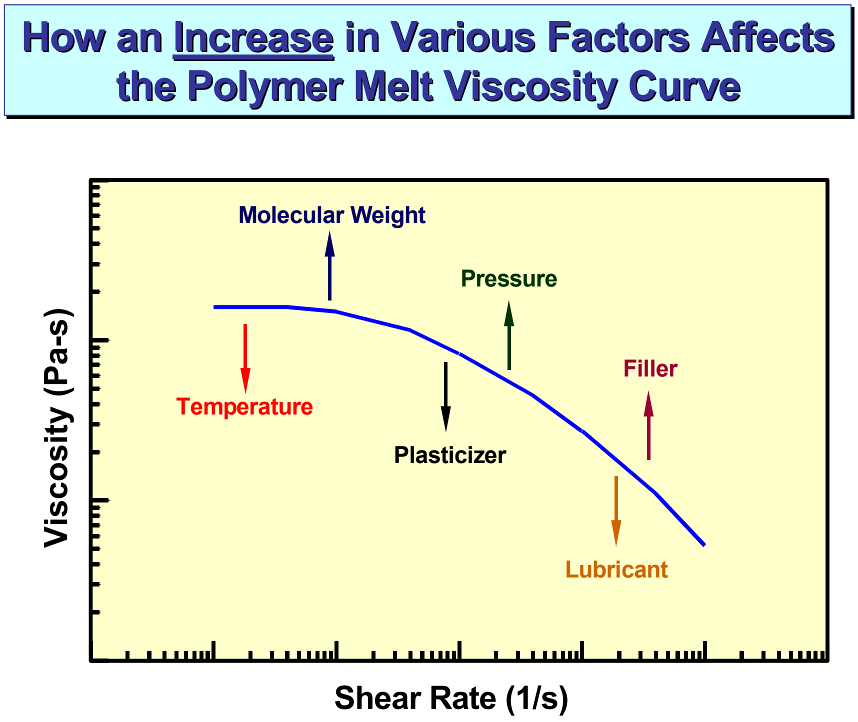

How an Increase in Various Factors Affects the Polymer Melt Viscosity Curve

Figure 19.

13.6 Thermal Stability

All of the discussions above have assumed that the polymer or plastic resin remains unchanged by the thermal conditions present in the test or process. As most polymers are organic (carbon based) compounds they are generally unstable towards exposure to the high temperatures they experience in conversion processes. For this reason the processes are generally designed to expose the polymer to the minimum time (residence time) possible. When a polymer is exposed to an □olysulfone high temperature for a short period of time or just a hot temperature for a long time it can be affected in one of two ways. Chemical bonds in the molecules can be broken to produce smaller molecules or the polymer can continue to react with other molecules or may crosslink to form larger molecules. (See Figure 20.) The former behavior can be seen in polymers such as PET, the nylons, and PMMA, while PVC provides a good example of the latter. In either case the melt viscosity will be affected. As shown in the earlier section, the molecular weight of a polymer has a very string effect on its melt viscosity. Thus degradation of the polymer chain will be seen as a decrease in the viscosity, while continued polymerization or crosslinking will be reflected in an increase. (See Figure 21.) In addition to affecting the melt viscosity of the resin, these processes invariably degrade the final mechanical properties of the finished part.

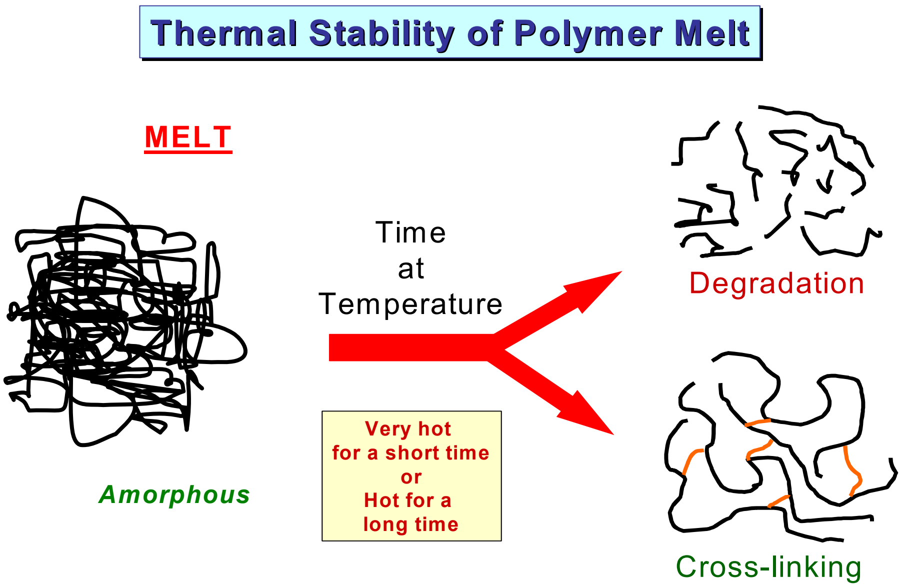


Figure 20.

As a result of the effect of temperature on the properties of a finished part, it is important to obtain a measure of the thermal stability of polymer or plastic resin at the temperatures used in the process. As the viscosity is very responsive to changes in the molecular weight of the polymer, it provides a sensitive measure its thermal stability.The

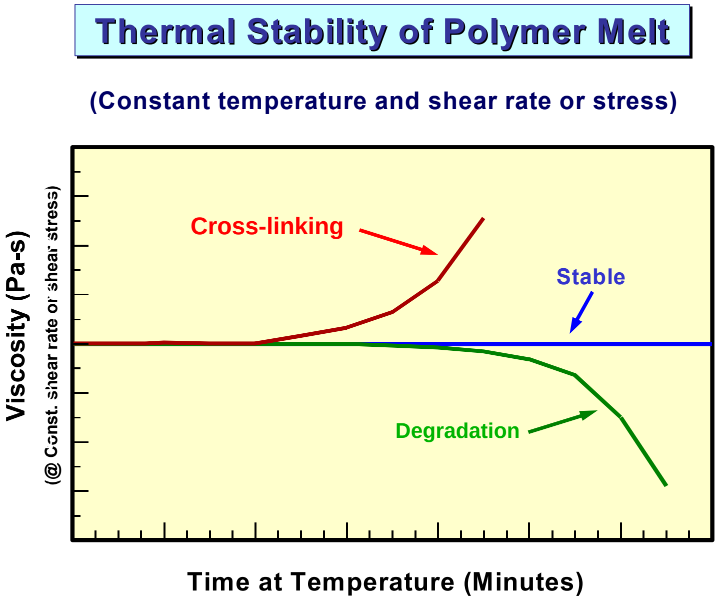


Figure 21.

rate at which degradation or crosslinking occurs in a polymer or plastic, at a given temperature, can easily be measured on a capillary rheometer. (See Figure 21.) In this test, sometimes called a “time sweep”, the rheometer is set up to perform measurements at one shear rate (or stress) at the set temperature. (It is best to use a moderately low shear rate to obtain the highest sensitivity.) When the test is initiated a first measurement of viscosity is acquired. The rheometer is then stopped for a pre-set period of time, after which another measurement is made. This procedure, which is usually controlled by a computer, is repeated until a pre-set total test time is reached. This test can then be repeated at a series of different temperatures. When the viscosity verses time data are fit to a line, one can obtain a measure of the rate of degradation or cross-linking. As an example of the data obtained from this test, Figure 22. shows the results from a series of “time sweeps” for Nylon 6/6 at a series of different temperatures. These data can then be used to set a “processing window” for this resin. (A similar test can be carried out using the MFR Tester – See the segment on MFR Testing in the Applications Section.)

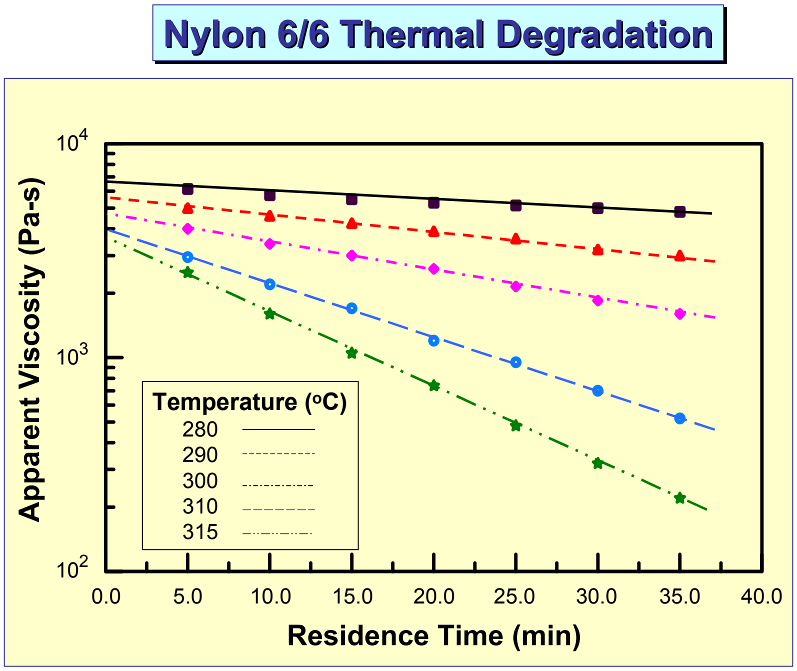


Figure 22.

13.7 Bagley, Rabinowitsch And Head Corrections

The flow curve that is most commonly produced from capillary rheometry data is one in which the shear stress at the capillary wall (τ_w) is plotted against the apparent shear rate at the capillary wall ($\dot{\gamma}_{a,w}$). These two material properties are obtained using the formulae:

$$\tau_w = \Delta P R_c / 2L_c \quad \text{and} \quad \dot{\gamma}_{a,w} = 4Q/\pi R_c^3$$

It is also common practice to define apparent viscosity (η_a) by the equation

$$\eta_a = \tau_w / \dot{\gamma}_{a,w}$$ (The symbol μ_a is sometimes used instead of η_a.)

The Rabinowitsch Correction

The Rabinowitsch Correction is a correction applied to viscosities, obtained from a capillary rheometer, to rectify the data for the non-Newtonian character of that fluid. For Newtonian fluids the apparent shear rate at the wall is equal to the true shear rate ($\dot{\gamma}_w$). However, for non-Newtonian fluids, such as polymer melts, the two are not equal but are related by the equation

$$\dot{\gamma}_w = [(3n^*+1)/4n^*]\ \dot{\gamma}_{a,w}$$

Where $n^* = [\Delta \log(R\Delta P/2L)]/[\Delta \log(4Q/\pi R)^3]$

This equation is referred to as the Rabinowitsch Equation and the term in square brackets is known as the Rabinowitsch Correction. While in theory the magnitude of the correction could range from 1 to ∞, the maximum error in the viscosity at any shear rate has been shown to be 15% when n* is 0.23. Generally, it is less than 15% when dies of L/D of 20:1, or greater, are used.

Approximate Method (Macosko, pp 242-4)

When one compares the true shear rate at the wall and the apparent shear rate, it can be shown that they are equal near the wall. (See Figure 15) It has been determined that this occurs at a point that is 83% of the capillary radius. Thus an approximate value of the shear rate at the wall can be found from the relationship

$$\dot{\gamma}_w = (0.83)\ \dot{\gamma}_{a,w}$$

It has been shown that this approximation produces an error of less than 2% for a range of n values from 0.2 to 1.3. The main danger in using this approximation is when the fluid is very strongly shear thinning ($n \leq 0.1$), where significant error occurs.

Correction: Use and Application. It should be borne in mind that:

1. For comparative purposes applying the correction will not alter the comparability of the data.

2. For a tubular die the relationship between shear stress at wall and the apparent shear rate at wall is unique and does not depend on the size of the tube or capillary.
3. The apparent flow curve ($\dot{\gamma}_{a,w}$ vs. τ) can be used for calculating data for flow through slits with a maximum error of as little as 3%, which is within the accuracy of most measurements.

For these reasons, the only occasion where it is necessary to use the correction is for research or for design purposes, where it is required that the true shear rate be known. For practical scale up purposes it is not important. A knowledge of n* is useful, however, as a measure of the degree of non-Newtonian behavior of the melt. The lower the value of n*, the more non-Newtonian the melt.

The Rabinowitsch-Mooney Correction

Corrects shear rate at the wall
for non-Newtonian fluids.

$$\dot{\gamma}_w = \left[\frac{3n+1}{4n}\right]\left(\frac{4Q}{\pi R^3}\right) = \left[\frac{3n+1}{4n}\right]\dot{\gamma}_{w,a}$$

Where:

$$n = \frac{d\ln(R\Delta P/2L)}{d\ln(4Q/\pi R^3)}$$

= “Flow Behavior Index” (Power Law)
(= Slope of τ_w vs. γ - Varies with shear rate.)

$\dot{\gamma}_{w,a}$ = Apparent wall shear rate

Effect of Flow Index on Shear Rate

Flow Index (n)	(3n + 1) / 4n
1.00	1.00
0.75	1.08
0.67	1.12
0.50	1.25
0.33	1.51
0.25	1.75
0.10	3.25

Figure 23.

The Bagley Correction

The Bagley Correction, also known as The Bagley Entrance Correction, is possibly of greater practical importance than the Rabinowitsch correction.

There is an incorrect assumption in the basic analysis for flow through a tube that all of the energy involved in forcing the material through a tube is absorbed over the length of the tube. In reality, some energy is used in funneling molten polymer molecules from the barrel or reservoir into the die. Much of this energy absorption is due to that involved in deforming the polymer molecules as they are suddenly subjected to an increase in elongation just above the die. This required extra energy input appears as equivalent to an increase in the effective length of the die.

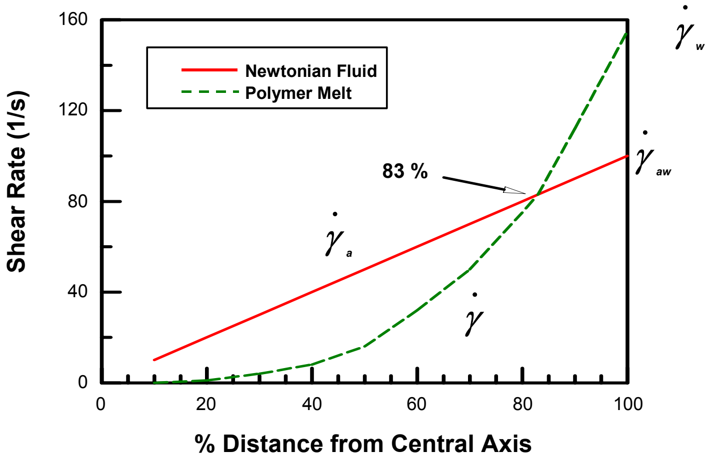


Figure 24.

Bagley measured the pressure drop (ΔP) against $\dot{\gamma}_{w,a}$ using a series of dies with the same diameter, but different L/D ratios. The subsequently derived plots of ΔP against L/D at constant shear rate showed an effective increase (e_o) in length/diameter ratio, which can be obtained by reading off the negative intercept of the ΔP-vs.-$\dot{\gamma}_{w,a}$ plot. In this case the true shear stress is given by

$$\tau_{true} = \Delta P/[2(L/R) + e_o]$$

Some measure of the error involved in not considering the Bagley correction may be gauged by considering a tube with a L/R ratio of 10/1 and a polymer melt with a Bagley correction factor (e_o) of 5. Ignoring the correction would give a wall shear stress of ΔP/20 whereas using the correction will give a value of ΔP/30, a 50% error!

Alternatively, one can determine the value of ΔP at each shear rate when the line in the ΔP-vs.-$\dot{\gamma}_{w,a}$ plot reaches L/R = 0. This value, designated as ΔP_o, represents the pressure drop for a “zero length” die. Since the die has zero length we can assume that no shearing takes place and the entire pressure drop is due to the extension of the polymer molecules. (Cogswell has used this assumption to develop a method and equations for the measurement of extensional viscosities with the capillary rheometer. If one uses a “zero length” or very low L/D die it is possible to easily obtain relative values of the extensional viscosities of different polymers.) Thus if we subtract this pressure from the total measured pressure, we can calculate the true shear stress.

$$\tau_{true} = (\Delta P - \Delta P_o) / 2(L/R)$$

The Bagley Correction

Corrects shear stress for entrance pressure drop.

$$\tau_w = \frac{(\Delta P)R}{2(L + e_o R)} = \frac{\Delta P}{2(L/R) + e_o} = \frac{\Delta P - P_o}{2(L/R)}$$

Where:
e_o = End Correction Factor
P_o = Pressure Drop
at L/D = 0

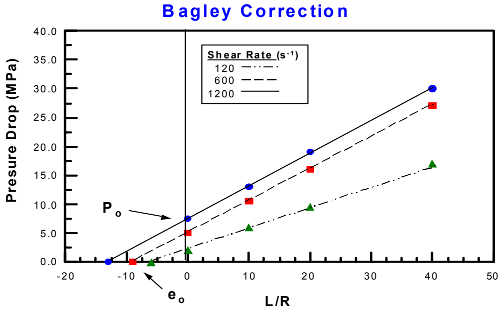


Figure 25.

Yet another method of correcting for the entrance effect, similar to that discussed above, is that known as the Couette-Hagenbach method. This is a ‘difference’ method in which two dies of different lengths L1 and L2 are used and for each of which the output Q for a series of pressure drops ΔP are obtained. Since for each die at a given shear rate the entrance effect is the same, the pressure drop and length of the shorter die can be subtracted from those of the longer die to give an estimate of the pressure drop ΔP1-ΔP2 for a hypothetical die of length $L_1 - L_2$. From this, the true shear stress at wall may thus be obtained from the formula

$$\tau_w = (\Delta P_1 - \Delta P_2) / 2(L_1 - L_2)$$

While this approach does correct for the entrance effects, it gives no idea of the magnitude of the error, which may be of interest in scale-up.

Head Corrections.

In some rheometers, and particularly those used for measuring flow rate (MFR or MFI), the force used to push melt through the die is measured above the melt in the reservoir (usually by measuring the weight or force put onto the melt.) There will be some error in the flow curve calculation if pressure losses in the reservoir are ignored. It may be shown that when the length of melt in a reservoir of radius R_b is L_b and the length and radius of the capillary are L_c and R_c, respectively, the ratio of the pressure drop in the reservoir or barrel (ΔP_b) to the pressure drop in the capillary or die (ΔP_c), for a true power law fluid, is given by:

$$\Delta P_b/\Delta P_c = (L_b/L_c)\ (R_c / R_b)^{(3n^*+1)}$$

In the determination of melt flow rate, most standards now specify that measurements must be made with the piston within fairly closely defined limits above the die. This is done to assure that, in all measurements, the amounts of material in the reservoir are similar.

Combined Rabinowitsch and Bagley Corrections Of Shear Rate and Shear Stress

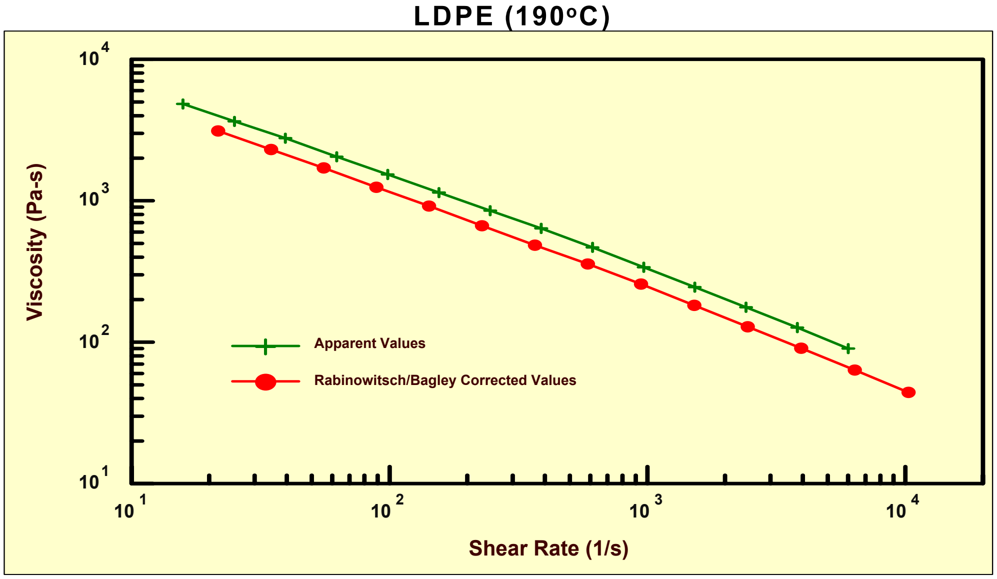


Figure 26.

Wall Slip.

Flow analysis generally assumes that there is no slip of the melt at the wall of the capillary. However, this assumption is not necessarily true (particularly at high shear rates.). If such slip exists, then a form of plug flow is superimposed on the normal laminar flow pattern. It has been shown [Lupton and Regester, Polymer Engineering & Science 5 235 (1965)] that if the wall slip velocity is V_a, Q is the volumetric flow rate, and R_c is the capillary radius, then:

$$4Q/\pi R^3_c = 4V_a\ (1/R_c) + X\ )$$

where **X** is a function of the shear stress.

To obtain a correction for this a series of flow curves is produced using a set of dies of varying radius R_c. Then, using measuring $4Q/\pi R^3$ at a given value of shear stress, a plot may then be obtained of $4Q/\pi R^3_c$-vs-$1/R_c$. The slip velocity will then be one quarter of the slope of this plot. This may then be repeated at other shear stresses and this will enable a plot of slip velocity against shear stress to be developed.

