Practical Rheology Section 2

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 1o 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.

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.

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 crosssection, 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
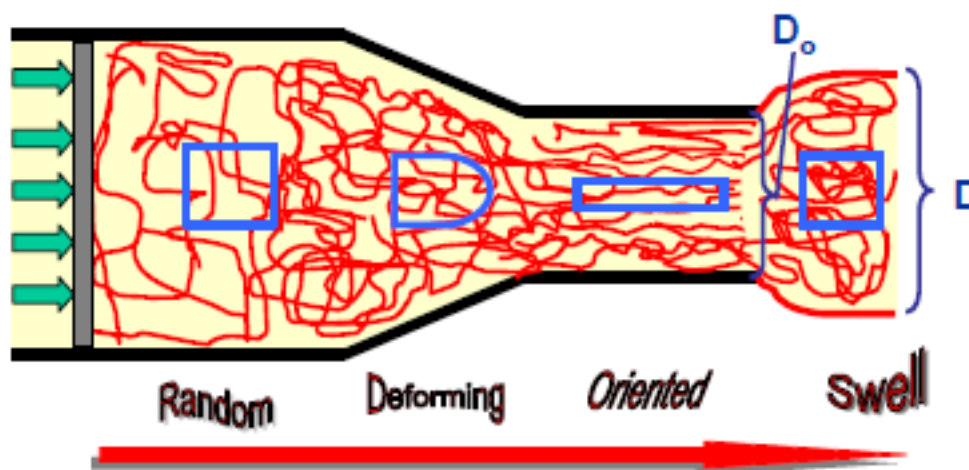
has been greatest.

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

Random   Deforming   Oriented   Swell

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.
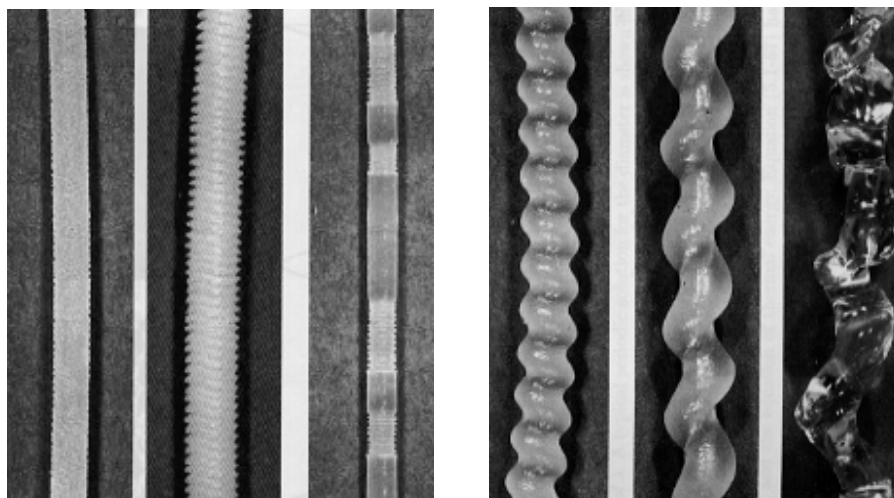
Sharkskin.

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 (γc) is inversely proportional to the die radius ®. (i.e.γc 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).

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

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From lab to production,
providing a window into the process

Raw Materials | Verification (MFR) C=(MFR)... | Pressure & Temperature | Sustainability | Material Analysis | Profitability Scrap Reduction Quality Improvement

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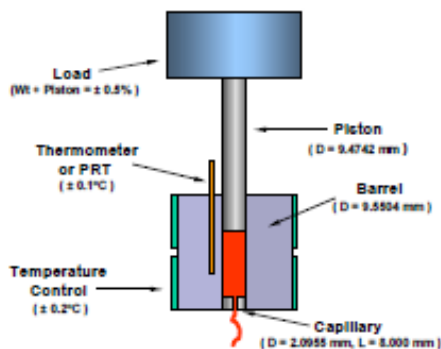
>Mass / time measured. (g/10 min.)
>MFR α 1/Viscosity
>May be related to, but not a
  strict function of, MW.

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

MFR = MFI = m x 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

FR(A) = m x 600/tA

Where m is the average mass extruded (m) within the cut-off interval tA (expressed in seconds). By Method B the flow rate is calculated from FR(B) = $\pi R2 \times L \times A \times 600/tB$.

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 tB 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 / πR2 L)(tB/tA)

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.

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.).

## 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
$Q = 71.630 (S)$
and the relationship for shear rate is
$\gamma\bullet = 91.203 S/R^3 c$
when the capillary radius (Rc) is in mm and the piston speed (S) is in mm/s.

The Capillary Rheometer
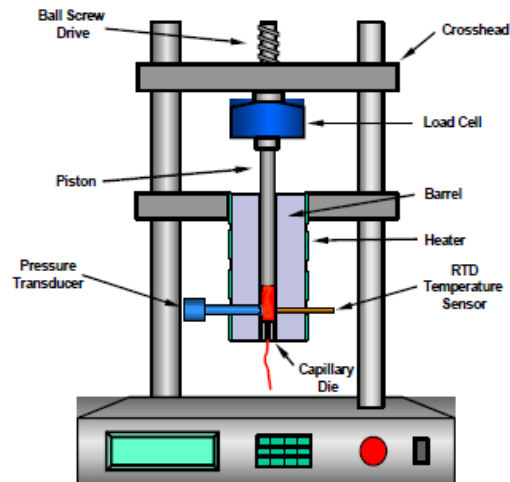
➤A driven piston provides a constant volume flow (Shear Rate) or pressure (Shear Stress).

➤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.

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.