14. MEASUREMENT OF EXTRUDATE SWELL

Die swell is also known as die swell, swelling ratio or puff-up ratio and is defined as the ratio of the diameter of the extrudate to the diameter of the die.

Errors due to drawing down. Accurate measurement, and interpretation of extrudate swell requires care. When it is measured on samples extruded downwards from a capillary rheometer the weight of the extrudate may to cause drawing down (stretching). Drawing down can be avoided by extruding into a bath, containing a liquid of the same density as the polymer, located immediately below the die. The effect of draw down, however, may be more conveniently minimized in other ways.

Minimization of errors. Draw down may be minimized graphically. Measurements of extrudate diameter are made at several points away from the leading end of the extrudate (obtained when cutting the extruded sample at the die outlet). By means of a graph, the theoretical die swell at this leading edge may be found by extrapolation. There is little loss in accuracy if the experimenter always makes the measurements at the same distance from the leading edge. The distance chosen is that at which the extrudate swell is approximately a maximum.

Circular cross-section. To ensure that a circular cross-section is obtained from the die or capillary, the extrudate must be given time to freeze while suspended since it can distort if allowed to lie on a surface before it has hardened. This distortion may be a problem when extruding unvulcanized rubber compounds, as extrudates made from such soft materials may distort under their own weight even when cold.

Diameter Determination.

Providing the extrudate is smooth and circular, the measurements of diameter may be made using a projection microscope. If a laser micrometer is available, very accurate measurements (of the extrudate and of the die) can be made relatively easily. Such data may be logged into the computer of interfaced to the rheometer. (This is the method used with the Dynisco Polymer Test LCR 7001.) If the sample is not round and smooth or if the extrusion exhibits sharkskin or melt fracture the best procedure is to weigh (M) a known length (L) of the extrudate. From these data and knowledge of the density (ρ), the extrudate diameter (D) can be calculated from the equation:

$$D^2 = 4M/\pi\rho L$$

Since it is usually required to know the ratio of the product diameter/die diameter, it is satisfactory to use the density of the solid polymer. In the case of crystalline polymers, however, the density will depend on the rate of cooling from the die. For accurate measurement the density should be obtained from the extruded sample.

Measurement of Extrudate Swell

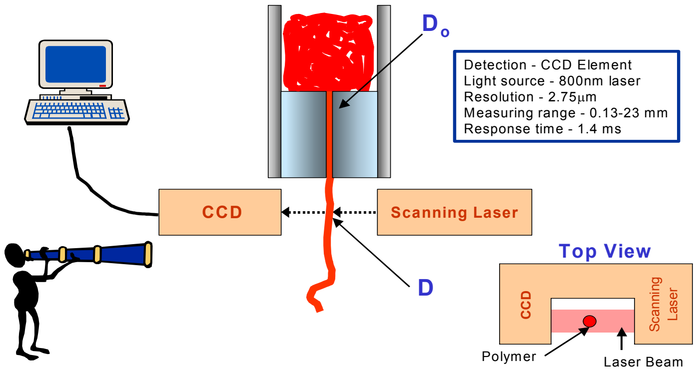


Figure 27.

Errors due to molecular factors. For semi-crystalline thermoplastics, estimates for the extrudate swell of large diameter slow cooling industrial extrudates, obtained from fast cooling small laboratory samples, may show some error. A source of this error may arise from the freezing of the extrudate before the polymer molecules have had a chance to recoil or relax after emergence from the die. This is a greater problem with small diameter extrudates and thus a source of scale up error. Error in the laboratory samples may be reduced by allowing them to anneal at a temperature 50-60ºC, above the glass transition temperature. On occasion it may be desired to know the ratio of the melt diameter/die diameter. In this case the melt density must be used in the formula above. When projection microscopy is used, the measured value of the diameter of the solid extrudate should be multiplied by the ratio solid density/melt density.

Viscosity and Extrudate Swell as a Function of Shear Rate

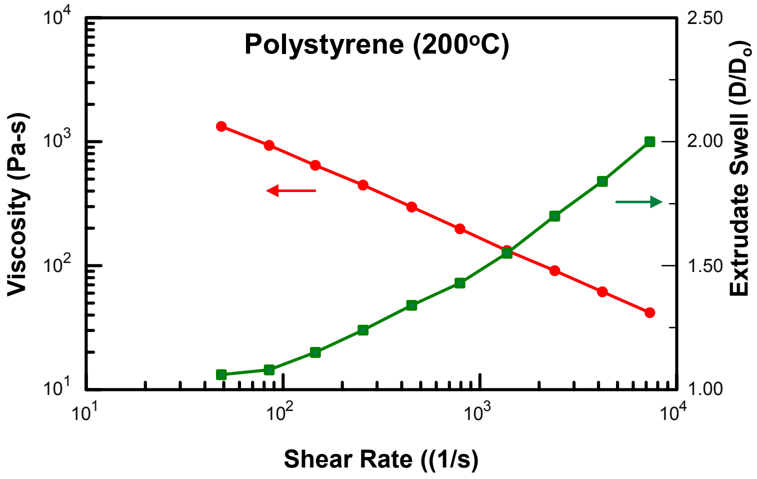


Figure 28.

15. APPLICATIONS OF RHEOLOGICAL DATA

15.1 Novel Applications Of The MFR Tester

The ability of the standard MFR instrument to characterize polymers is considered by some to be rather limited. However, the capabilities of this instrument for polymer testing go well beyond those achievable strictly by the standard tests. Several of these applications are discussed below.

<u>Shear Thinning of the Melt</u> – The MFR test is sometimes criticized for being a single point test. Because of their nature, the flow properties of polymers usually vary with the force or rate at which they are deformed. As a result of the orientation of the polymer molecules, their flow rate often increases faster than expected as the deformation rate or force is increased. Therefore, a function rather than a point will best describe their flow behavior. This behavior can be gauged with the MFR tester by measuring the melt flow rates generated using a series of two or more different weights. The slope of the curve obtained by plotting the weight verses the MFR will give a measure of this "shear thinning" function [See Yoo, H.J., et. al., SPE ANTEC, Technical Papers, Vol. XXXIX, pp. 1444-47 (1993)]. For some polymers this slope can be roughly related to its molecular weight distribution. (See Figure 25.) Note in the figure that resins PE-2 and PE-5 have the same MFR in the standard low load (2.16 Kg) test, but are very different at the higher loads. Thus, whereas the standard MFR test would indicate that the resins are the same, they are not.

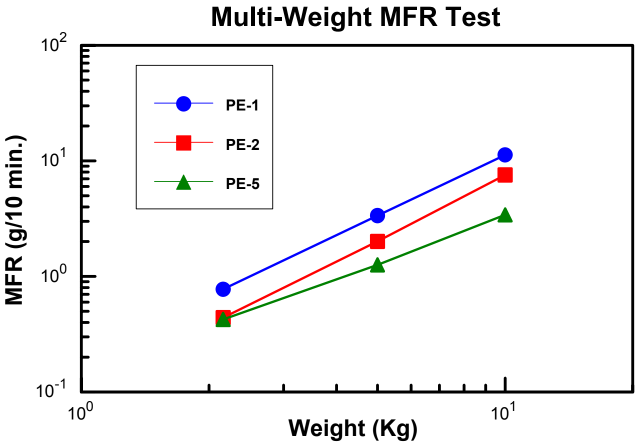


Figure 29.

<u>Extrudate Swell</u> – When polymer melt emerges from a die the extrudate may swell so that its cross-section, after it leaves the die, is significantly greater than that of the die orifice. This source of this swelling is from the extension or, orientation, of polymer molecules as they pass through a die. On exiting the die the molecules tend to re-coil back to their original configuration, which causes the extrudate to expand perpendicular to the flow. The extrudate swell is defined as the ratio of the extrudate diameter to that of the die. This value is very important to anyone extruding a profile, where dimensions are critical.

The melt index test itself will not give a measure of extrudate swell. However, a semi-quantitative measure of the relative swell values for a product can be obtained from measurement of the length the polymer strands produced during equal extrusion times. The shorter the strand the greater will be the extrudate swell. All other things being equal, a material that swells more is more "elastic" and will show less sag in thermoforming operations.

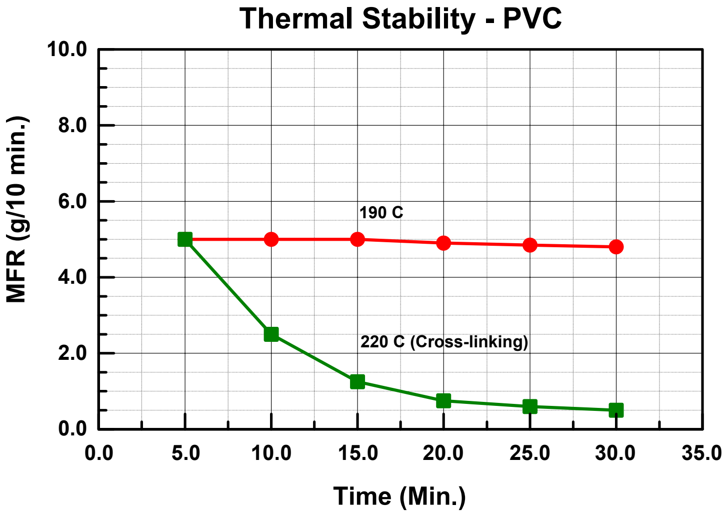


Figure 30.

Thermal stability – The stability of a polymer product at processing temperatures will often determine if a material can be successfully formed into useful products that don't fail in service. While the melt indexer is often used to determine if a material has degraded, after the fact, it can also be used to determine if a virgin material has the stability required to stand up to a process. To do this one need only set up the MFR test by the standard procedures. Then a separate timer should be started once the barrel is filled and the piston inserted. Next conduct a standard Method A or B test noting the MFR and the completion time from the timer. While supporting the weight and piston, pause for a period of time, say five or ten minutes and then, run another test and record the MFR and time. This procedure can be repeated several times. The results, plotted as MFR verses time at temperature, will then reflect any changes taking place in the resin and the rate at which they occur. An increase in MFR will indicate that the polymers are degrading, while a decrease will indicate the possibility of cross-linking taking place (See Figure 26.). This test can be repeated at other temperatures to establish the "processing window" of a material.

Intrinsic or Relative Viscosities – Intrinsic or relative solution viscosity measurements have traditionally been used to estimate the molecular weights of polymers. They are extensively used in the manufacture of PET, nylons, and other polymers. These tests, however, are time consuming, require laboratory facilities, and necessitate the disposal of the frequently unfriendly solvents used. The melt viscosity, and therefore the MFR of a polymer, is also directly related to its molecular weight. (In fact, it is five times more sensitive than the solution viscosities.) Thus a relationship exists between the two methods and MFR measurements can be used to determine solution viscosities. Figure 27 shows that a semi-log plot of the MFR of several intrinsic viscosity standards produces a straight line. Thus once this relationship is established the IV can be determined from MFR in a short time and without the use of unfriendly solvents. [See Reilly, J.F. and Limbach, SPE ANTEC, Proceedings Vol. XXXVIII, pp 812 – 15(1992)].

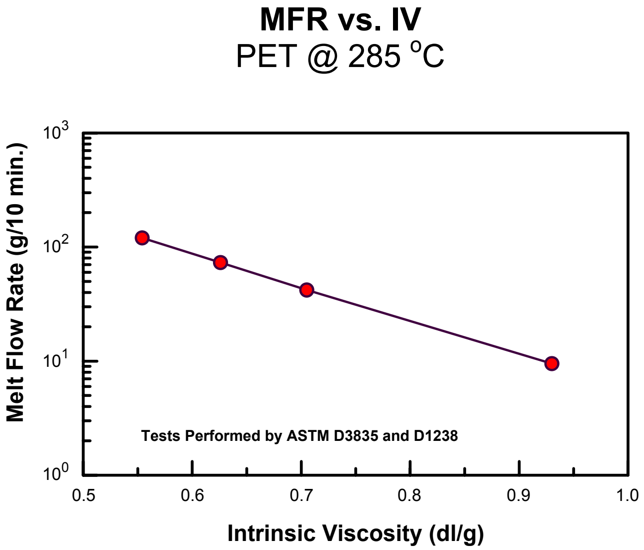


Figure 31.

15.2 Correlation Of Polymer Melt Rheology To MFR

A correlation of the shear flow based melt rheology to melt flow index (MFR, g/10min) or melt volume index (MVR, cc/10min) is made by the following procedure: 1.) Match the shear stress achieved in the melt indexer on shear stress verses shear rate curve. 2.) Determine the shear rate achieved at this shear stress. 3.) Calculate the volumetric flow rate from the shear rate and die geometry.

Method

The MFI test is performed under a condition of constant stress. The stress exerted upon a molten polymer in the melt flow indexer is calculated from the weight of the piston and standard weight, piston face area, and the die geometry. A table of these stress values for the ASTM D-1238 test specification is shown below. (Similar values can be calculated for the ISO 1133 test.)

Shear Stresses in ASTM D-1238 Tests

Test Load (weight + piston) (g)	Shear Stress (psi)	Shear Stress (kPa)
325	0.4256	2.932
1050	1.3750	9.474
1200	1.5714	10.827
2160	2.8318	19.511
3800	4.9762	34.286
5000	6.5476	45.113
10000	13.0952	90.226
12500	16.3690	114.256
21600	28.318	195.11

A laboratory capillary rheometer can be used to obtain a measure of the MFI by a determining of the volumetric melt flow rate from a curve of shear stress verses shear rate, at constant temperature. Such a curve is shown below.

As shown in Figure 28 below, a horizontal line at the shear stress in the MFI test is extended to the curve. The corresponding shear rate is determined from a vertical line dropped to the shear rate axis. A second order polynomial fit of the rheometer data is used in the LabKARS Software to interpolate these values. (A Rabinowitsch Correction is performed on the data prior to interpolation.) The resultant shear rate is used in the volume flow rate equation, with the dimensions of the melt flow indexer die, to determine the flow rate in the indexer at that shear rate.

$$\textbf{\textit{Volumetric Flow Rate}} = \boldsymbol{Q} = \frac{\mathbf{600}\,\dot{\gamma}\,\pi\,\boldsymbol{R_c^3}}{\mathbf{4}} = \mathbf{0.542}\,\dot{\gamma}$$

Where R_c^3 = MFI die radius in cm (0.20955/2) and the constant 600 converts from units of 1/seconds to 1/ 10 minutes. (From the above it can be seen that to a first approximation the volumetric flow rate is about one half the shear rate at the melt flow indexer stress level.) The above equation produces the melt volume index (MVI) in cc/10 minutes. The melt flow index (MFI) in g/10 minutes is obtained when the MVI is multiplied by the polymer melt density at the test temperature. Note: Flow in the short (L/D=3.818) melt flow indexer die is not all shear flow. When extensional effects produce a significant fraction of the pressure drop, the predicted MFI will tend to be higher, since extensional effects are ignored in the calculation. If, however, two rheometer dies are used the entrance effect can be estimated and a more accurate MFI produced.

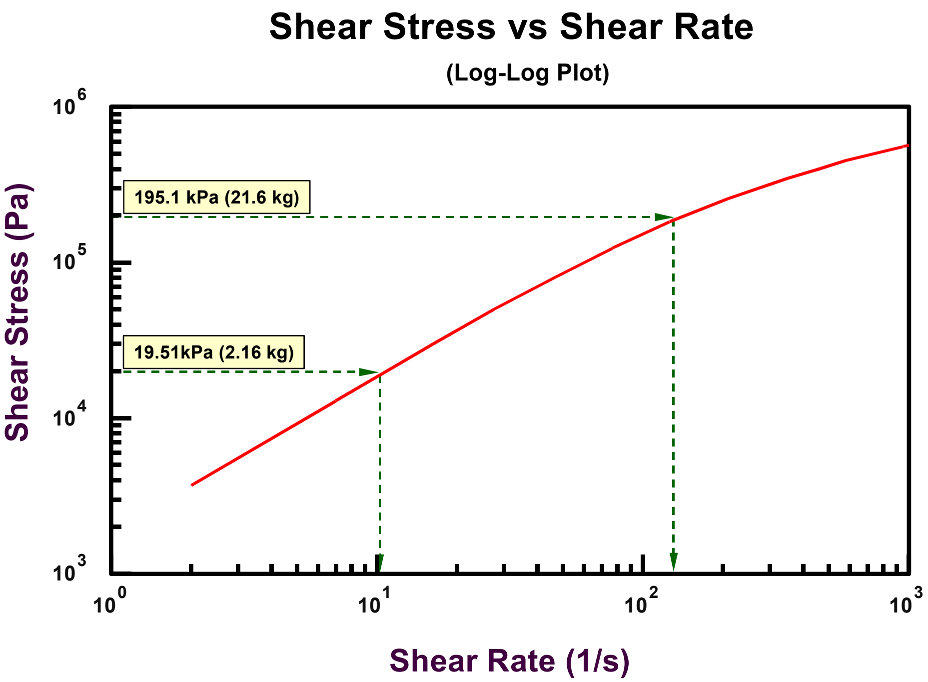


Figure 32.

15.3 Applications In Extrusion Pressure Drop In A Die

Pressure is required to force a liquid, such as a polymer melt, through an extrusion die. In the case of extrusion dies this pressure is usually produced by an extruder screw that pumps material to the die face where pressure is built up by the restricting effect of the die.

Simple Die Characteristics

In the case of a simple extrusion die of any shape, where the cross-section of the channel is constant from its inlet to exit:

1. The pressure is greatest at the die entry.
2. The pressure is virtually zero at the die exit (and for most purposes may be equated with zero).
3. The pressure drop from the inlet to the exit is linear.
4. When the inlet pressure is denoted by ΔP and the length of the die is L, $\Delta P/L$ is constant along the whole length of the tube.

Calculation Of Pressure Drop In A Capillary Die

The pressure drop in a constant cross-section die (which is fed from a reservoir of material at the die head) is related to the output rate, the die dimensions, and the melt viscosity. For a simple rod die, the pressure drop is calculated by the following procedure:

1. Determine the apparent wall shear rate from the formula $\dot{\gamma}_{w,a} = 4Q/\pi R^3$.
2. Read off the wall shear stress (τ_w) corresponding to this shear rate value from the flow curve for the appropriate polymer at the extrusion temperature.
3. Calculate the pressure drop (i.e., the pressure developed at the back of the die parallel) from the shear stress by the formula $P = 2L (\tau_w) / R$ where L is the length and R the radius of the parallel portion of the die.

Calculation Of Pressure Drop In A Slit.

For a slit die the shear rate is given by

$$\dot{\gamma}_{a,w} = 6Q/Wh^2$$

where w is the width of the slit and H its thickness (or depth). The flow curve, even though it may have been prepared from capillary data, may then be used to read off the corresponding shear stress. In turn the pressure drop is obtained from the expression

$$P = 2L\,\tau_w / H$$

Calculation Of Pressure Drop In A Tapered Capillary Die

In the case of a tapered die, the radius at the inlet is called R_1 and at the outlet R_2. As with the capillary die, the shear rate is first determined applying the capillary formula using the inlet radius. The shear stress at that shear rate is determined from the flow curve. The pressure drop is then given by:

$$P = [2\,\tau_1 / 3\tan\theta] / [R_1 / R_2)^3 - 1].$$

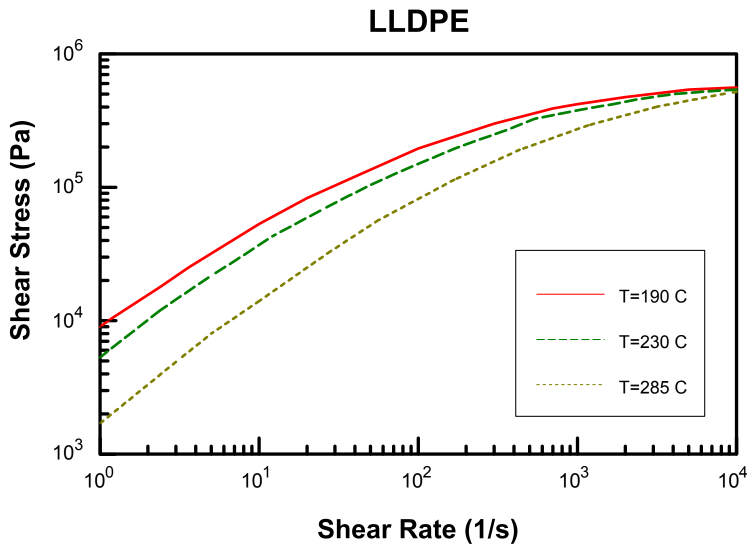


Figure 33. Polymer Flow Curves Used for Determinations of τ_w

Sizing Of Die Components

The cross-section of an extrudate will not always be the same as the outlet cross-section of the die from which it has been extruded. There are three reasons for this:

1. Shrinkage of the extrudate on cooling.
2. Extrudate or die swell.
3. Draw down (stretching of the extrudate on emergence from the die).

During rheology testing, die swell measurements can be made relatively easily. A common use of such measurements is to size die components. The magnitude of the shrinkage is usually quite small and since die swell measurements are usually based on cold extrudates this factor is usually built into any die swell assessment. Whereas die swell increases the cross section, drawing down reduces it.

Correction Factors.

The relationship between the cross-section dimension of an extrudate **E** and the cross-sectional dimension of a die **D**, is:

$$\mathbf{E = sdD.}$$

In this equation, **s** is the die swell ratio at the wall shear rate occurring during extrusion. **D** is the draw down factor defined by $\sqrt{(\mathbf{L_d - L_u})}$. $\mathbf{L_d}$ is the length of material produced in a unit of time in the process in which draw down has taken place and $\mathbf{L_u}$ is the length of material naturally extruded in unit time without any drawing down having occurred. (The square root term arises since it is the cross-sectional area rather than a single dimension e.g. diameter that decreases inversely with the extent of draw-down.)

Sizing Pipes.

A further complication arises in pipe manufacture, where it is common practice to inflate the tube to the inner diameter of a sizing die. In this case, if the outer diameter of the extrusion die annulus is $\mathbf{d_o}$ and that of the inner diameter of the sizing die annulus is $\mathbf{d_s}$, then the thickness of the pipe **T** will be related to the annular gap of the die, **A**, by the relationship:

$$\mathbf{T = s\sqrt{(L_d / L_u)}\ (d_s / d_o)A}$$

Estimation of Pressure Drops in Extrusion Dies

The relationships between pressure drop (**P**), output rate (the flow rate **Q**), and viscosity for various flow cross-sections may all be arranged to take the form

$$\mathbf{P = \eta \times R \times Q.}$$

Where **R** is called the die resistance.

Die Resistance.

Die resistance is a measure of the resistance of a flow channel to the passage of the polymer melt. For regular channels of simple shape it is easily calculated from their dimensions. For regular extrudate sections include rod (cylinder), sheet (rectangle), and pipe (annulus), the formulae for calculating the die resistance are:

1. **Rod or Cylindrical Channel**.

   Length = L; Radius = r; Diameter = d.

   Die resistance = $\mathbf{R = 8 (L) / \pi r^4 = 128 (L) / \pi d^4}$

2. **Rectangular Channel**.

   Length = L; Width = w; Thickness = t.

   TABLE T. When the width is more than 10 times thickness

   Die resistance = $\mathbf{R = 121 / w t^3}$

   b.) Where width is less than 10 times thickness

Die resistance = R = 121S / w t^3

S = Shape factor and is given in Figure 3.

3. **Pipe or Annular Channel.**

Length = 1; inner diameter =d_I, outer diameter = d_o, Gap thickness, t = 1/2(d_o-d_i)

Average diameter, d = 1/2(d_o + d_i)

Die resistance = R = 121 / π d t^3

Calculating Die Resistance (Example For Pipe Die Land.)

Consider a land of length 50 mm, with an internal diameter of 100 mm, and external diameter of 104 mm. The average diameter is 102 mm and the gap thickness is 2 mm. Using the formula given above:

Die resistance = R = 12.50 / π $(102.2)^3$ = 0.234 mm^{-3}.

Flow Rate

When calculating pressure losses, flow rates must be expressed as volume flow per unit time. If the mass flow rate, for a melt of density D at the processing temperature, is known as M (kg/h) then the volume flow rate (Q) in mm^3/s is:

$$Q = 278{,}000\ (M / D).$$

If a melt flow rate tester that can do a method B test is available the melt density (D) may be measured directly.

Correction Method For Plastic Melts

The fact that molten plastics are non-Newtonian introduces two complications in calculating pressure losses. First, the viscosity of molten plastic is not constant and second, the flow pattern in a channel is different from that of a simple Newtonian fluid. (The viscosity of a simple, or Newtonian fluid is a constant, which depends only upon the temperature.) These problems can be overcome by using apparent viscosities and representative values.

Apparent Viscosity.

If the shear stress at a particular shear rate is known for a plastic melt, then the ratio shear stress/shear rate is called the apparent viscosity. The apparent viscosity generally decreases as shear rate increases. To calculate pressure losses in a process it is necessary to have a graph of apparent viscosity against shear rate for the material at a particular temperature of the melt. These flow curves can be obtained from material suppliers, measured in the laboratory (see Figures 10 and 11 and the section on 'Rheology Equipment and Testing'), or it may be calculated approximately from the MFR of the plastics material. Figure 15 shows a flow curve that will be used as an example here.

Representative Values.

At a given overall output rate, the flow pattern of a molten polymer in a channel will differ from that of a simple Newtonian fluid. Figure 31 shows flow patterns through a 20mm diameter tube for a Newtonian and for a non-Newtonian fluid (polymer melt). The polymer melt is assumed to have a melt flow index (MFR) value of 0.3. Both materials have zero flow velocity at the walls of the tube and maximum flow velocity in the center of the tube. For the same output rate (and hence the same average flow velocity) the polymer melt has a lower maximum velocity and more of a plug like flow. The flow velocity is nearly constant across the middle of the tube and decreases rapidly near the walls. As a result, the shear rate, which controls the localized rate at which layers flow over each other, is greater near the walls in the case of the polymer melt than for a Newtonian. Near the walls of the flow channel there can be a large difference in shear rates as shown in Figure 30.

There is a fairly complex way of relating Newtonian and non-Newtonian shear rates at the wall called the Rabinowitsch correction. However, it is simpler to consider the situation where the two lines in Figure 31 intersect. Here Newtonian and non-Newtonian shear rates are equal. The value of shear rate at this point is called the representative value. By using this value it is possible to calculate pressure drops using a method similar to that used for Newtonian fluids (see W. Michaeli in his book 'Extrusion Dies').

Representative Shear Rate

It has been found that the position of the representative shear rate in a flow channel is nearly constant for plastic melts. For a tube, it is at 83% of the distance from center to walls. The formulae for calculating the representative shear rates are as follows:

For a rod die: $\dot{\gamma}^* = 3.3Q/\pi r^3$

For a rectangular channel: $\dot{\gamma}^* = 4.6\, Q/b\, t^2$

For an annulus: $\dot{\gamma}^* = 1.46\, Q/d\, t^2$

Flow Through a Die for a Newtonian Fluid and a Non-Newtonian Polymer Melt

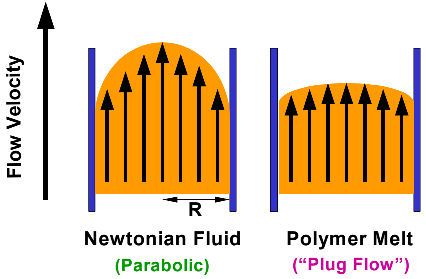
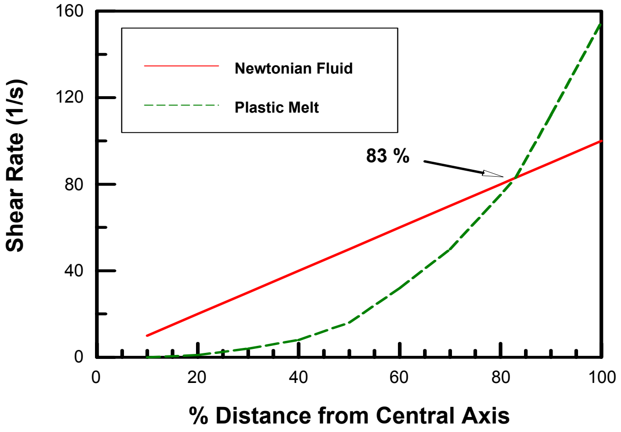


Figure 34.



Shear Rates in a Die

Figure 35.

Representative Viscosity

Once the representative shear rate is determined, the flow curve for the plastic melt is used to find the apparent viscosity of the melt at this shear rate. This apparent viscosity is called the representative viscosity (η_R) and if substituted in the equation

$$P = \eta_R \times R \times T,$$

it may be used to calculate pressure drops.

Pressure Drop Calculation Using Representative Viscosity

Suppose the pipe die whose die resistance was calculated above, extrudes plastic melt at 180 kg/h, the melt has a density of 800 kg/m³, and its flow properties are as shown in Figure 15.

Flow rate: $Q = 278{,}000 \times 180/800 = 62{,}550\ \text{mm}^3/\text{s}$.

Representative shear rate: $\dot{\gamma}^* = 1.46 \times 62550 /\_\ 102 \times 2^2 = 224\ \text{s}^{-1}$

From the flow curve, the representative is viscosity (@ 230 °C in Fig. 19) is 940 Pa-s (N s / m²).

Pressure drop: $P = \eta_R \times R \times Q = 940 \times 0.234 \times 62550 = 13760000\ \text{N/m}^2$
$= 13.76\ \text{MN/m}^2$ or 2005 psi.

Flow Resistance Of Complete Dies

Most dies may be considered as a number of connecting sections. The die resistance depends most on the smallest dimension of the channel cross-section (for example, the thickness of a slot die or on the gap thickness of a pipe die). Thus flow resistance is usually greatest across the die land and one should first calculate the die resistance and pressure drop of this section of the die. Only when this is satisfactory is it then necessary to calculate pressure drops for the other die sections. The total pressure drop will then be the sum of the pressure drops for each section.

15.4 Applications In Injection Molding.

Pressure Drop in a Runner and Runner Sizing

A runner is the channel that connects an injection mold cavity to the sprue bush where the polymer melt is first introduced to the mold. Runner sizing is very important, but often the decision regarding its size is made at the mold design stage, without actually molding the component. Melt flow data obtained in the laboratory, however, can be used to calculate the optimum runner size.

A great deal of energy is often wasted in this important process. This is because it is necessary to apply considerable pressure to the polymer melt in order to fill an injection mold quickly. The molds used are often designed without using flow data and as a consequence, runners (the flow channels), are frequently made too large. This means that the high injection molding pressures used are transmitted into the cavity requiring excessive clamping pressures to hold the two mold halves together. If these pressures are reduced, the process will be simpler, cheaper, and more energy efficient to operate. One way of doing this is to size the runners so they are as small as possible, consistent with mold filling and packing. As the runner is often the thickest part of the molding, any reduction in runner cross-section will also reduce the cooling cycle and speed up production. In addition, smaller runners will result in less material wasted or required to be reworked, thus reducing costs.

Runners.

These melt flow channels (the runners) are often of circular cross-section, although trapezoidal sections are common because of their ease of manufacture. The cross-sections of these channels are generally constant from the inlet to the exit. Normally polymer melt fills a mold extremely quickly (in less than one second.) and the amount of heat transfer to the mold is relatively small. From a rheological point of view, flow through the runner may be assumed to be the same as that through a circular die and the pressure drop can be calculated. (For a trapezoidal runner, it is assumed that the pressure drop is the same as that for the largest circular runner that fits neatly within the trapezoidal cross-section.)

Injection Pressure.

Most injection molding machines have available approximately 20,000 psi (140 MN^2) of injection pressure. Of this about 10,000 psi may be lost in the runner system and still leave enough to pack the injection mold. To size a runner we first select a runner that seems to be representative and calculate the pressure drop through one of that cross-section. If the pressure drop obtained is too large or too small, then the calculation is repeated, using slightly different runner sizes, until the ‘correct’ amount of pressure drop is obtained. If the inlet pressure is denoted by ΔP and the length of the runner is L then, as the pressure drops linearly from the inlet to the exit, $\Delta P/L$ is constant along the whole length of the runner.

Information Required.

For a runner feeding only one cavity the information required is:

- The thermoplastic material to be used for the component.
- The weight of each component.
- The density of the thermoplastic material.
- A flow curve for the material at the melt temperature being used in the process.

In order to calculate the runner size it is necessary to convert the gravimetric values into volumetric values (i.e. g/s into m^3/s). To calculate Q, the volumetric flow rate, it is necessary to know the density of the material at the injection molding temperature. This is relatively easy to obtain if an MFR machine, which is capable of doing a method B determination, is available. If not, the advice of the material supplier may be sought. (Generally, the density of a plastic material at molding temperatures may be considered to be roughly 0.75 times that of the room temperature value.) Ideally, the flow properties of the plastic material should be measured over a range of shear rates, using a high shear rate rheometer, to construct a flow curve. It may, however, be possible to obtain such a flow curve from the material manufacturer.

Calculation Of Pressure Drop (ΔP)

The pressure drop in a constant cross-section runner (fed from a reservoir of material in the nozzle or sprue bush) is related to the flow rate, the die dimensions, and the melt viscosity. For a circular cross-section runner it may be calculated by a relatively simple procedure.

Method 1

A. Select a runner diameter. (For example, 6mm/0.25in.)
B. Calculate the runner volume.
C. Calculate the volume of the molding.
D. Calculate the working volume (V) (mold volume + runner volume).
E. Calculate the volumetric flow rate (Q). (Assuming that the mold filling time is 1 second if the value is not known from experience.) If the mold filling time is t seconds then Q = V/t. If a 1 second fill time is used, Q will be numerically equal to V but will have different units.
F. Calculate the apparent wall shear rate ($\dot{\gamma}_{w,a}$) from the formula $\dot{\gamma}_{w,a} = 4Q/\pi R^3$.
G. Read off the wall shear stress (τ_w) corresponding to this shear rate value from the flow curve appropriate to the material.
H. Calculate the pressure drop (ΔP – i.e. the pressure developed at the beginning of the runner) from the shear stress by the formula $P = 2L\tau_w / R$ – (where L is the length and R the radius of the runner).
I. If the pressure drop is less than 10,000 psi (70 MNm²) then one should make the runner smaller and if greater than 10,000 psi (70MNm²), then one should make the runner larger. That is, re-size the runner as appropriate. (Since the designer will normally wish to keep the runner as short as possible the main variable here will be the runner diameter.)

Method 2.

This is the same as above except for stage E.

E. Calculate the volumetric flow rate (Q) from the barrel diameter (of the injection molding machine that is to be used) and of the ram speed (linear screw speed) during mold filling. If the cylinder diameter is D and the ram speed is S, then the rate of volumetric displacement by the ram, (which will be the same as that in the mold cavity) – Q will be:

$$Q = \pi D^2 S/4.$$

If it is not known what machine is to be used then it is possible to estimate the required machine size by assuming that the amount of displacement required in the injection barrel (V_i) is about 10% more than V as defined above i.e. $V_i = 1.1V$. This volume will be the ram area times the stroke of the ram. In practice this is usually about 3D so that the volume will be $(\pi D^2/4)3D$ or $3\pi D^3/4$. Thus $1.1V = 3\pi D^3/4$, or $D^3 = 0.467V$ from which the ram diameter D may be immediately found.

Optimizing Runner Sizes

We have shown that the use of flow curves, in association with standard rheological (flow) equations, enables us to determine the pressure loss that occurs when a molten thermoplastic material flows down a channel. We must, however, decide how much pressure can afford to be lost in the runner system that feeds the several cavities. Since an injection-molding machine has normal working pressures of 137-207MN m^2 (30,000psi), a pressure drop of 69MN m^2 (10,000psi) may reasonably be lost in the runner system.

Balanced And Unbalanced Runner Systems

The runner layout selected for this calculation is balanced, which means that the distance (or melt flow path) from the sprue entry to the gate entry is identical for each cavity in the mold. (All of the cavities are also assumed to be identical.) Use of a balanced runner system ensures that each cavity is:

1. Filled with molten material at the same time.
2. Subjected to the same amount of injection pressure, so that identical moldings produced in each cavity.

The above statements are based upon the assumption that the gate, dimensions, and cooling for each cavity are identical. Unbalanced runner systems require modifications to the individual branch runners and/or to the gates in order to produce identical moldings.

Information Required.

To calculate the optimum size of a balanced runner layout, some details of the mold and part must be known. These are as follows:

1. The number of parts in the mold.
2. The thermoplastic material to be used for the part.
3. The weight of each part.
4. The density of the thermoplastic material. (To calculate the runner size it is necessary to convert the gravimetric values into volumetric values, i.e. g/s into m^3/s.). If a flow rate tester is available, which can do Method B testing, the melt density can be easily obtained.

Runner Sections.

The following procedure is used for a runner layout having three sections (i.e. primary, secondary and tertiary runners). The same procedure can be lengthened or shortened to accommodate runner layouts having fewer or more sections. For each runner section, it is necessary to estimate how much plastic material will flow through that particular section or branch. For example, if the primary runner is centrally fed from the sprue, it can be assumed that the flow is split equally between each section. When calculating pressure drops, numerous calculations often need to be done. It is preferable, therefore, to devise a computer program, so that the laborious calculations can be easily handled.

Calculating The Pressure Drop (∆P).

See the previous section on 'Pressure Drop in a Runner and Runner Sizing', for calculating the volumetric flow rate (Q) Methods 1 and 2.

A. Select a runner diameter.
B. Select the runner configuration (which will establish the lengths of the various runner branches).
C. Name the runner sections.
D. Calculate the runner volume.
E. Calculate the volume of the molded part.
F. Calculate the working volume (V) (feed system volume plus molded part volume).
G. Calculate Q the volumetric flow rate.
H. Calculate the shear rate ($\dot{\gamma}_{w,a}$).
I. Use a flow curve for the material to read off the shear stress corresponding to this shear rate.
J. Calculate the pressure drop (∆P) in the primary runner.
K. Calculate the volumetric flow rate for each of the secondary runner branches (Q). This will be Q/N where N is the number of secondary runners and Q is the amount of material flowing through the secondary runner.
L. Calculate the shear rate ($\dot{\gamma}_{w,a}$) for the secondary runner.
M. Read off the shear stress from the flow curve.
N. Calculate the pressure drop (∆P) in the secondary runner.
O. Crosscheck the calculations up to this stage.
P. Calculate the volumetric flow rate (Q) for the tertiary runner. If there are M tertiary runners per secondary runner this will be Q/MN.
Q. Calculate the shear rate ($\dot{\gamma}_{w,a}$) for the tertiary runner.
R. Read off the shear stress from the flow curve.
S. Calculate the pressure drop (∆P) for the tertiary runner.
T. Add together the pressure drops for each of the runner sections to obtain the total pressure drop for the complete runner system.

Optimization.

The mold designer will naturally try to keep the runner lengths as short as possible. This will largely be determined by the arrangement of mold cavities. A computer program may be written to test a variety of configurations and runner diameters, to determine which will give the best balance of pressure drop and runner scrap. One approach is to make the assumption that a 10,000psi pressure drop in the runners will be acceptable. The best design will be the one that gives this figure with the minimum amount of total runner volume.

Optimizing The Runner Layout For A Multi-Cavity Mold

The techniques, used to calculate optimum runner diameters for a given material/mold combination, can also be used to determine the configuration of the runner layout for a multi-cavity mold. The mold used to produce these components can be laid out in various ways. Each cavity may be fed from a central sprue by means of its own runner or the cavities can be grouped into sets, with each set being fed from a secondary runner. Calculations were performed for the following group sizes using two different thermoplastic material, general purpose (GP) grades of acrylonitrile butadiene styrene (ABS) and polycarbonate (PC).

Size Of Group	Number Of Primary Runners
1	24
2	12
3	8
4	6
6	4
8	3
12	2

Calculations showed that the configuration of 3 cavities by 8 branches (i.e. The 24 cavities are laid out in groups of three. Each group of 3 cavities is fed by its own main runner.) is the most efficient runner design. For this configuration the pressure drop and the material usage, is the least, or most economical, of all the layouts considered.

Different Runner Sizes

The runner diameter can be selected so that (1.) the runner diameter is constant throughout the runner configuration or (2.) the runner diameter is different for each section, or branch, of its configuration. Thus a different diameter is used for each of the primary, secondary, tertiary, and quaternary runners. By reducing the diameter of the secondary, tertiary and quaternary runner sections it is possible to reduce the percentage of material in the runner without significantly changing the pressure drop for the runner configuration.

Specifying the Clamping Force for an Injection Molding Machine.

Since the pressure in a liquid acts in all directions, it follows that when a polymer melt is injected under pressure into a mold, there is a force developed that will tend to open the mold. In trying to assess this mold opening force it is useful to distinguish what it will be at two different instants of time during the molding operation; just before the mold is completely filled, (i.e.; while the melt is still flowing) and at the start of the packing stage, just after the mold has filled.

Mold Opening Forces During Cavity Filling.

During the cavity filling phase there will be pressure losses, due to shear flow, along the entire flow line; from the front of the injection ram, through the barrel, nozzle, sprue, runner, gate and mold cavity. Where there is converging flow, such as in the nozzle areas, extensional flow will contribute to the pressure losses. It is in theory possible to calculate the pressure losses at each stage, but, generally, it is sufficient to divide the total pressure drop (between the injection ram face and the blind end of the mold cavity) - P_{total} into three components:

a) The pressure drop up to the injection nozzle exit (ΔP_n).
b) The pressure drop in runner and sprue (ΔP_r).
c) The pressure drop in the mold cavity (ΔP_m).

The pressure drop up to the injection nozzle exit, ΔP, is obtained by measuring the pressure generated during an air shot at the correct volumetric injection rate (Q). Generally, there is approximately a 10% pressure difference between the injection line pressure and the nozzle pressure.

b) The pressure drop in the runner and sprue (P_r). The pressure drop in the sprue is usually ignored, as the cross-sections here are quite large. Since the sprue is usually at right angles to the runners and mold cavity, its contribution to the mold opening force is negligible.

P_r is calculated by the following procedure:

i. Use Q to determine the shear rate at the runner wall ($4Q/\pi R^3$ where R is the runner radius).
ii. Use the flow curve for the particular polymer at the melt temperature being employed to find the shear stress (τ_w) corresponding to the shear rate.
iii. Calculate P_r from the equation $P_r = 2L(\tau_w)/R$ where L is the length of the runner. (See Pressure drop in a runner and runner sizing.)

d) The pressure drop in the mold cavity (P_m). Assuming that P_{total} is known, then P_m may be obtained by the expression

$$P_m = P_{total} - \Delta P - P_r$$

P_m is the pressure drop between the gate and the blind end of the mold just before the mold completely fills. At that moment the pressure at the front end will be zero. As the pressure varies from point to point, it is necessary to find the average pressure over the whole of the projected area of the mold cavity in order to calculate the total mold opening force. Two useful, simple, cases may be identified:

i) A simple rod or bar shaped cavity. Here it may be assumed that the pressure drop changes linearly from one end to the other and the average pressure at any point can be assumed to be $P_m/2$. The mold opening force due to melt in the mold cavity F_m will be given by

$$F_m = AP_m / 2$$

where A_m is the projected area of the mold cavity.

It is now necessary to determine the mold opening force due to the runner. This will be obtained by multiplying the projected area of the runner by the average pressure in the runner. The projected area will be 2RL and the average pressure will be $P_m + P_r / 2$. Thus the total mold opening force (F) due to cavity and runner will be given by

$$F = (A_m P_m / 2) + 2RL(P_m + P_r / 2).$$

ii) A center-gated disc mold. For this type of mold, it is estimated that the force is given by

$$F_m = P_m \pi R^2_m \; [n / (n+2)]$$

where n is an experimentally determined constant and R_m is the radius of the disc. (Barrie, Plastics and Polymers 37 463, (1970))

Similar arguments may be made for multi-cavity molds involving several runners.

Mold Opening Force After Cessation Of Flow.

During the packing stage there should, in theory, be complete transmission of pressure between the ram (the screw tip) and the blind end of the cavity – up to the moment that the gate freezes. In practice, however, there is some pressure loss. The mold opening force may be calculated from the expression

$$F = P_{total} A G$$

where A is the total projected area of mold cavity plus runners and G is the correction factor. G is usually in the range 0.8-0.9, but may be as low as 0.7 in extended runner systems.

Mold Locking Force.

The above calculations yield estimates of the maximum opening pressure while melt is still flowing and after the mold has filled. The locking force employed, measured in tons, must exceed the higher of these two values. The clamping pressure, measured in tons per square inch, is based upon the projected area of the component and is often of the order of 2.5 tons/ in^2. It is, therefore, possible to obtain a good idea of the clamping force required from a relatively simple calculation.

16. SOLVING PRODUCTION PROBLEMS THROUGH UNDERSTANDING FLOW BEHAVIOR

In this section a number of problems are considered, which can be solved without calculations, but simply with an understanding of flow behavior.

Qualitative Application Of Rheological Concepts

Since most processes for shaping rubbers and plastics involve flow, it might be expected that rheological concepts are widely used in problem solving. In practice, however, quantitative applications are somewhat limited, because of the complex flow behavior of polymer melts, the complex flow patterns involved in shaping operations (e.g. the filling of an injection mold), and the fact that cooling often occurs while the melt is still flowing. Nevertheless, a qualitative understanding of flow behavior can often help to overcome processing problems.

Effect Of Flow Channel Shape

For a flow channel of a fixed cross-sectional area, greater flow rates occur when the channel is circular than when it is in the form of a slit. The narrower the slit (even when the cross-sectional area is the same) the lower the flow rate (under a constant delivery pressure). This difference is relevant if attempts are being made to extrude complex shapes, where the extruded cross-section is made up of components of different thickness and shape.

If, for example, the extrudate cross-section is in the form of a dumbbell with two almost spherical parts being bridged by a slit, flow will tend to be faster through of the round sections and slower through the bridging slit. This will lead to stretching, and possibly tearing, of the central section of the extrudate. Even greater problems may occur when the extrudate cross-section is like a half dumbbell, or key cross-section, with one circular section attached to a slit. In this case the extrudate will tend to curl up as it leaves the die.

While such designs are best avoided, the problem may be solved by reducing the parallel portion of the die in those regions where the flow is slowest (i.e., in the slit zones). Throttling the flow in the regions where flow is fastest, by the insertion of a pin or mandrel into the flow channel at the entrance to the die parallel, may also be effective.

Unbalanced Flow In Tubular Extrusion

Tubing is made by extruding polymer through the annular gap between the walls of a circular die and an inserted pin or mandrel. It is sometimes found that the inside wall of the tube has a number of transverse ripples. These ripples arise from variations the flow velocity through the die in the radial direction.

In a simple rod die the flow rate is highest in the center of the die and zero, or almost zero, at the wall. (With simple liquids, such as water, the velocity profile is parabolic in shape, while with polymer melts it is somewhat flatter). If one were to extrude over a very thin pin (of a thickness approximating to that of a thin piece of wire) the velocity profile would be little affected. (The flow rate a short distance from the thin pin would be much greater than the flow rate the same distance from the die wall.) As the diameter of the pin increases the difference will decrease, but, to a greater or lesser extent, the flow rates will still be higher nearer to the pin than to the die wall. Since the melt is coming out faster on the inside of the tube this will tend to cause buckling and hence rippling on the inside of the tube. One way of reducing this is to fit a restrictor bulge or ring around the pin to slow up the flow in this region.

Uneven Die Swell

As a general rule, die swell increases with shear rate and decreases with the length of the die parallel. If a complex section is being extruded, with different cross-sections, then different shear rates will exist at the walls of the different cross-sections. The shear rates will be highest where the cross-section is the least. It may be possible to compensate for these differences when carrying out die sizing (see the section entitled 'Sizing of Die Components'). However, if it is found that swell at one point is lower than elsewhere, then the die parallel at that cross-section may be reduced to compensate. If this is done, one should machine the back end of the die parallel to ensure that all changes in cross-section are gradual.

Die Swell And Parison Sag During Blow Molding.

In extrusion blow molding it is common to extrude a parison vertically downwards. The tube diameters, while tending to increase due to die swell, will also tend to decrease as the parison sags under its own weight. While the swell effect will be independent of parison length the sag will increase as the tube length increases. It is possible to compensate for this by using a tapered die and pin, which move axially with respect to each other, to open the die gap during the extrusion of the parison. The parison pin movement may be programmed either as the result of trial and error experiments or by use of theoretical data.

Extrudates Exhibiting Melt Fracture Or Sharkskin.

It is often found that surface defects on an extrudate have a regular pattern on the surface. With large diameter extrudates this is likely to be due to sharkskin. With smaller diameter products it is probably to be due to melt fracture. If the defects are transverse to the direction of flow it is probably a form of sharkskin. If they are helical in form, then it is probably melt fracture. These phenomena and their characteristics are discussed in the section entitled "Elastic Effects in Polymers".

If problem is identified as one of melt fracture, then the following possibilities should be considered:

1. Reduce output rate (not usually commercially desirable).
2. Increase the melt temperature (increases cooling times).

3. Increase the taper of the die entry.
4. Taper the ‘die parallel’ up to 10 degrees.
5. Use a polymer with lower molecular weight.

If the problem is identified as sharkskin, then the following possibilities should be considered:

1. Reduce output rate.
2. Vary the die temperatures.

Either raising or lowering of the die body temperature may help, while extra heating of the die exit may be particularly beneficial.

Short Injection Moldings

Assuming that the injection stroke length has been correctly set (so that the correct mass of material is delivered to the mold), failure to fill the mold cavities arises because the polymer has frozen before filling is complete. Raising the melt temperature will both reduce the melt viscosity and increase the time taken for the melt to freeze. If this is carried to excess, however, the polymer may degrade or the cooling times may be become excessively long. One may also increase the mold temperature, however, this may lead to an unacceptably long cooling time. It also may be possible to use an easier flowing grade, if such a material is available. Failing this, it may be better to re-site the gate to reduce the length of flow path required. Computer programs are available that optimize gate positions and enable visualization of mold filling operations.

17. SYSTEMS OF UNITS

c.g.s. – Centimeter-gram-second. A system of measurement that uses the centimeter (cm) as the basic unit of length, the second(s) as the basic unit of time, and the gram (g) as the basic unit of mass. The derived unit of force is the dyne (dyn). This system is sometimes known as the CGS or cgs System.

f.p.s. – Foot-pound-second. A system of measurement that uses the foot (ft) as the basic unit of length, the second (s) as the basic unit of time, and the pound as the basic unit of force (force i.e. lbf). The unit of mass is the slug. This system is sometimes known as the FPS gravitational, imperial, or British Engineering system of units. Also known as FPS or fps System.

i.p.s. – Inch-pound-second. A system of measurement that uses the inch (in) as the basic unit of length, the second(s) as the basic unit of time, and the pound force (lbf or psi) as the unit of force. This system is sometimes known as IPS or ips System.

m.k.s. - Meter-kilogram-second. A system of measurement that uses the meter (m) as the basic unit of length, the second(s) as the basic unit of time and the kilogram (kg) as the basic unit of mass. The derived unit of force is the □olysu (N). This system is sometimes known as MKS or mks System.

MKSA metric. See S.I.

S.I. – Système International d'Unités. An international system of units now widely used for scientific and technical work. The seven basic units are the meter (length), kilogram (mass), second (time), ampere (electric current), Kelvin degree (temperature), mole (amount of substance) and the candela (luminous intensity). There are supplementary units for plane angle (radian) and solid angle (steradian) and some SI derived units that have special symbols, which include the Newton and Pascal. Certain other non-SI units are permitted, such as cm and ºC. SI units were derived from the MKS system and are sometimes known as MKSA metric.

PROPERTY	SYMBOL	SYSTEM OF MEASUREMENT			
		c.g.s.	f.p.s.	i.p.s.	S.I.
Shear Stress	τ	dyn cm^2	lbf ft^2	lbf in^2	Nm^2
Shear Rate	$\dot{\gamma}$	s^{-1}	s^{-1}	s^{-1}	s^{-1}
Apparent Viscosity	η	dyn s cm^2	lbf s ft^2	lbf s in^2	Pa-s

VISCOSITY TERMS.

Shear stress is usually designated by the Greek letter τ and has the units of force per unit area. 1 dyn cm² = 0.002 088 lbf ft² = 0.000 014 5 lbf in² or psi.

Shear rate is usually designated by the Greek letter gamma with a dot above the letter, that is, gamma dot or $\dot{\gamma}$. No matter what system of units is used, it is represented by 1/time (in seconds) or reciprocal seconds or s^{-1}.

Apparent viscosity. Dividing τ (the shear stress) by the corresponding $\dot{\gamma}$ (the shear rate) gives the viscosity (η_a) at a particular shear rate. This is an apparent viscosity: In practice the word 'apparent' is often omitted. Apparent viscosity has the units of force per unit area times time (in seconds). See Dynamic viscosity.

Dynamic viscosity. An alternative name for the coefficient of viscosity of a fluid. The usual symbol is η. In the c.g.s system, the units are dyn s cm² or 'poise' (P).

One poise = 1P = 0.1 Pa-s = 0.1 Nsm^{-2} = 0.00014 5 lbf s in^{-2}.

One Pascal second = 1 Pa-s = 1 Nsm^{-2} = 0.102 kgf s m^{-2} = 10 P = 0.00145 lbf s in^{-2}.

Kinematic viscosity. The kinematic viscosity is obtained by dividing the coefficient of viscosity (the viscosity) of a fluid by its density. The units are Stokes = cm^2s^{-1} or ft^2s^{-1}.

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Tables

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19. TABLES

TABLE 1.

UNITS CONVERSION

KNOWING	MULTIPLY BY	TO GET
BAR	1.013	ATMOSPHERES
BAR	14.50	POUND PER SQUARE INCH
BRITISH THERMAL UNITS	1.056	KILOJOULES
BRITISH THERMAL UNITS	778.2	FOOT POUNDS
CALORIES	4.184	JOULES
CENTIMETERS (CM)	0.3937	INCHES
CENTIMETERS	0.01	METERS
CENTIPOISES	0.01	POISES
CENTIPOISES	0.001	PASCAL-SECONDS
CENTISTOKES	0.01	STOKES
CUBIC CENTIMETERS	0.061	CUBIC INCHES
CUBIC INCHES	16.387	CUBIC CENTIMETERS
DYNES	0.00001	NEWTONS
DYNES/SQUARE CENTIMETER	0.1	NEWTONS/SQUARE METER
FEET	0.3048	METERS
FEET PER MINUTE	0.0051	METERS PER SECOND
FEET PER MINUTE	0.305	METERS PER MINUTE
FOOT POUNDS	1.356	JOULES
FOOT POUNDS PER SECOND	1.356	WATTS
GAUGE	0.254	MICRONS
GRAMS	0.0353	OUNCES
GRAMS PER CUBIC CENTIMETER	0.58	OUNCES PER CUBIC INCH
HORSEPOWER	745.7	WATTS
HORSEPOWER	550	FOOT POUNDS PER SECOND
INCHES	25.4	MILLIMETERS
JOULES	0.738	FOOT POUNDS
KILOGRAMS	1000	GRAMS
KILOGRAMS	0.001	METRIC TONNES

KNOWING	**MULTIPLY BY**	**TO GET**
KILOGRAMS PER CENTIMETER	2.205	POUNDS PER INCH
KILOGRAMS PER CUBIC METER	0.06243	POUNDS PER CUBIC FOOT
KILOGRAMS PER SQUARE CENTIMETER	14.223	POUNDS PER SQUARE INCH
KILOGRAMS PER SQUARE METER	3.278	OUNCES PER SQUARE FOOT
KILOGRAMS PER SQUARE METER	0.2048	POUNDS PER SQUARE FOOT
KILOGRAMS PER SQUARE CENTIMETER	2.016	POUNDS PER SQUARE INCH
KILOJOULES	0.9478	BRITISH THERMAL UNITS
KILOJOULES	1000	JOULES
KILOWATTS	737.6	FOOT POUNDS PER SECOND
KILOWATTS	1.341	HORSEPOWER
LITERS	1.024	CUBIC INCHES
LITERS	0.264	GALLONS US
LITERS	2.114	PINTS (US LIQUID)
LITERS	1.054	QUARTS
LONG TONS.See TONS (LONG)		
MEGAPASCALS	145	POUNDS PER SQUARE INCH
MEGAPASCALS	10	BAR
METERS	100	CENTIMETERS
METERS	10	DECIMETERS
METERS	3.28	FEET
METERS	1000	MILLIMETERS
METERS PER SECOND	196.86	FEET PER MINUTE
METERS PER MINUTE	3.28	FEET PER MINUTE
METRIC TONNES	0.98	TONS (LONG)
METRIC TONNES	1.1023	TONS (SHORT)
MILLIMETERS (MM)	0.0394	INCHES
MILLIMETERS	39.37	MILS
MILS	25.4	MICRONS
MILS	0.0254	MILLIMETERS
NEWTONS PER SQURE METER	10	DYNES PER SQUARE CENTIMETER

KNOWING	**MULTIPLY BY**	**TO GET**
NEWTONS PER SQUARE METER	0.02088	POUNDS FORCE PER SQUARE FOOT
NEWTONS PER SQUARE METER	0.000145	POUNDS FORCE PER SQUARE INCH
OUNCES	28.35	GRAMS
OUNCES	0.0625	POUNDS
OUNCES PER CUBIC INCH	1.73	GRAMS PER CUBIC CENTIMETER
PASCAL-SECONDS	10	DYNE-SECONDS PER SQUARE CENTIMETER
PASCAL-SECONDS	1	KILOGRAM PER SQUARE METER PER SECOND
PASCAL-SECONDS	1	NEWTONS-SECONDS PER SQUARE METER
PASCAL-SECONDS	0.02088	POUNDS FORCE-SECONDS PER SQUARE FOOT
PASCAL-SECONDS	0.000145	POUNDS FORCE-SECONDS PER SQUARE INCH
POISES	100	CENTIPOISES
POISES	0.1	PASCAL-SECONDS
POISES	0.1	NEWTON-SECONDS PER SQUARE METER
POISES	0.1	KILOGRAM PER METER PER SECOND
POUNDS	0.4536	KILOGRAMS
POUNDS FORCE PER SQUARE INCH	SEE POUNDS PER SQUARE INCH	
POUNDS PER CUBIC FOOT	16.02	KILOGRAMS PER CUBIC METER
POUNDS PER SQUARE INCH	2.307	FEET OF WATER
POUNDS PER SQUARE INCH	2.036	INCHES OF MERCURY
POUNDS PER SQUARE INCH	703.1	KILOGRAMS PER SQUARE METER
POUNDS PER SQUARE INCH	0.0703	KILOGRAMS PER SQUARE CENTIMETER
POUNDS PER SQUARE INCH	0.0069	MEGAPASCALS
RELATIVE DENSITY SEE SPECIFIC GRAVITY		

KNOWING	MULTIPLY BY	TO GET
SHORT TONS SEE TONS (SHORT)		
SPECIFIC GRAVITY	62.4	POUNDS PER CUBIC FOOT
SPECIFIC GRAVITY	16.39	GRAMS PER CUBIC INCH
SPECIFIC GRAVITY	0.58	OUNCES PER CUBIC INCH
SPECIFIC GRAVITY	0.036	POUNDS PER CUBIC INCH
SQUARE FEET	0.093	SQUARE METERS
SQUARE INCHES	645	SQUARE MM
SQUARE METERS	10.76	SQUARE FEET
SQUARE MM	0.0016	SQUARE INCHES
SQUARE YARDS	0.8354	SQUARE METERS
THOU. SEE MILLS		
TONS (LONG)	1.016	METRIC TONNES
TONS (LONG)	1.12	TONS (SHORT)
TONNES (METRIC).SEE METRIC TONNES		
TONS (SHORT)	0.907	METRIC TONNES
TONS (SHORT)	0.8928	TONS (LONG)
YARDS	0.914	METERS

TABLE 2.

STANDARD (BASED ON ISO AND ASTM) ABBREVIATIONS FOR SELECTED THERMOPLASTICS.

Abbreviation	**Name.**
ABAK	acrylonitrile-butadiene-acrylate (was A/B/A in ISO)
ABS	acrylonitrile-butadiene-styrene
A/B/A	See ABAK
A/CPE/S	See ACS
ACS	acrylonitrile-chlorinated polyethylene-styrene (was A/CPE/S in ISO)
AES	acrylonitrile-ethylene-propylene-diene-styrene (was A/EPDM/S in ISO)
A/EPDM/S	See AES
A/MMA	See AMMA
AMMA	acrylonitrile-methyl methacrylate (was A/MMA in ISO)
AS	acrylonitrile-styrene (SAN is more usual in Europe)
ASA	acrylonitrile-styrene-acrylate
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CN	cellulose nitrate
CP	cellulose propionate
E/EA	See EEAK
EEAK	ethylene-ethylene acrylate (was E/AK in ISO)
E/MA	See EMA
EMA	ethylene-methacrylic acid (was E/MA in ISO)
E/P	See EP
EP	Ethylene-propylene (was E/P in ISO)
EPDM	ethylene-propylene-diene
E/TFE	See ETFE
ETFE	ethylene-tetrafluoroethylene (was E/TFE in ISO)
EVAC	ethylene-vinyl acetate
EVAL	See EVOH
EVOH	ethylene-vinyl alcohol (was EVAL in ISO)
FEP	fluorinated ethylene-propylene
LCP	liquid crystal polymer
MABS	methyl methacrylate-butadiene-styrene
MBS	methacrylate-butadiene-styrene
PA	polyamide

Abbreviation	**Name.**
PAEK	polyaryletherketone
PAI	polyamideimide
PAK	polyacrylate
PAR	polyarylate
PAUR	poly(ester urethane)
PB	polybutene-1
PBAK	poly(butyl acrylate)
PBT	poly(□olysulfo terephthalate)
PC	polycarbonate
PCTFE	polychlorotrifluorethylene
PE	polyethylene
PEBA	poly(ether block amide)
PEEK	polyetheretherketone
PEEKK	polyetheretherketoneketone
PEEST	polyetherester
PEI	poly(ether imide)
PEK	polyetherketone
PEKEKK	polyetherketoneetherketoneketone
PEKK	polyetherketoneketone
PEOX	poly(ethylene oxide)
PES	poly(ether sulfone)
PESTUR	poly(ester urethane)
PET	poly(ethylene terephthalate)
PEUR	poly(ether urethane)
PFA	perfluoro alkoxyl alkane
PFEP	perfluoro(ethylene/propylene)
PI	polyimide
PIB	polyisobutylene or polyisobutene
PMMA	poly(methyl methacrylate)
PMP	poly-4-methylpentene-1
PMS	poly-α-methylstyrene
POM	□olysulfones□lene or, polyacetal or, polyformaldehyde
PP	polypropylene
PPE	poly(phenylene ether)
PPOX	poly(propylene oxide)
PPS	poly(phenylene sulfide)
PPSU	poly(phenylene sulfone)
PS	polystyrene
PSU	□olysulfones
PTFE	polytetrafluoroethylene
PUR	polyurethane
PVAC	poly(vinyl acetate)
PVAL	poly(vinyl alcohol)
PVB	poly(vinyl butyral)

Abbreviation	Name.
PVC	poly(vinyl chloride)
PVDC	poly(vinylidene chloride)
PVDF	poly(vinylidene fluoride)
PVF	poly(vinyl fluoride)
PVFM	poly(vinyl formal)
SAN	styrene-acrylonitrile
S/B	styrene-butadiene
S/MS	styrene-α-methylstyrene
SMA	styrene-maleic anhydride
VC/E	See VCE
VC/MMA	See VCMMA
VC/VDC	See VCVDC
VC/VAC	See VCVAC
VC/MA	See VCMAK
VC/OA	See VCOAK
VC/E/MA	See VCEMAK
VC/E/VAC	See VCEVAC
VCE	vinyl chloride-ethylene (was VC/E in ISO)
VCEMAK	vinyl chloride-ethylene-methyl acrylate (was VC/E/MA in ISO)
VCEVAC	vinyl chloride-ethylene-vinyl acetate (was VC/E/VAC in ISO)
VCMAK	vinyl chloride-methyl acrylate (was VC/MA in ISO)
VCMMA	vinyl chloride-methyl methacrylate (was VC/MMA in ISO)
VCOAK	vinyl chloride-octyl acrylate (was VC/OA in ISO)
VCVAC	vinyl chloride-vinyl acetate (was VC/VAC in ISO)
VCVDC	vinyl chloride-vinylidene chloride (was VC/VDC in ISO).

The above abbreviations may be modified by the addition of up to four specified letters after the abbreviation for the polymer under discussion. For example, PS could become PS-HI when high impact polystyrene is being described. In the case of PE, this would become PE-LD when low-density polyethylene (LDPE) is being described.

When mixtures are made from two or more polymers (blends or alloys), ISO 1043 suggests that the symbols for the basic polymers be separated by a plus (+) sign and that the symbols be placed in parentheses. For example, a mixture of * polymethyl methacrylate and * acrylonitrile-butadiene-styrene should be represented as (PMMA+ABS)

When referring to a copolymer it is recommended (ISO) that an oblique stroke / be placed between the two monomer abbreviations. (For example, E/P for an ethylene propylene copolymer.) The oblique strokes may be omitted when common usage so dictates according to ISO 1043-1:1987 (E).

TABLE 3.

SOME COMMON ABBREVIATIONS AND TRADE NAMES FOR THERMOPLASTICS AND THERMOPLASTIC ELASTOMERS.

Abbreviation	Common Name	Common Trade Names or Trade Marks.
ABS	Acrylonitrile butadiene styrene	Cycolac; Lustran
AMS	Alpha methyl styrene	Elite HH
ASA	Acrylonitrile styrene acrylate (AAS)	Luran S
BDS	Butadiene styrene block copolymer	K resin; Styrolux
CA	Cellulose acetate	Cellidor; Tenite
CAB	Cellulose acetate butyrate	Cellidor; Tenite
CAP	Cellulose acetate propionate	Cellidor; Tenite
CN	Cellulose nitrate	Celluloid; Xylonite
CP	Cellulose propionate (CAP)	Cellidor; Tenite
CPE	Chlorinated polyethylene (PE-C)	Bayer CM; Tyrin CM
CPVC	Chlorinated polyvinyl chloride (PVC-C)	Lucalor
EA-MPR	Elastomer alloy melt processable rubber Or melt processable rubber	Alcryn
EA-TPV	Elastomer alloy thermoplastic vulcanizate	Santoprene
ECM	Ethylene-carbon monoxide	Carilon: Ketonex
ETFE	Tetrafluorethylene-ethylene copolymer	Tefzel
EVA	Ethylene vinyl acetate copolymer (EVAC)	Evatane
EVAL	Ethylene vinyl alcohol copolymer	Clarene; Eval
EVOH	Ethylene vinyl alcohol copolymer	Clarene; Eval
FEP	Fluorinated ethylene propylene (TFE-HFP)	Teflon FEP
HDPE	High density polyethylene (PE-HD)	Lupolen HD; Rigidex
HIPS	High impact polystyrene (TPS or IPS)	Lustrex; Polystyrol
LCP	Liquid crystal polymer	Vectra; Xydar
LDPE	Low density polyethylene (PE-LD)	Alathon; Hostalen
MBS	Methacrylate butadiene styrene	Paraloid
MDPE	Medium density polyethylene (PE-MD)	Fortiflex
MPR	Melt processable rubber or, elastomer alloy melt processable rubber	Alcryn
PA	Polyamide or nylon	
PA 6	Polyamide 6 or nylon 6	Akulon K; Ultramid
PA 11	Polyamide 11 or nylon 11	Rilsan B
PA 12	Polyamide 12 or nylon 12	Rilsan A; Grilamid
PA 46	Polyamide 46 or nylon 46	Stanyl
PA 66	Polyamide 66 or nylon 66	Maranyl; Zytel
PA 610	Polyamide 610 or nylon 610	Brulon; Perlon N

Abbreviation	Common Name	Common Trade Names or Trade Marks.
PAA 6	Polyaryl amide or, poly-m-xylene-adipamide (PA MXD6)	Ixef
PAN	Polyacrylonitrile	Acrilan; Barex; Orlon
PBT	Polybutylene terephthalate	Pocan; Valox
PC	Polycarbonate	Lexan; Makrolon
PCT	Polycyclohexanedimethylol terephthalate	Thermx;
PCTFE	Polychlorotrifluorethylene	Hostaflon C2; Kel-F
PE	Polyethylene	Alathon; Lupolen
PEBA	Polyether block amide (TPE-A)	Pebax
PEEK	Polyether ether ketone	Victrex PEEK
PEEL	Polyether ester (TPE-A or YPBO)	Arnitel; Hytrel
PE-HD	Polyethylene-high density	Lupolen HD; Rigidex HDPE
PEI	Polyether imide	Ultem
PEK	Polyether ketone	Hostatec
PEKK	Polyether ketone ketone(from DuPont)	
PE-LD	Polyethylene- low density	Alathon; Lupolen LD
PE-MD	Polyethylene- medium density	Fortiflex
PE-VLD	Polyethylene- very low density	Norsoflex
PET	Polyethylene terephthalate	Arnite A; Techster E
PES	Polyether sulphone (sulfone)	Victrex
PI	Polyimide	Vespel
PK	Polyketone	Carilon
PMMA	Polymethyl methacrylate (acrylic)	Diakon; Plexiglas
PMP	Polymethyl pentene	TPX; Crystalor
POM	Polyoxymethylene or, acetal or, polyformaldehyde	Delrin; Hostaform
POM-H	Acetal homopolymer	Delrin and Delrin II
POM-CO	Acetal copolymer	Hostaform; Ultraform
PP	Polypropylene	Profax; Propathene
PPE	Polyphenylene ether (see PPO)	
PPO	Polyphenylene oxide-usually modified polyphenylene oxide (PPO-M)	Luranyl; Noryl
PPS	Polyphenylene sulfide (sulphide)	Fortron; Ryton
PPPS	Polyphenylene sulfide sulfone (polyphenylene sulphide sulphone)	Ryton S
PPVC	Plasticized polyvinyl chloride (PVC-P) Plasticised polyvinyl chloride (PPVC)	Solvic; Vinnol
PS	Polystyrene (GPPS or PS-GP)	Lustrex; Polystyrol
PSU	Polysulfone (polysulphone)	Udel
PTFE	Polytetrafluoroethylene	Fluon; Teflon
PVC	Polyvinyl chloride	Corvic; Geon
PVDC	Polyvinylidene chloride copolymers	Saran

Abbreviation	**Common Name**	**Common Trade Names or Trade Marks.**
PVDF	Polyvinylidene fluoride	Dyflor; Kynar
PVF	Polyvinyl fluoride	Tedlar
SAN	Styrene acrylonitrile copolymer	Lustran SAN; Tyril
UPVC	Unplasticized polyvinyl chloride (PVC-U) Unplasticized polyvinyl chloride (UPVC)	Corvic; Geon
RMPP	Rubber modified polypropylene a TPO (also known as RRPP or PP/EPDM)	Uniroyal TPR; Keltan
SBS	Styrene butadiene styrene block copolymer or thermoplastic elastomer styrene based (TPE-S)	Cariflex TR; Solprene
SEBS	Styrene butadiene styrene block Copolymer (saturated) or thermoplastic Elastomer styrene based (TPE-S)	Cariflex
TPE	Thermoplastic elastomer (rubber)	
TPE-A	Polyether block amide (PEBA)	Pebax
TPE-E	Thermoplastic elastomer – ether ester or polyether ester elastomer	Arnitel; Hytrel
TPE-OXL	Thermoplastic elastomer – polyolefin based with crosslinked rubber	Levaflex; Santoprene
TPE-S	Thermoplastic elastomer styrene based (usually styrene butadiene styrene block copolymer)	Cariflex TR; Solprene
TPE-U	Thermoplastic polyurethane (TPU)	Elastollan; Estane
TPO	Thermoplastic polyolefin – may be a blend, (see RMPP), a thermoplastic vulcanizate (see TPV) or a reactor made product	
TPR	Thermoplastic rubber (elastomer)	
TPU	Thermoplastic polyurethane	Elastollan; Estane
TPV	Thermoplastic vulcanizate (a TPE with crosslinked rubber)	Santoprene
ULDPE	Ultra low density polyethylene (ULDPE)	
VLDPE	Very low density polyethylene (ULDPE)	Norsoflex

TABLE 4.

SUGGESTED TEMPERATURES (°C) AND LOADS (Kg) FOR MFR TESTS.

Material	Temperature (°C)	Load (Kg)
Acetal (POM-H & POM-CO)	190	2.16 or 1.05.
Acrylic (PMMA)	230	1.2 or 3.8.
(a) Acrylonitrile butadiene		
styrene (ABS)	200	5.0.
(b) Acrylonitrile		
butadiene styrene (ABS)	230	3.8.
(a) Cellulose esters	190	0.325 or 2.16 or 21.6.
(b) Cellulosic esters		
(CA, CAB CP)	210	2.16.
Nylon 66 (PA 66)	275	0.325.
Nylon 6 (PA 6)	235	1.0 or 2.16 or 5.0.
Polychlorotrifluorethylene (PCTFE)	265	12.5.
(a) Polyethylene (PE)	125	0.325 or 2.16.
(b) Polyethylene	190	0.325 or 2.16 or 10 or 21.6.
® Polyethylene	310	12.5.
Polycarbonate (PC)	300	1.2.
Polypropylene (PP)	230	2.16.
(a) Polystyrene (PS or HIPS)	190	5.0.
(b) Polystyrene	200	5.0.
® Polystyrene	230	1.2 or 3.8.
Thermoplastic polyester (PBT or PET)		
(a) Polyterephthalate	210	2.16
(b) Polyterephthalate	250	2.16
® Polyterephthalate	285	2.16.
Polyphenylenesulfide (PPS)	315	5.0.
Unplasticized PVC (UPVC)	175	21.6.

TABLE 5.

SUGGESTED TEMPERATURES FOR HIGH SHEAR RATE RHEOMETRY.

Polymer (Abbreviation)	Test Temperature (°C/°F)	Range (°C/°F)
ABS	240/464	230-270/446-518
ASA	260/500	250-280/482-536
BDS	220/428	190-230/374-446
EVA	180/356	140-225/284-437
FEP	350/662	300-380/572-716
HDPE	240/464	205-280/401-536
HIPS	240/464	200-270/392-518
LDPE	210/410	180-280/350-536
LLDPE	210/410	160-280/350-536
PA	See PA 6, PA 11, PA 12 & PA 66	
PA 6	250/482	230-280/446-536
PA 11	255/491	240-300/464-572
PA 12	255/491	240-300/464/572
PA 66	280/536	260-290/500-554
PBT	250/482	220-260/428/500
PC	300/572	280-320/536-608
PE	See HDPE, LDPE and LLDPE	
PEEK	370/698	360-380/680-716
PEI	380/716	340-425/640-800
PET	275/527	260-300/518-572
PES	360/680	330-380/626-716
PMMA	240/464	210-270/410-518
POM-CO	205/401	190-210/374-410
POM-H	215/419	190-230/374-446
PP	240/464	220-275/428-527
PPE	See PPO	
PPO	280/536	260-300/500-572
PPS	320/608	290-360/554-680
PPVC	180/356	175-200/347-392
PS	220/428	200-250/392-482
PSU	360/680	330-380/626-716
PVC	See PPVC and UPVC	
PVDF	225/437	220-250/428-482
SAN	240/464	200-270/392-518

Polymer (Abbreviation)	Test Temperature (°C/°F)	Range (°C/°F)
RMPP	240/464	220-275/428-527
UPVC	195/383	185-205/364-401
TPE	See TPE-A, TPE-E, TPE-S, TPE-U and TPE-OXL	
TPE-A	200/392	185-240/364-464
TPE-E	220/428	195-255/383-491
TPE-S	170/338	150-200/302-394
TPE-U	200/392	180-230/356-446
TPE-OXL	190/374	180-200/356-392

TABLE 6.

HEAT CONTENT OF SOME PLASTIC MATERIALS.

Material Abb.	Melt Temp (°C)	Mold Temp (°C)	Temperature Difference (°C)	Specific Heat (J/Kg /^{O}k)	Heat to be Removed (J/g)
FEP	350	200	150	1600	240
POM	205	90	115	3000	345
SAN	240	60	180	1968	354
PC	300	90	210	1750	368
ABS	240	60	180	2050	369
PMMA	260	60	200	1900	380
PPS	320	135	185	2080	385
PS	220	20	200	1970	394
ASA/AAS	260	60	200	2010	402
HIPS	240	20	220	1970	433
PPO	280	80	200	2120	434
PA 6	250	80	170	3060	520
LDPE	210	30	180	3180	572
PA 66	280	80	200	3075	615
PP	260	20	240	2790	670
HDPE	240	20	220	3640	801

Table 7

GLASS TRANSITION TEMPERATURES (T_G) AND MELTING TEMPERATURES ™ OF SOME POLYMERS IN ^{O}C.

ABBREV.	MATERIAL NAME	T_g	T_m
ABS	acrylonitrile-butadiene-styrene	105	
AS	acrylonitrile-styrene – see SAN		
CTA	cellulose triacetate	105	306
CTB	cellulose tributyrate		183
CAP	cellulose tripropionate		234
FEP	fluorinated ethylene-propylene		271
HIPS	high impact polystyrene	100	
IPS	isotactic polystyrene	100	240
IPMMA	isotactic polymethyl methacrylate	45	160
PA 6	nylon 6	50	215
PA 11	nylon 11		185
PA 12	nylon 12		175
PA 46	nylon 46		295
PA 66	nylon 66	55	265
PA 610	nylon 610	40	227
PAA 6	polyaryl amie/an aromatic nylon	90	236
PAN	polyacrylonitrile	80/104D	
PAR	polyarylate	180	
PB	polybutene-1	-25	126
PBAK	polybutyl acrylate	40	195
PBT	polybutylene terephthalate	30	225
PC	polycarbonate	150	225
PCTFE	polychlorotrifluorethylene	49	220
PE-HD	high density polyethylene		130
PE-LD	low density polyethylene	-20	120
PE-LLD	linear low density polyethylene		127
PEEK	polyetheretherketone		334
PEI	polyether imide	215	
PEK	polyetherketone	154	367
PEOX	polyethylene oxide	-56	66
PET	polyethylene terephthalate	69	260

ABBREV.	MATERIAL NAME	T_g	T_m
PMMA	polymethyl methacrylate	99	
PMP	poly-4-methylpentene-1	55	250
PMS	poly-α-methylstyrene	120	
POM-CO	□olysulfones□lene/acetal copolymer		165
POM-H	□olysulfones□lene/acetal homopolymer	-13	175
PP	polypropylene	0	165
PPE	polyphenylene ether	210	
PPOX	polypropylene oxide	-62	75
PPS	polyphenylene sulfide	85	282
PS	polystyrene	100	
PSU	□olysulfones		190/230
PTFE	polytetrafluoroethylene	126	327
PVAC	polyvinyl acetate	30	
PVAL	polyvinyl alcohol	50/70	D
PVC	polyvinyl chloride	87	212
PVDC	polyvinylidene chloride	-25	190
PVDF	polyvinylidene fluoride		177
PVF	polyvinyl fluoride	-20	200
SAN	styrene-acrylonitrile	105	
SP	saturated polyester – see PBT and PET		
SPMMA	syndiotactic polymethyl methacrylate	110	>200

D = decomposes before melting.

Table 8

SOME THERMAL PROPERTIES OF THERMOPLASTIC MATERIALS (^{O}C).

MATERIAL	T_g	T_m	SP	HDT		VSP
				(0.45 Mpa)	(1.8 Mpa)	
ABS	105		94	96	84	95
HIPS	100		84	85	72	86
PA 66	55	265	180	183	75	185
PE-HD		130	115	75	45	125
PE-LD	-20	120		45		85
PMMA	99		95	97	80	90
POM-H	-13	175	170	120	165	175
PP	0	165	145	140	60	150
PS	100		92	97	90	98

T_g = glass transition temperatures

T_m = melting temperature

SP = cantilever softening point test

VSP = Vicat softening point test

HDT = heat distortion temperature

TABLE 9

SUGGESTED DRYING CONDITIONS FOR EXTRUSION MATERIALS

(Based on suggested drying conditions for Injection molding materials.)

Abbrev.	Water Abs.	Hot Air Drying		Desiccant Drying	
	(%)	(Temp ^{0}C)	(# of hours)	(Temp ^{0}C)	(# of hours)
ABS	0.2 to 0.35	70 – 80	2 – 4	70 – 80	2
HIPS	0.08	70	2 – 3	70	1 – 2
LDPE	<0.2	65	3	80	1 to 1.5
HDPE	<0.01	65	3	80	1 to 1.5
LLDPE	<0.2	65	3	85	1 to 1.5
PP (H + CO)	<0.2	65	3	85	1 to 1.5
PA 6	1.6	80	16	105	12
PA 66	1.5	85	16	105	12
PMMA	0.3	75	2 to 4	90	3 to 4
PPVC	-	-	-	-	-
UPVC	<0.2	65	3	80	1 to 1.5

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Appendix

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FIGURES

Title **Page**

Appendix I

TESTING, STATISTICS AND QUALITY CONTROL

Successful quality control of a product requires not only that the product meets its specification, but, requires monitoring of the process to ensure that adverse changes are not occurring - even though the product is still within specification. If this is not done, a situation may arise where, within a short space of time, high reject rates may develop. Such problems may be anticipated by the use of statistical quality control (SQC) methods (also know as statistical process control or SPC). Furthermore, the use of such methods may avoid the acceptance of specification limits that may be difficult to hold in production.

TESTING FOR CONSISTENCY.

While it is the quality of the end-product that is important, clearly it is necessary that the raw materials, and products of intermediate stages, should also be of acceptable quality. For this reason, quality control (QC) should be considered for all stages of production. Extensive testing is expensive, but fortunately, in practice, it is often found that a small number of tests can give a good guide for the consistency of quality. For example, when using polyethylene, a check of melt flow rate (MFR or MFI) and density can often provide adequate information on raw material consistency. In the case of injection molding, simple tests such as visual appearance, product weight, and oven stability may be sufficient, however, for critical applications further testing may be necessary.

SPECIFICATION AND TOLERANCE LIMITS

The manufacture of a product commonly involves meeting specification limits, which have been agreed upon by customer and supplier. For a given product there may be several such limits. One of these could be a particular dimension. For example, it may be specified that the dimension should be 10.00±0.02cm or between 9.98 and 10.02cm. The value of 10.00cm is called the nominal value. (It should be noted that the plus and minus deviations need not be equal.)

INHERENT VARIATIONS.

Before agreeing to specification limits it is important to understand that in a process there will always be some natural variation in the product (For example, variations in dimensions or weight.) - even when no external modifications have been made to the process. These are known as unassigned or inherent variations. Such variations may be analyzed statistically as outlined below.

MEAN AND STANDARD DEVIATION.

Any statistical analysis first requires a calculation of the arithmetic mean (or average) and the standard deviation. If we have five values ($N=5$) of a variable x, which have magnitudes of 5,3,7,4 and 6, the mean (X) is obtained by adding up the five numbers (the total $25 = \Sigma x$) and dividing by N to give an arithmetic mean or average of 5. The formula used is:

$$\mathbf{X=\Sigma x/N.}$$

By a similar calculation it can be shown that the five numbers 8,0,1,9 and 7, have the same mean, but they have a greater variation (they are more widely spread). The most useful measure of such a spread, called the standard deviation, is given by the formula:

$$\boldsymbol{\sigma} = \sqrt{[\Sigma(x-X)^2 / N]}.$$

THE NORMAL OR GAUSSIAN DISTRIBUTION.

It is often found that the inherent variations in a variable quantity closely follow that of the theoretical Gaussian (Normal) distribution. The Gaussian distribution may be expressed graphically as a plot of the frequency (f) with which a particular value of the variable occurs against the value of the variable (x). This symmetrical and bell shaped curve is centered at the arithmetic mean. The greatest concentration of values is found near the mean. The farther away from the mean value, the lower the frequency. If the mean and standard deviation are known then the Normal curve may be defined. Even in those cases where the plot of f verses x does not give a good Gaussian fit, when a sample of a few individuals is taken, and a sample average calculated (X), the plot of f verses the sample mean (X) is Gaussian. In this case the true distribution mean, or grand mean, may be given the symbol μ (or X with a superimposed double bar).

SOME NORMAL DISTRIBUTION CHARACTERISTICS

It may be shown that in a Gaussian distribution:

- 50% of the results are within 0.6745 $\boldsymbol{\sigma}$ of the mean,
- 68.26% are within 1 $\boldsymbol{\sigma}$
- 95% are within 1.96 $\boldsymbol{\sigma}$
- 95.44% are within 2 $\boldsymbol{\sigma}$
- 99.74% are within 3 $\boldsymbol{\sigma}$ and,
- 99.8% are within 3.09 $\boldsymbol{\sigma}$ (of the mean).

These limits are a direct consequence of the properties of the Gaussian distribution and are often referred to as the natural tolerance limits.

In the case of a distribution of means of samples of size N, 50% of the results are within 0.6745 $\boldsymbol{\sigma}/\sqrt{N}$ of the grand mean (with the other limits similarly adjusted by the factor 1 $\boldsymbol{\sigma}/\sqrt{N}$). Because it occurs so often the expression $\boldsymbol{\sigma}/\sqrt{N}$ is known as the standard error of the mean.

CONFIDENCE LIMITS.

It follows from the above that if a large number of samples of size N are taken from a Gaussian distribution, 95% of the samples will lie within the range μ±1.96 **σ** /√N or, put another way, there is a 95% probability that the true mean μ will lie in the range X ±1.96 **σ** /√N. These are sometimes known as the 95% confidence limits. Similarly the expression X ±3.09 **σ** /√N is sometimes referred to as the 99.8% confidence limit.

ESTIMATING

The expressions used to obtain confidence limits are only strictly correct if the standard deviation is known accurately. In practice we have to estimate this from the standard deviation of a sample and, it may be argued, that in this case the best estimate of the standard deviation, as obtained from a sample, is given by:

$$\boldsymbol{\sigma = \sqrt{[\Sigma(x-X)^2 / (N-1)]}}$$

t-DISTRIBUTIONS

When the standard deviation is obtained from a sample, it is necessary to replace the Gaussian distribution by a series of distributions known as the t-distributions, which depend on the sample, size. In this case the 95% confidence limits will be given by X± t0.05 **σ** /√N. Some values for t at the 95% and 99.9% levels are given in the following table.

Degrees of Freedom	**1**	**2**	**3**	**4**	**6**	**8**	**10**	▶
t(95%)12.74	4.30	3.18	2.78	2.45	2.31	2.23	1.96	
t(99.9%)	637.6	31.6	12.94	9.61	5.96	5.04	4.59	3.29

Degrees of freedom may be defined as any of the independent variables constituting a statistic. In this case, the number of degrees of freedom is equal to N-1.

SETTING LIMITS.

The product of a process is subject to a measure of variability that is quantified by the natural tolerance limits or confidence limits. It is important, therefore, to realize that if the specification limits are set too closely, high wastage or reject rates will occur, unless changes are made to the process to reduce variability. Wherever possible, and when data are available, the supplier and the purchaser should agree to adopt specification limits roughly equal to the 99.8% limits or a spread of approximately six standard deviations about the mean. This will produce low reject rates, for the particular criterion involved, providing the average mean value of the property attained during production coincides with the middle value of the specification limit. Any divergence from this will lead to a considerable increase in reject rates.

SIGNIFICANCE TESTING.

Significance testing is used to determine the level of probability that the difference in values between two (or more) sets of results is significant and not simply due to random scatter of results.

THE NULL HYPOTHESIS

The approach adopted here is to say that there is no significant difference between two sets of results (the Null Hypothesis) and then to calculate the probability that this hypothesis is correct. If the probability of the hypothesis being true (that is, there is no significant difference) is less than 5%, it is concluded that the difference is significant. If it is less than 0.1% the difference is said to be highly significant. If the difference is significant, then this means that the probability that the differences in the data are not simply due to random scatter is at least 95%. If the difference is highly significant then it is almost certain that the two sets of results are different.

SIGNIFICANT DIFFERENCE OF A SAMPLE MEAN FROM A GRAND MEAN

In this example we will consider whether the sample average of 4 melt flow rate (MFR or MFI) readings is significantly different from a grand, or universal mean. Such a grand mean, given the symbol μ, may have been obtained by averaging previous test results. In this case $\mu = 7.0$.

Let the four measured MFR values be 7.20, 7.24, 7.12 and 7.34. From these data we calculate that $X = 7.225$ and $\boldsymbol{\sigma} = 0.091$.

The formula for t is:

$$\mathbf{t = |X-\mu|/(\sigma/\sqrt{N}).}$$

Where N is the number of tests in the sample and the vertical bars mean that the + or - differences are ignored. In this case $t = (7.225-7)/(0.091/\sqrt{4}) = 4.95$.

Since there are four samples, in this case the number of degrees of freedom (N – 1) is 3. From the above table it can be seen that the probability that the result is from a distribution with a grand mean of 7.0 is less than 5%, but more than 0.1%. (t (95%) is 3.18 and t (99.9) is 12.94.) We thus reject the Null Hypothesis and state that the difference is significant at the 5% level. If the probability were less than 0.1% we would be even more confident in rejecting the null hypothesis and would say that the difference is highly significant at the 0.1% (1 in 1000) level. (For the probability to be less than 0.1% we would have to have a number >12.94. If the answer were a number less than 3.18 then we would accept the null hypothesis.)

SIGNIFICANT DIFFERENCE BETWEEN TWO SAMPLE MEANS

In this case the formula for t is given by; $t = X_a - X_b / S_d$. Where X_a and X_b are the larger and smaller sample means respectively and S_d is known as the standard error of the mean difference. It is given by:

$$\mathbf{S_d = S_c\sqrt{[N_a + N_b)/N_aN_b]}}$$

Where $S^2_c = [\boldsymbol{\sigma}^2_a (N_a - 1) + \boldsymbol{\sigma}^2_b (N_b - 1)] / (N_a + N_b - 2)$ and N_a = the number in sample A and N_b is the number in sample B. In this situation the number of degrees of freedom is given by $N_a + N_b - 2$.

As an example, consider two samples of polyethylene that have each been tested for melt flow rate using five samples. The results are as follows:

Sample A	7.22	7.26	7.31	7.34	7.10	$X_a = 7.246$
Sample B	7.05	7.12	7.00	7.08	6.98	$X_b = 7.046$

From these data we calculate $S^2_c = 0.00603$ and $S_d = 0.049$. Hence, $t = (7.246 - 7.046)/0.049 = 4.08$. For eight degrees of freedom the difference is significant at the 5% level, but not at the 0.1% (1 in 1000) level. We thus reject the Null Hypothesis and state that the difference is significant at the 5% level. If the probability were less than 0.1% we would be even more confident in rejecting the null hypothesis and would say that the difference is highly significant.

QC WITH AVERAGE AND RANGE CHARTS

A quality control chart (QCC) (sometimes called process control charts) will show how well a process is operating. It will reveal whether the process is functioning correctly, if the process has progressed out of control, or if it is about to drift out of control. The tendency of a machine or material to shift out of control, or out of specification, can, therefore, be spotted before rejects have been produced. To get the information required, it is necessary to take samples at predetermined intervals, perform measurements, record the data, plot the measurements on the chart, assess the results and then, take appropriate action.

VARIABLES AND ATTRIBUTES

A variable is a property that arises from measurements and is thus subject to variations. These measurements may be weight, length, tensile strength, melt flow rate (MFR) and so on. An attribute, on the other hand, is a property that either is or is not possessed by the product. (For example, pass-fail, go-no go, satisfactory-defect.) Quality control systems may be use either variables or attributes, but the procedures used will differ. While attribute testing provides only limited data, it is often simpler to carry out and may be adequate for the purpose.

QC CHARTS FOR SAMPLING BY VARIABLES

To get reasonable results it is necessary to keep two charts for each measurement: one chart that shows the average value (X) of the measurement and another that shows how much variability there is in that particular sample. (For example, the average of 9, 10, 11, 9 and 11 = 50/5 = 10 and the average of 6, 10, 14, 8 and 12 also = 50/5 = 10. The second set of numbers, however, is obviously more variable). Unless variability is plotted we may, unknowingly, be producing items which vary too much. While the best measure of spread of results is the standard deviation, it is easier, and almost as good with small samples, to plot the range (R also known as 'w'). The two charts are then known as the Mean chart and the Range chart. These two charts, together with the data files, are generally located on one sheet known as the quality control (QC) chart.

WARNING AND ACTION LINES.

Warning and action lines are 'limit lines' that are found on the process control chart. The horizontal scale is marked off as a time scale (or as sample numbers in order of testing) and the vertical scale is marked off with values of the property being tested. Most of these charts have 5 lines. There is an average value (determined during the set-up period), two sets of lines above the average line and, two sets of lines below. The first of the upper lines is called the Upper Warning Limit (UWL) and the second is called the Upper Action Limit (UAL). The first lower line is called the Lower Warning Limit (LWL) and, the second is referred to as the Lower Action Limit (LAL). These lines correspond to probability points on the normal distribution curve. They are normally set so that, if the product is being produced with the normal variation in values of the tested property 95% (or 1 in 20) of these values will lie within the Warning Limits. 99.9% of the test values will lie within the Action Limits. Since 1 in 40 of the results may be expected to lie above the upper warning limit and approximately 1 in 1000 above the upper action limit, these limits are sometimes known as the 1 in 40 and 1 in 1000 limits respectively.

RANGE CHART LIMITS.

The range chart usually has 3 lines. There is an average value (determined during the set-up period) and a set of two lines above the average line. The first upper line is known as the Upper Warning Limit (UWL) and the second upper line is known as the Upper Action Limit (UAL). The lower lines, known as the Lower Warning Limit (LWL) and the Lower Action Limit LAL), may easily be calculated, but this is often not done, as a small range is acceptable

MEAN CHART LIMITS.

The warning limits for the mean chart are calculated based on the fact that 95% of the results may be expected to be in the range $X \pm 1.96\sigma/\sqrt{N}$. In practice, it is normal to estimate the value of σ, the sample standard deviation, from the mean range (i.e. the average difference between the highest and lowest value obtained in each sample) using the equation $\sigma = Rd$ where d is a constant dependent on the sample size and R is the mean range. Therefore, the values for the mean warning limits (MWL) will be given by:

$$\mathbf{MWL = M \pm 1.96Rd/\sqrt{N} = M \pm A_wR.}$$

Where $A_w = 1.96d/\sqrt{N}$ and M is the grand mean of the sample means. The grand mean is often denoted by a capital X with a double bar superimposed. The mean action limits (MAL) are given by $MAL = M \pm A_aR$ where $A_a = 3.09d/\sqrt{N}$. Some figures for A_a and A_w are given in the following table.

Samples size N	2	3	4	5	6	7	8	9	10	12
A_w	1.23	0.67	0.48	0.38	0.32	0.27	0.24	0.22	0.20	0.17
A_a	1.94	1.05	0.75	0.59	0.50	0.43	0.38	0.35	0.32	0.27

THREE LINE CHARTS.

Some average control charts only have three lines on them: the average value, the upper control limit (UCL) line and the lower control limit (LCL) line. The two lines are obtained by adding three standard deviations (+3 σ) to the average and subtracting three standard deviations (-3 σ) from the average. These boundaries produce the limits of approximately 1 in 1,000. In this system there are no warning limits and it is common practice to use five measurements (N=5) in a sample. As with the previous system the standard deviation may be estimated from the mean range.

RANGE CHART.

In addition to a chart of the means it is also useful to produce a chart that displays the scatter of results in a sample. In practice a range chart is most commonly used. In this case the range warning limits (RWL) are given by RWL + D_wR and the range action limits (RAL) by RAL = D_aR. Some values for D_w and D_a are given in the following table.

Sample size N	2	3	4	5	6	8	10	12
D_w (upper)	2.81	2.17	1.93	1.81	1.72	1.62	1.56	1.51
D_w (lower)	0.04	0.18	0.29	0.37	0.42	0.50	0.54	0.58
D_a (upper)	4.12	2.99	2.58	2.36	2.22	2.04	1.94	1.87
D_a (lower)	0.00	0.04	0.10	0.16	0.21	0.29	0.35	0.40

A simpler range chart is often used with just the Upper Control Limit, which for a sample of size N=5 is given by 2.11R.

USE OF A QCC FOR VARIABLES

A QCC is typical used to check the product of a manufacturing process, such as a polymerization process. In this case we will assume that earlier studies have shown that measurements of melt flow rate give a good guide to consistency of quality. Let us also assume that we wish to monitor two supposedly identical processes more or less simultaneously. For example, a particular reactor may be operated with two alternating shifts or there may be two supposedly identical adjacent reactors. To set up charts we carry out the procedure outlined below. The procedure described will be for the QCCs involving warning and action limits. Clearly the process is simpler where just two control limits are used.

SETTING UP A QCC.

During a period when there are no production problems samples are taken and each tested N times. (Assume N=5.) From these 5 measurements we calculate the sample mean X and note the difference in value between the highest and the lowest result. This is the range (R) of the sample. We then in turn, average all the sample means to get the grand mean μ, or X double bar, and average the values of R to get the mean range R. From these data, using the formulas given above, we calculate the warning and action limits.

GRAPHICAL REPRESENTATION.

A vertical line is drawn on the left hand side of a piece of paper and on the center of the line is marked the value of the grand mean. A horizontal line is normally drawn through this point. Horizontal dashed lines are then drawn from the vertical axis at points corresponding to the warning limits. Similar, but differently patterned lines are drawn for the action limits. A range chart may be constructed in a similar way immediately below the means chart. At the bottom of the lower chart a horizontal line is marked off with the sample number as they become available for testing.

RECORDING.

As the samples are produced, and tested, the mean and range results are recorded graphically on the charts. If there is some known difference in the way that the samples were obtained (for example, from a different reactor or shift), it is useful to denote the different sets of results using a different color or symbol. The data should be plotted on the charts and then subjected to the interpretation described in the next section. If the interpretation concludes that the process should be investigated, the limits should not be used until the process has been inspected and put back into control, when new limits may be calculated.

INTERPRETATION.

Providing the operator understands the probability of getting the particular result(s) that he/she has obtained, interpretation is largely a matter of common sense. Let us consider some examples.

1. A plotted result occurs that is above the upper warning limit on the chart of the means. Such a result may be expected on 1 occasion in 40. If, however, the next sample also gives the same result the chances of two such results occurring is less than 1 in 1600 and therefore the process must be investigated immediately.
2. A plotted result is outside the upper action limit. This is clearly an indication that the process has changed and it must be investigated.
3. Graphical plots may indicate a drift in the results, even though initially they are within the limits. If the cause of the drift is not investigated and controlled, not only may QCC limits be exceeded, but product specification limits may also eventually be exceeded. This is a good example of anticipating trouble before it becomes serious.

4. Graphical plots, where there are two or more sets of samples (for example, from different reactors), may show different patterns for the two sets much more clearly than tables of numbers. This will help to pinpoint where an investigation may be needed.

The above comments although introduced above with respect to means charts, also apply to the range charts.

QCCs FOR ATTRIBUTES

This will be dealt with only briefly here without any reference to theory. If we are concerned with recording the number of defective items in a batch, the mean action limit (MAL) in this case, is given by $MAL = Np3.09 \pm \sqrt{[Np(1-p)]}$. Where p is the average proportion or fraction of defective items in the batch. The inner warning limits are obtained by substituting 1.96 for the 3.09 figure in the above equation.

If we are concerned with the number of defects in a piece of material (e.g. the number of pinholes in a length of film), it may be shown that if the average number of defects is Y, then the Number Action Limits and Number Warning Limits are given respectively by:

$$Y \pm 3.09\sqrt{Y} \text{ and } Y \pm 1.96\sqrt{Y}.$$

SETTING UP STATISTICAL PROCESS CONTROL (SPC).

For quality assurance and/or quality control systems to work effectively it is essential that everyone is totally dedicated to the concept of quality. Before any strategy is implemented or documents prepared, there must be commitment from senior management and discussions with key people throughout the organization. Those responsible for implementing the quality strategies must be provided with the correct equipment and with clear and precise directions. The duties of everyone involved must be publicized and the effect of their contribution on the quality of the end-product/service must be defined.

QA AND TQM.

Quality assurance (QA) aims for zero defects and to get the job done right the first time. The emphasis is on preventing defects and on building in quality at every stage of a process. The impetus for improvement must come from the top of the organization and then it must involve everyone from the directors down to the shop floor personnel. Such total quality management (TQM) requires a change of attitude and a commitment on the part of everyone to zero errors/defects and, to supplying products that meet the customer's requirements. All departments in an organization must be committed, not just the production department. Ideally the function of a quality control (QC) department is to reassure everyone that the quality is being maintained.

QUALITY CONTROL INSPECTORS

Quality control inspectors are usually necessary and such people must be regarded as members of the team. The inspectors must be trained in quality control (QC)/statistical process control (SPC)) techniques, so they can interpret QC/SPC data effectively. QC/SPC will only work if the people who analyze the data do so correctly and if they act sensibly to correct faults after information analysis.

QC WITH AVERAGE AND RANGE CHARTS

Quality control charts (QCC) (sometimes known as process control charts) show how well a process is operating. As explained in the previous section they will show if the process is functioning in an acceptable way, if the process has moved out of control, or if it is about to drift out of control. The tendency of a machine to drift out of control can, therefore, be spotted before rejects have been produced. However, to get the information required, it is necessary to take samples, or measurements, at predetermined intervals, perform measurements, or comparisons, record the data, chart the measurements, assess the results and then, take appropriate action.

IMPLEMENTING SPC.

It is suggested that a manual data collection and interpreting system be tried before a computer-based system is installed. Once the concept has been tried and proven then the information so gathered may be used to define what precisely is wanted.

1. Communicate with your customer to ensure that the correct characteristics are being subjected to SQC/SPC control.
2. Ensure that all personnel are involved, committed and have the right training.
3. Carry out a production capability analysis to establish that the process can consistently meet the customer’s requirements.
4. If necessary, modify the production plant or process until the correct production capability is obtained.
5. Ensure that any computer software will handle the data and give the information that is required.
6. Once both you and the customer are satisfied with the production process, enter the SPC details into the SPC computer.
7. Decide, after consultations with the customer, on the frequency of the checks to be carried out by the SPC inspectors.
8. Ensure that the SPC inspectors enter the information into the SPC computer as specified or that the measuring instruments enter the information directly into the SPC computer.
9. Display and retain the information against a production run identification,
10. Assess the results and then, take appropriate action.

USE OF RHEOMETERS FOR SQC/SPC

Rheological measurements are valuable for determining if a product is within specification and the process involved is under control. They may be used to measure the flow properties of polymer immediately after polymerization, of a compound after blending, or incoming resins purchased by a fabricator. Experience will determine what specific data are most useful to measure. These data may include melt viscosity at one or more shear rates, melt index, melt density or critical shear rate for onset of melt fracture. Statistical packages are available with some rheometers that allow one to establish limits for each variable selected and print out a detailed conformance report for a sample. Such a package is resident in the LabKARS for Windows Software included with all ***Dynisco Polymer Test*** 7000 Series of capillary rheometers.

ON-LINE RHEOMETERS

The term on-line rheometers refers to rheometers have been developed for continuous automated monitoring of viscosity or melt flow rate in manufacturing processes. These systems are generally mounted on an extruder or reactor from which they extract and test a sample of molten polymer, which may be discarded or returned to the process. Generally, the resin sampled from the process is taken up by a small melt pump, which precisely meters the melt through a capillary or slit die. One or more pressure transducers monitor the pressure drop across the die.

To measure the viscosity the rheometer melt pump is run at a constant rate and the pressure drop across the die is measured. From the volume flow rate produced by the pump, the pressure drop and the die dimensions, values of the shear rate and shear stress are calculated. The viscosity is then calculated from these values. When melt flow rate is required, the system is run at constant pressure. (The pressure used is generally the same as that produced in an ASTM lab test.) From the pump speed and its volume flow per revolution and the die dimensions the melt volume flow/time can be determined. When the melt density of the polymer is known the melt flow rate (MFR) in grams/10 minutes can be calculated.

Because they can continuously monitor a process on-line rheometers have been used for SPC for many years. The continuous data stream from these instruments provides “real-time” information on a process without the delay for lab tests. This enables SPC to be applied to real-time control of the process. Recently these rheometers have also gained acceptance in quality control and are being used to certify resins for shipping to customers.

AUTOMATIC QUALITY CONTROL

Because of the power of the microprocessor, it is now relatively easy to incorporate features that verification product quality during manufacture. Verification of product quality at the point of manufacture can be documented in statistical process control (SPC) records. The average, or set, value of a monitored value may be automatically displayed, together with appropriate control limits. During production the data is gathered and displayed. Production drifts, or trends, can, therefore, be easily spotted and, out-of-specification products rejected completely or, diverted for inspection.

Appendix II

A METHOD FOR STATISTICAL ANALYSIS OF CAPILLARY RHEOMETER DATA

It is well known that the flow behavior of a molten polymer cannot be fully described by a single data point, but is best represented by a function. As the viscosity generally changes with the stress or rate of shear, a single point measurement only describes one unique viscosity related to a unique set of test parameters. When these parameters (rate, pressure, temperature) are changed the viscosity will probably change. Thus the melt flow rate measurement may be a poor predictor of polymer melt behavior.

As we have shown earlier (See Chapter 11. “High Shear Rate Rheometry”), the capillary rheometer is well suited for producing the data that describe the behavior of a polymer’s melt viscosity as a function of shear rate or shear stress. In fact the data produced can cover the range of rates or stresses seen in many conversion processes. Since the mode of operation of the capillary rheometer is similar to many conversion processes (The first extruders and injection molding machines used rams rather than screws.) these instruments produce data that can be used to predict “processability”.

The processability or “true” consistency of a resin can only be predicted from a function or curve that describes its behavior in an actual conversion process. If one can quantify the entire curve then it can be used to assure a resin’s consistency and suitability for a conversion process. To accomplish this we must establish the variability in the viscosity verses shear rate (or stress) curve for a material, due to machine, material, methodology, environment and man. The steps needed to do this are:

1. Define a standard “good” resin, or typical production samples, or a series of lots that process well in your process.

2. Using this resin, generate statistically significant number (optimally 20 or more) viscosity curves over the range of shear rates (or stresses) existing in the process. (This may be done, for example, during product development or in the normal course of QA testing.)

3. Use these data to determine the mean values of viscosity and their $\pm$ 3 σ deviations at each shear rate (or stress).

4. Plot these data on a normal viscosity versus shear rate (or stress) graph. The +3 σ and -3 σ values about the mean viscosity values produce what we call a “tube”. (See Figure 36.) These values can also be considered as the upper and lower control limits (UCL and LCL).

Statistical Analysis of Rheological Data

The Rheology "Tube"

Plot of the mean viscosity vs. shear rate.

The (+/-) 3 sigma values to produce a "Tube" around the curve.

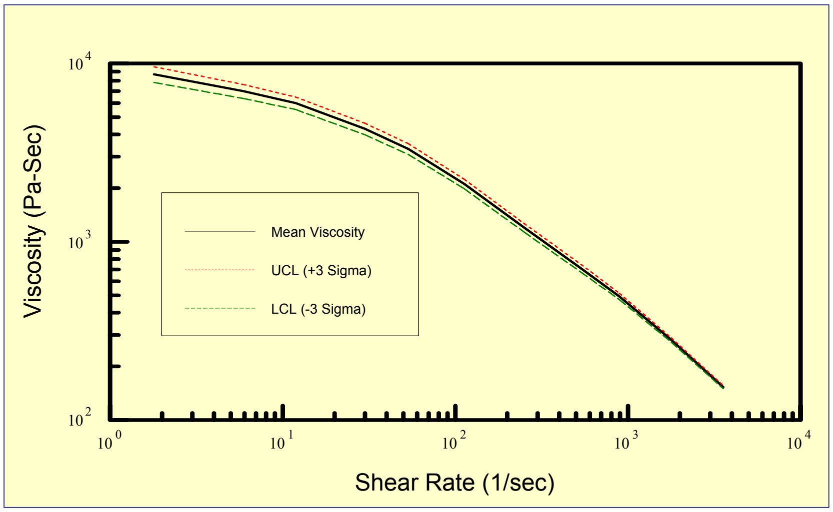

Figure 36.

The "tube" defines the natural variability of that material, machine, and man in the lab test. Generally, for an in control measurement, the material (resin) will provide the largest source of variability represented by the "tube". [The latter two variables may be kept under control by periodically checking the instrument performance "tube" with a stable lab calibration standard (e.g.; LLDPE or polypropylene) as is done in the rheometer manufacturing process.][1] When the complete rheology curve for a test resin falls within the "tube" it is within the established specification for that material, over the entire range of rates it will see in processing. If the curve, or any part of the curve, falls outside of the "tube" it is considered to be out of specification. The way, in which the curve moves out of the "tube", it's direction, slope, or shape, will provide an indication of what change has taken place in the product. These may include changes in molecular weight or molecular weight distribution (from degradation or cross-linking), branching, or variations in composition. (See Figure 37.) The algorithms required to perform this analysis are found in the LabKARS Software supplied with the ***Dynisco Polymer Test*** LCR 7000 Series of capillary rheometers.

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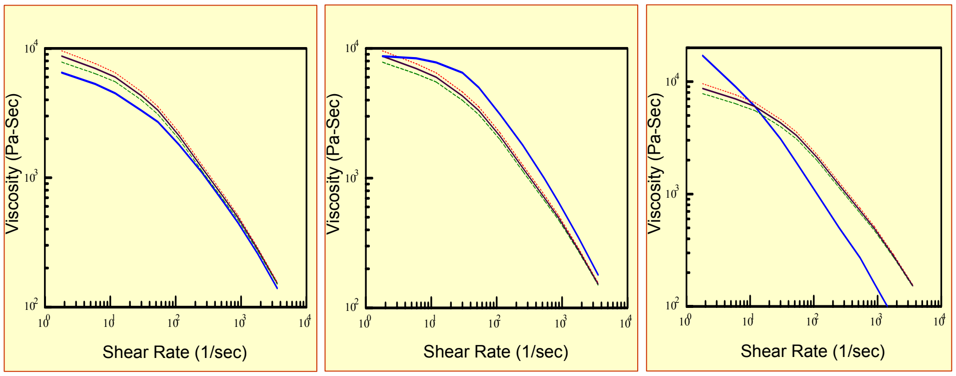
[1] Reilly, J.F., "A Practical Method for Improved Rheological Analysis", Technical Papers Vol XLII, p. 2370, SPE ANTEC (1996).

Effect of the Change in Molecular Structure on Melt Viscosity

The Rheology “Tube”

Simulated



Molecular Weight **Molecular Weight Distribution** **Branching**

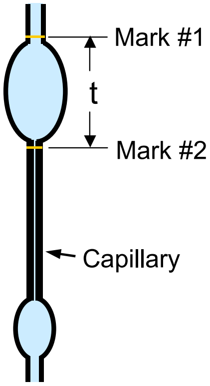
Figure 37.

Appendix III

Prediction of Solution Viscosities from Melt Viscosity and Melt Flow Rate

The dissolution of even a small amount of polymer in a solvent causes a significant increase in the solution viscosity. For this reason and the simplicity of the measurement, solution methods have been extensively used in the characterization of polymeric materials for many years. Figure 38 shows a table containing definitions of many of the different solution viscosities that are frequently used. Of these various viscosities the intrinsic viscosity, which defines a theoretical reduced or inherent viscosity achieved when the concentration of polymer approaches zero, (See Figure 39.) is related to the size of the molecules and thus to their molecular weight. As a result, the intrinsic viscosity and the reduced and inherent viscosities are often used in process and quality control for specification of polymers such as PVC, nylon and PET. The relationship between the intrinsic viscosity and molecular weight, developed from the Einstein Viscosity Equation, is quantified in the Mark-Howink-Sakaruda Equation:

Molecular Weight (Size) from Polymer Solution Viscosity



Capillary Viscometer

t_0 = time for solvent
t = time for solution
η= viscosity

Solution Viscosities

(Constant Solvent & Constant Temperature)

Common Name	IUPAC Name	Symbol and Defining Equation
Relative Viscosity	Viscosity Ratio	$\eta_{rel}=\eta/\eta_0=t/t_0$
Specific Viscosity	-------	$\eta_{sp}=\eta_{rel}-1=\left(\eta-\eta_0\middle/\eta_0\right)=\left(t-t_0\middle/t_0\right)$
Reduced Viscosity	Viscosity Number	$\eta_{red}=\eta_{sp}/c$
Inherent Viscosity	Logarithmic Viscosity Number	$\eta_{inh}=\ln\left(\eta_{rel}\right)/c$
Intrinsic Viscosity	Limiting Viscosity Number	$\left[\eta\right]=\left(\eta_{sp}/c\right)_{c=0}=\left[\ln\left(\eta_{rel}\right)/c\right]_{c=0}$

Figure 38

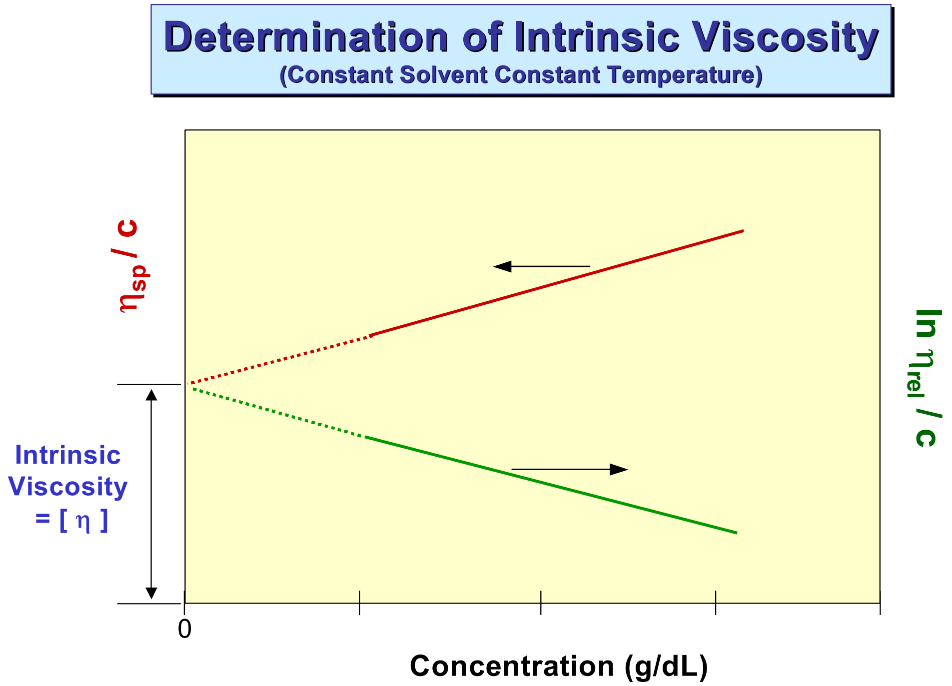


Figure 39.

$$[\eta] = K (M_v)^a \qquad (1.)$$

where: **M_v** is the "viscosity average molecular weight".
(May also be **M_w** or **M_n**.)
K and **a** are called the "Mark-Howink Constants"

Values of the "Mark-Howink Constants", for a polymer in a particular solvent at a specified temperature, are determined from the correlation of the intrinsic viscosities with molecular weights, of a series of polymer samples, measured by an absolute method (such as M_w from light-scattering). Values of these constants can be found in the literature (For example "The Polymer Handbook" edited by Brandrup and Immergut, published by Wiley-Interscience.) for a wide range of polymers in various solvents and at several temperatures. Generally, the magnitudes of the exponent constant "a", that are found in the literature, range between values of 0.6 and 0.8. A plot of the intrinsic viscosity verses weight average molecular weight (M_w) for nylon 6 is shown in Figure 40.

The melt viscosity of a polymer is very strongly affected by its molecular weight. [See Section 13.4, (pg. 52) "Effect of Molecular Weight and Molecular Wight Distribution on Polymer Flow" and Figure 41.] Extensive experiments on linear (non-branched) polymers, with a range of molecular weights, have shown that, above a "critical"

Relationship of Intrinsic Viscosity to Molecular Weight

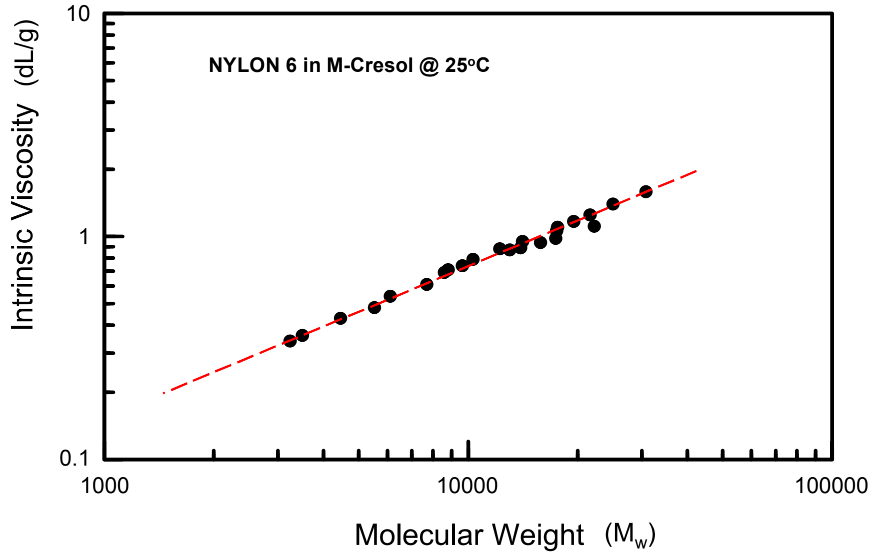


Figure 40.

Melt Viscosities of PET Resins with Different IVs

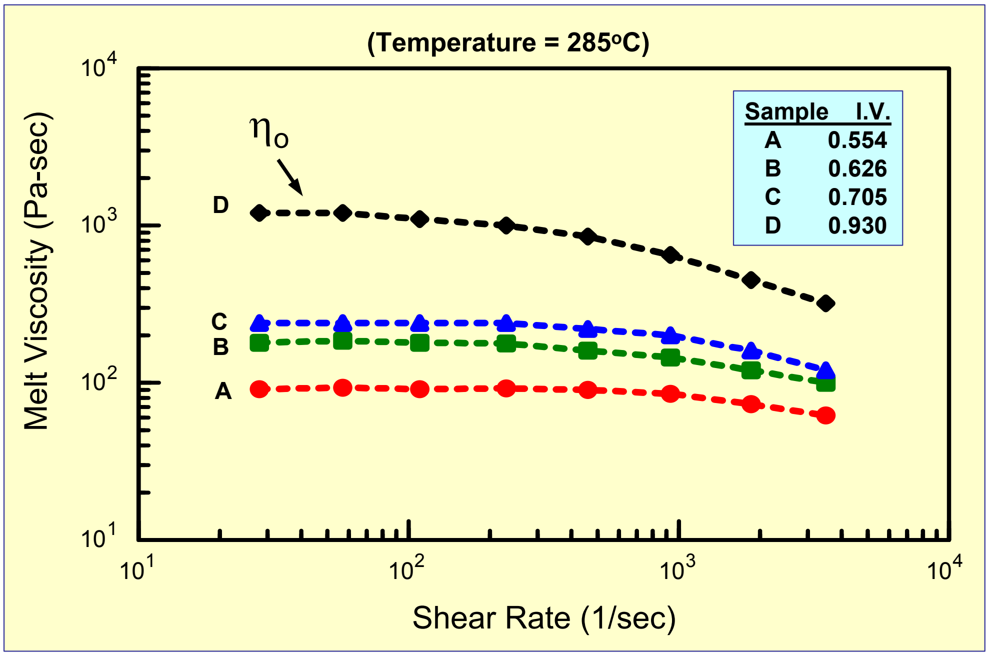


Figure 41.

value (M_c), the melt viscosity (at constant temperature) is related to the weight average molecular weight (M_w) through the relationship:

$$\eta_o = K' (M_w)^{3.4} \quad (2.)$$

Where: η_o is the Newtonian or "zero shear rate" melt viscosity
M_w is the weight average molecular weight
K' is a constant.

(Below the critical molecular weight the exponent = 1. As the shear rate increases above the "zero shear rate" range the exponent decreases towards a value = 1 at infinity.)

Looking at the equations for intrinsic viscosity and melt viscosity we can see that they are both a function of molecular weight. It can be shown that the viscosity average molecular weight and the weight average molecular weight are close in value ($M_v \cong M_w$). In addition, the M_w is very frequently used to obtain the Mark-Howink Constants. The melt viscosity, however, is much more sensitive to the molecular weight with it's exponent of 3.4, relative to 0.6 to 0.8 for the solution measurement. We can develop a relationship between the two viscosities in the following manner:

For the Mark-Howink Equation:

$$[n] = K(R M_w)^a \quad (1.)$$

$$\ln[n] = a\ln(M_w) + a\ln(R) + \ln(K) \quad (1a.)$$

And for the expression for melt viscosity:

$$\eta_0 = K'(M_w)^{3.4} \quad (2.)$$

$$\ln(\eta_0) = 3.4\ln(M_w) + \ln K' \quad (2a.)$$

Combining the equations equal through molecular weight we get:

$$\ln[n] = \frac{a}{3.4}\ln(\eta_0) + K'' \quad (3.)$$

$$\ln[n] = 0.215\ln(\eta_0) + K'' \quad (3a.)$$

Equation 3 shows that the two viscosities are related through a linear equation where the slope is the Mark–Howink Constant a divided by 3.4 and the constant K" is the y intercept. When we insert a value of 0.75 for "a" for PET (in Phenol/TCE @ 30°C), the value for the slope in 3a becomes 0.215.

From Equation 3 we can see that, for any polymer, we can establish a relationship between melt viscosity and intrinsic viscosity if we have two or more standards for which both values are known. If we know the Mark-Howink Constant "a" for the resin, as in Equation 3a, then, since the slope is constant, all we need is one standard to establish the constant K" and the relationship between the viscosities. Figure 42 shows a plot of the data for PET from Figure 41. (The IV is plotted in a linear scale for clarity since the slope of the log-log plot is very steep.)

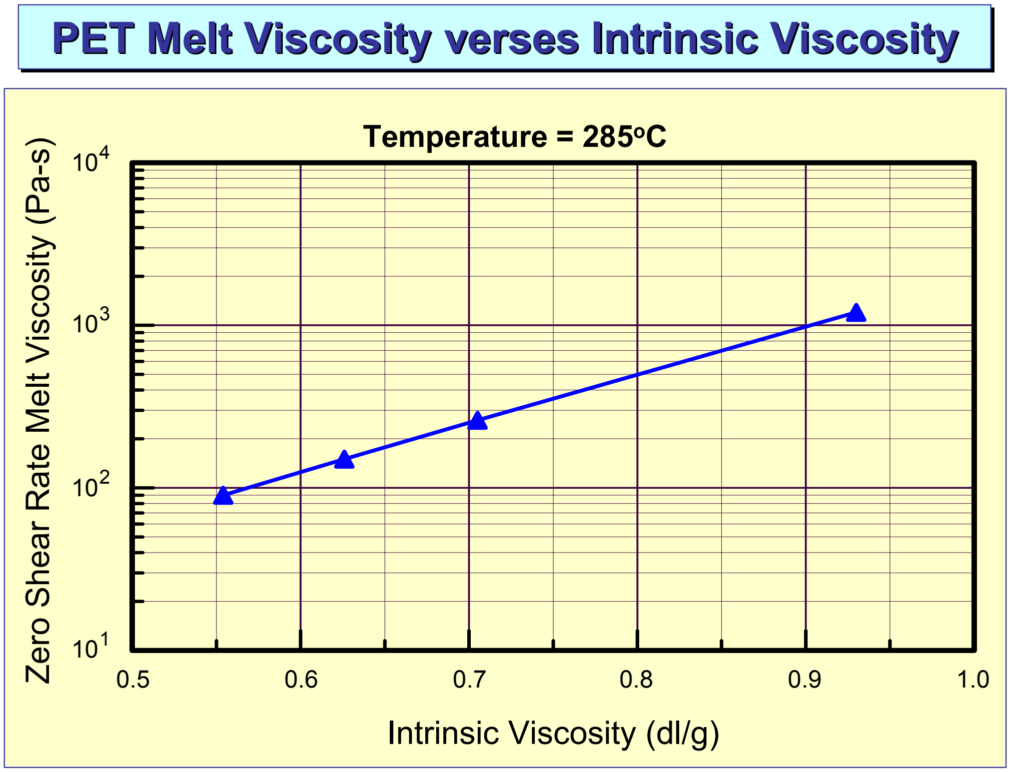


Figure 42.

It can be shown that a similar relationship exists between the melt flow rate (MFR) and solution viscosity. Figure 43 shows a plot of data from ASTM tests D1238 and D4603 for a PET resin. (Note that the slope is reversed.)

The determination of the intrinsic or another solution viscosity from melt viscosity or melt flow measurements has found a wide acceptance in industry. Besides the fact that the melt measurement is much more precise, it also eliminates the environmental and disposal issues regarding the aggressive solvents used for the solution measurements. In addition, melt flow and viscosity tests are much better suited to automation and in process measurements and can provide timely input for process control.

PET Melt Flow Rate verses Solution Viscosity

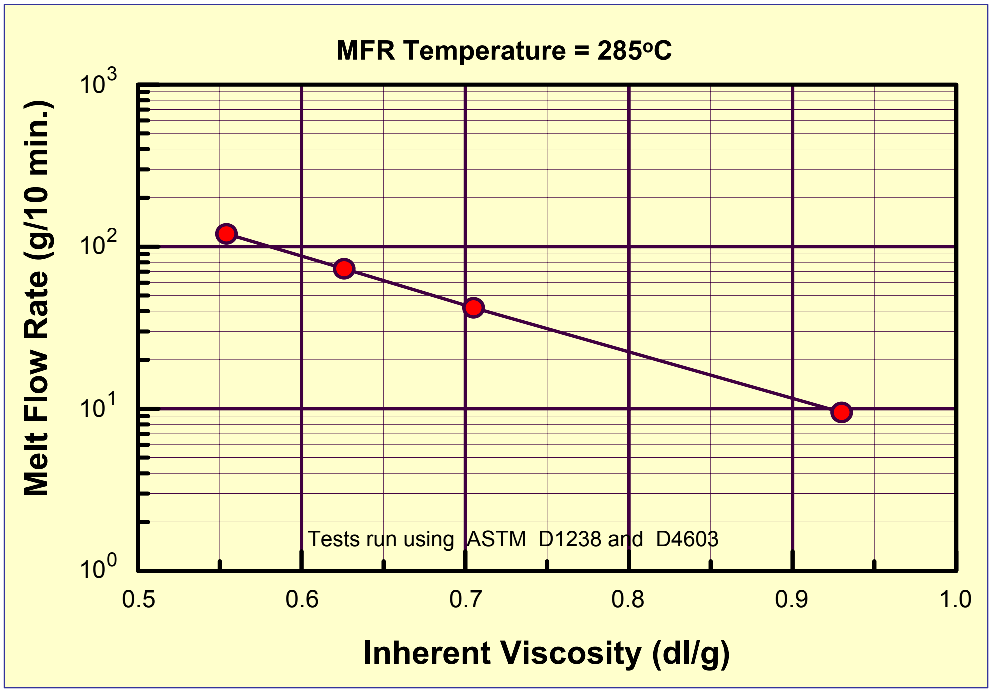


Figure 43.

Appendix IV

MEASUREMENTS OF EXTENSIONAL VISCOSITIES WITH A CAPILLARY RHEOMETER

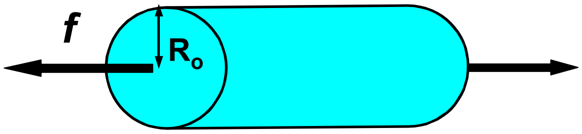
The shear flow of a molten polymer is an important and unique characteristic of these materials. It reflects the basic molecular structure of the macromolecules and, as discussed earlier, is often used to characterize polymer resins. It may also dictate the performance of a material in conversion processes and, therefore, is widely used in the plastics industry for quality and process control.

Not all processes, however, subject the molten polymer only to shear, but also to tensile stresses such as those seen in fiber extrusion, film forming, and blow molding. In such processes extensional viscosities may be more important than the shear viscosities. Figure 44 shows the definitions of extensional stress, strain and strain rate for a fiber

.

Flow of Polymer Melts

Extensional Deformation



Extensional Strain **Extensional Strain Rate** **Extensional Stress**

$$\varepsilon = \ln \frac{L}{L_0} \qquad \dot{\varepsilon} = \frac{1}{L}\frac{dL}{dt} \qquad \sigma_e = \frac{f e^{\dot{\varepsilon} t}}{\pi R_0^2}$$

L_o = Original length   *L = Length after deformation*

Figure 44.

Similar expressions exist for other geometries.

Unlike shear viscosities, which generally show a decline with deformation rate, the extensional viscosities can either decrease (strain thinning) or increase (strain hardening). (See Figure 45.) For example, in stable fiber spinning it is important to have a material that will strain harden in order to prevent fiber breakage. In blow molding, a strain thinning material will tend to make parisons that have thin walls at the corners, as extra pressure is needed to fill these regions. A strain hardening material will maintain a more uniform thickness in these areas.

Shear and **Extensional** ***Viscosities***

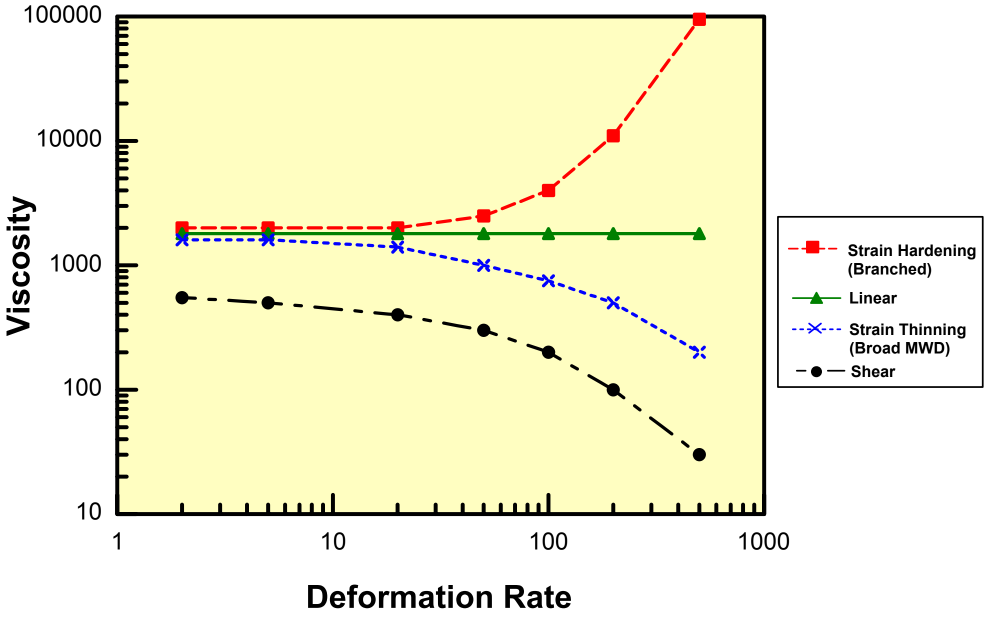


Figure 45.

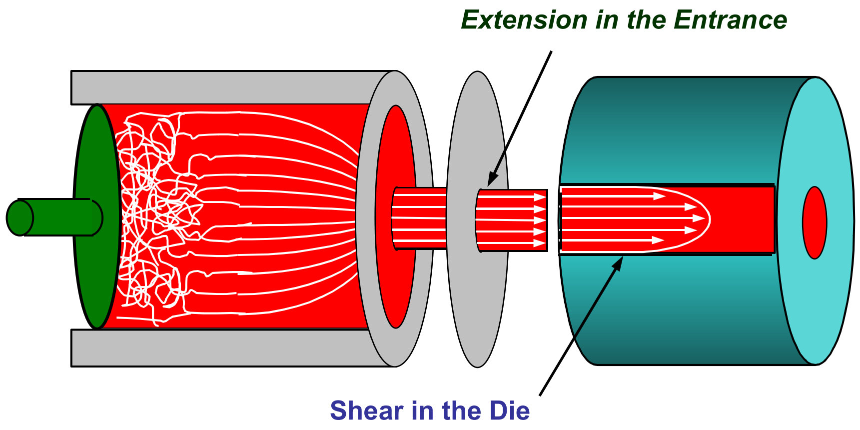
There have been numerous approaches developed for the measurement of extensional viscosities, however, the most practical method in use today is one developed by F.N. Cogswell [1]. He observed that as a melt flows from a reservoir into a die the streamlines converge and accelerate, producing a strong extensional flow. If the length of the orifice through which the melt exits is very small or “zero”, one can then assume that the pressure drop observed is due predominantly to extension. (See Figure 46.) (A rigorous mathematical treatment of this analysis can be found in references 2 and 3.) From this model he developed the set of equations for the calculation of extensional stresses, rates and viscosities shown below.

---

[1] Cogswell, F.N., Polymer Eng. and Sci., 12, 64 (1972).
[2] Cogswell, F.N., J. Non-Newtonian Fluid Mechanics 4, 23 (1978).
[3] Shroff, R.N., et. al., Trans. Society of Rheology 21, (3) 429 (1976).

Measurement of Extensional Rheology

Entrance and Die Flow



Cogswell's Equations

Determination of extensional properties

Extensional Stress = $\sigma_E = \frac{3}{8}(n+1)P_0$

Extensional Rate = $\dot{\varepsilon} = \dfrac{4\eta\dot{\gamma}^2}{3(n+1)P_0}$

Extensional Viscosity = $\lambda = \dfrac{9(n+1)^2}{32\eta}\left(\dfrac{P_0}{\dot{\gamma}}\right)^2$

Figure 46.

The use of the Cogswell Equations requires the determination of the quantities P_o, (the pressure drop across a "zero length die"), $\dot{\gamma}$ and η (the shear rate at the die wall and viscosity in fully developed flow), and n, (the power law exponent). A standard capillary rheometer may be used to make these measurements, however, this often proves to be cumbersome, as several runs have to be made to obtain one set of values. A capillary rheometer can, however, be modified to contain two “bores” or barrels in the same heated block. This allows the simultaneous testing of more than one sample of material with capillaries of different length or diameter. A diagram of such an instrument is shown in Figure 47. In this instrument two pistons are driven, by a ball screw drive system, through the two barrels. The shear rates generated by each barrel are determined by the piston drive speeds and die geometry. High temperature pressure transducers mounted above the dies measure the pressures developed in each barrel during a test. The shear stresses are calculated from the measured pressures and die characteristics. The main use of this instrument has been to provide all of the data needed for a Bagley Correction in a single run.

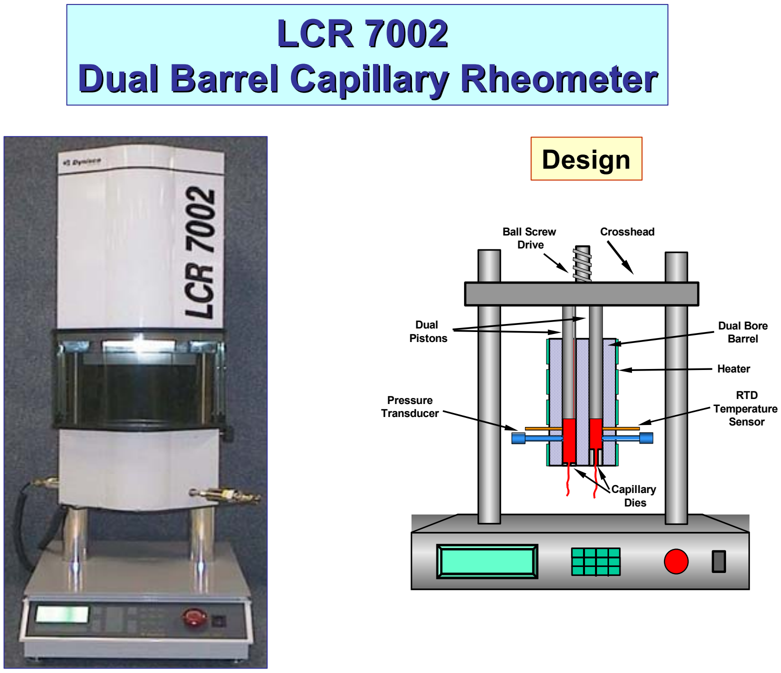


Figure 47.

In this application, dies of the same diameter, but different lengths are used. These generally include a die with L/D > 20 and a second with L/D < 1. The pressure drop at “zero length” (P_o) is obtained from the extrapolation of a linear fit of the pressure verses L/D for the two dies at each shear rate tested. The shear viscosities and rates are determined from the piston speeds, dimensions of the long die, and the pressures generated across this die. The value of n at each shear rate is calculated from a polynomial fit to the shear stress verses shear rate curve generated by the long die. These computations are usually carried out by computer using software such as that available with the Dynisco Polymer Test LCR 7002 Capillary Rheometers. Figure 48 shows experimental results from measurements of the shear and extensional viscosities of a linear low-density polyethylene made with the LCR 7002 Capillary Rheometer.

Measurement of Extensional Viscosities

Experimental results

LLDPE @ 190 °C

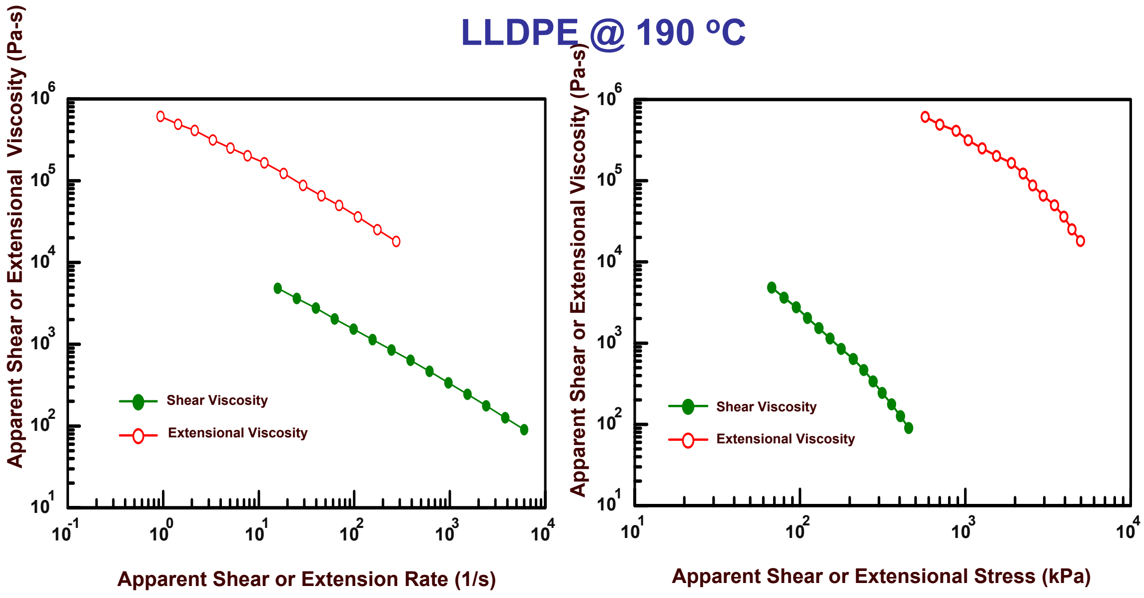


Figure 48.

Appendix V

ON-LINE RHEOMETERS

Generally, laboratory melt indexers and capillary rheometers have been used to generate rheological data for quality and process control in polymer manufacturing and processing. These instruments, however, require trained laboratory personnel and a significant turn around time to produce data for QA or process control applications. For these reasons, on-line rheometers, automated rheometers that are interfaced directly to a process, have been developed. Although several different kinds of on-line rheometers have been developed, most of the systems in use employ a capillary or slit die. These instruments have found acceptance for many years in the polyolefins manufacturing industry where large volumes of resin are produced and timely control of the process is required. Most of these rheometers are found on extruders (usually mounted between the end of screw and die head) although some have also been mounted on reactors. Recently, more specialized and compact instruments have been developed that facilitate their use in compounding and conversion processes.

On-Line Rheometer – "Bypass" Type

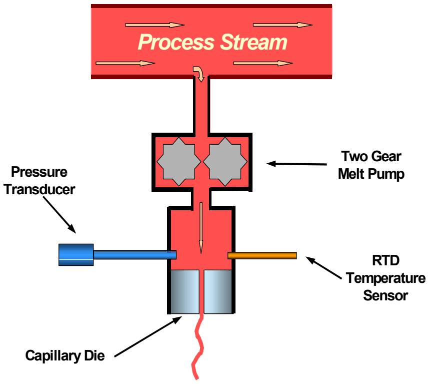


Figure 49.

The simplest form of the on-line rheometer is shown in Figure 49. In this instrument a melt metering pump samples polymer melt from a process stream and conveys it to a cavity containing a thermocouple (or RTD), pressure transducer and capillary die. The melt pump produces a precisely metered flow of the molten polymer through the capillary die and the pressure transducer measures the pressure drop produced. When this rheometer is run at a constant pump speed, the shear rate through the die is determined from the volume flow rate and die dimensions, while the shear stress is established from the pressure drop across the capillary die and its dimensions. Since the viscosity is defined as shear stress/shear rate, a continuous output of this material property can be calculated and displayed. These instruments, however, are more commonly run under pressure control to produce a continuous output of melt flow rate. The pressure is controlled so that a constant shear stress, equal to that produced in a standard MFR test, is produced. The dies used in this situation are similar to those used in the standard ASTM test. Under these operating conditions the melt volume flow rate is determined from the volume/revolution and speed of the melt pump. When the melt density of the molten polymer is known the melt flow rate (MFR) in grams/10 minutes can be calculated. Figure 50 shows melt flow rate data obtained from a bypass rheometer during the extrusion of a series polycarbonate samples with slightly different melt flow rates.

On-Line Measurement of MFR

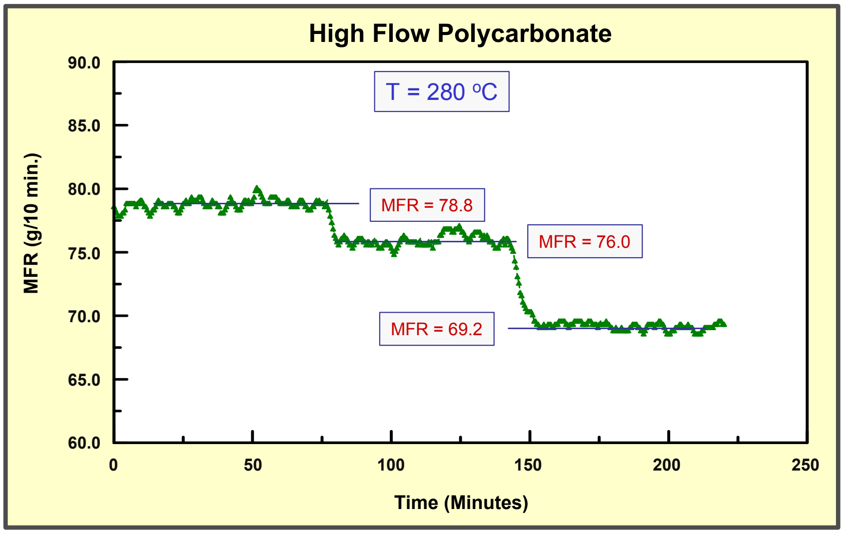


Figure 50.

Often it is desirable to return the tested resin to the process for financial, housekeeping, or safety purposes. To accomplish this, a second transducer and melt pump, are added to the outlet. The second pump serves to isolate the test from fluctuations in the process pressure and to return the melt to the process stream. An innovative new return stream (or "zero discharge") capillary die rheometer is shown in Figure 51. In this instrument, to simplify the design, the two "stacked" melt pumps are driven from one shaft by a single motor and transmission. A novel "annular" transfer line, which fits into a standard sensor port, is used to collect polymer and return it to the process. The inlet tube also projects into the process stream for better sampling of the flowing melt. Other types of return stream designs use slit dies to eliminate entrance corrections and “fast sampling” loops to reduce sampling delays.

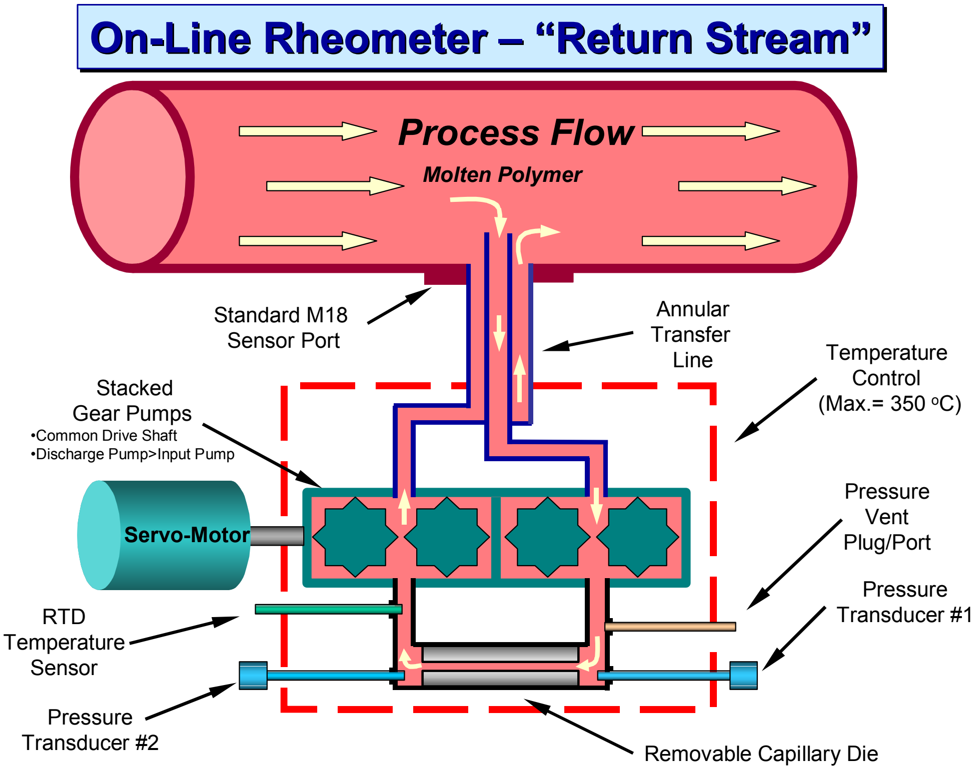

On-Line Rheometer – “Return Stream”

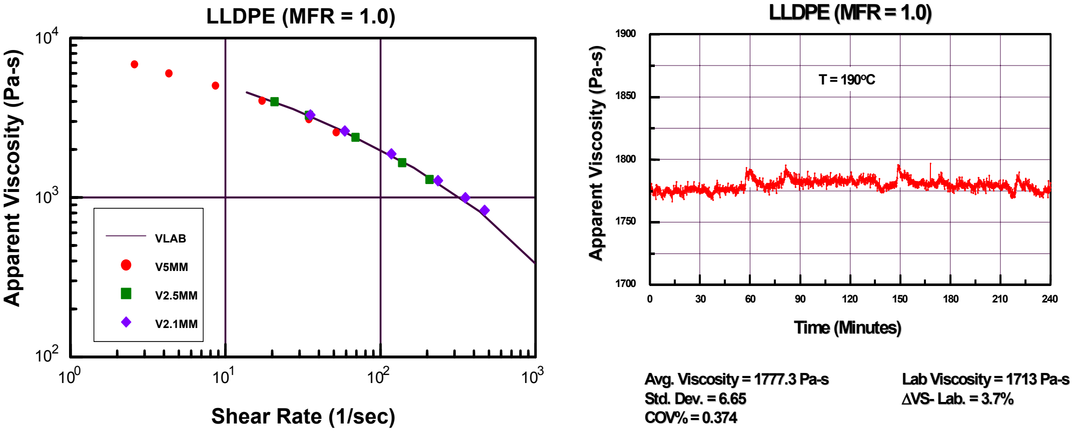
Figure 51.

Both bypass and return stream rheometers are available with two or more capillary or slit dies. For these rheometers a three-gear (or more) melt pump is used to divide the in coming melt stream between two (or more) melt chambers. In the rate control mode such rheometers are used to continuously produce multiple shear rates, provide the information to correct for entrance effects (See Bagley Corrections), or measure extensional viscosities (See Appendix III). In pressure control they can be used to continuously measure hi-load/ low load melt flow rate ratios (See section on Melt Flow).

The operations (temperature control, pump speed, etc.), data acquisition (pressure, temperature, pump speed, etc.), calculations (MFR, viscosity, etc.) and display of most on-line rheometers are controlled through a microprocessor, PC or DCS. These control system can be programmed to continuously step through a series of motor speeds in order to measure melt viscosities over a range of shear rates. By using an optimized selection of capillaries, pressure transducers, and motor speeds, it is possible to continuously generate viscosity curves, over a shear rate range of several decades. If the number of shear rates measured is optimized, it is possible to generate a complete new flow curve every five minutes.

Figure 46 shows the results of on-line viscosity measurements made with the Dynisco ViscoSensor return stream rheometer on a linear low-density polyethylene resin. The first chart, Figure 46a, shows an example measurements made at a number of different shear rates by using several different pump speeds (and dies). It can be seen that the viscosity values generated, lie very close to those generated in the laboratory with a capillary rheometer, represented by the solid line. Figure 46b shows a continuous measurement of viscosity at a fixed shear rate. Over a period of four hours the system shows a very high precision of measurement (better than that achieve in multiple laboratory tests) and good agreement with laboratory analyses. Tests with on-line rheometers consistently show that, when operated correctly, they consistently produce more precise results with a much faster response time than the laboratory. For these reasons and the drive towards increasing automation in manufacturing the acceptance of on-line rheometers in the plastics industry is rapidly expanding.

On-Line Measurements of Melt Viscosity



a.) Accuracy

b.) Precision

Figure 52.