

Rheology Conference
A Practical Approach
to Quality Control

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Rheology Conference

A Practical Approach to Quality Control

A Two-Day Conference

organised by

Rapra Technology Limited

held at

Rapra Technology Limited

Shawbury, Shrewsbury, Shropshire SY4 4NR, UK

1st and 2nd October 1998

A Two-Day Conference

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Why Rheology ?

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INTRODUCTION

It is often thought that rheology (the study of flow) is too esoteric to be of practical use. This paper sets out to show that this is not so. The knowledge of the flow properties of materials is of practical importance. Processes where fluids are subjected to flow such as mixing, blending, extrusion, fibre spinning and the piping of fluids in chemical processes are all within the remit of this science. Indeed rheology is at the heart of many industrial processes from resin manufacture, oil extraction to sewage disposal.

THEORY

There are two ways in which a fluid can be made to flow, either by applying a shear stress or an tensile stress. These give rise to values for the shear viscosity and elongational viscosity of the material.

As the name implies the shear viscosity applies to those operations in which the fluid is sheared. Extrusion profiling, most mixing and pumping operations apply shear stresses to the fluid to make it flow. The shear viscosity, η , is related to the applied shear stress and the shear rate by the formulae shown in **Figure 1**. In the example shown, the bottom plate is stationary and the top plate causing the shearing of the fluid moves with velocity, v . The applied shear stress to the top plate, σ , causes the liquid at the wall of the plate to move to position B, thereby applying a shear strain of to each element of the fluid flowing along the stream lines indicated. It can be shown for simple fluids where the viscosity is directly proportional to the applied shear stress that the shear rate is given by dv/dh .

Not all processes subject the fluid to shear, some such as fibre spinning and blow moulding subject the material to tensile stresses. In such cases, the elongational viscosity is a more important parameter than the shear viscosity **Figure 2** shows how the elongational viscosity is expressed in terms of the tensile stress and the extensional rate.

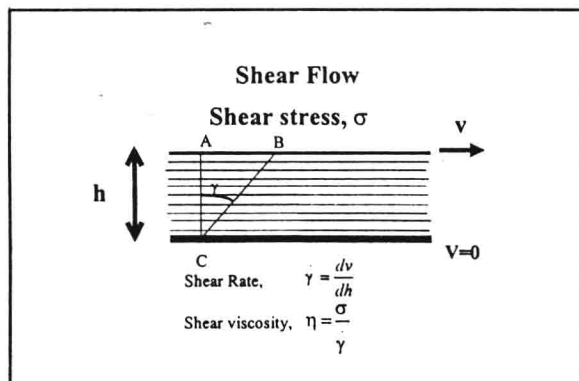


Figure 1
Shear Flow

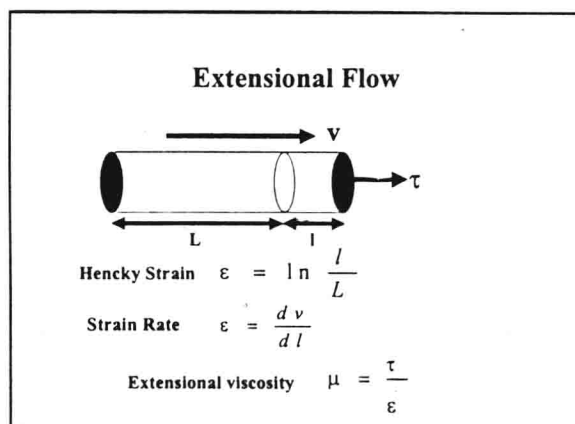


Figure 2
Extensional Flow

The above definitions hold for simple Newtonian fluids where both the shear viscosity and the extensional are linear functions of the shear stress and the extensional stress.

Not all fluids obey these simple rules, the viscosity of many materials, for instance polymer melts, are not linear functions of the applied stress and the viscosity of some materials are dependant on the length of time the strain rate has been applied.

INSTRUMENTATION

There are two main types of rheometer, rotational and capillary extrusion. In the former the fluid is contained within a gap between two co-axial cylinders (couette rheometers) or between two parallel plates. One of these surfaces is made to rotate, thereby subjecting the fluid to shear forces. The torque required to cause the rotating part to turn at a fixed angular velocity is measured. From the geometry of the system and these two parameters the viscosity of the sample can be calculated.

A couette rheometer shears the sample at a constant rate; however corrections must be made for end-effects. In the case of a parallel plate rheometer the shear rate applied to the fluid will increase along the radius. By making one of the plates slightly conical in geometry, less than 4° , it can be shown that the shear rate is essentially constant along the radius, **Figure 3**.

Cone-and-plate rheometers can work at very low shear rates less than 10^{-4} s^{-1} . Since polymer melts at these very low shear rates behave as Newtonian fluids and the viscosity is related to the molecular weight of the polymer by a simple power law, these instruments are ideal for calculating the molecular weight of the polymer melt. They are very sensitive instruments and can be used for measuring the viscosity of dilute solutions and how they vary with concentration.

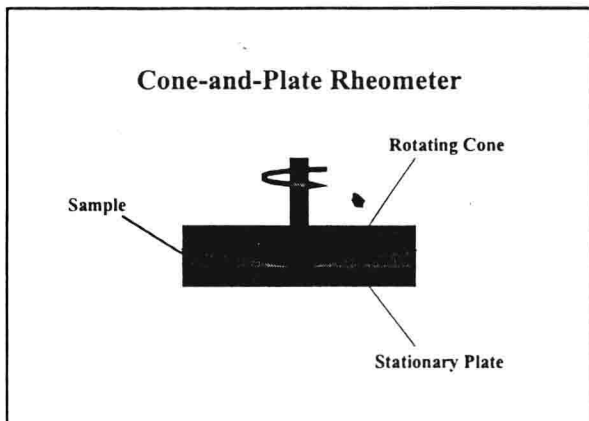


Figure 3
Cone and Plate Rheometer

Although the plate can be rotated at high velocity, meaningful data for polymer melts cannot be obtained at shear rates much greater than $10\text{s}^{-1(8)}$. This is because at higher shear rates flow instabilities particularly at the edges occur. So such rheometers cannot be used to investigate the behaviour of polymer melts at the high shear rates encountered in industrial processes such as injection moulding, extrusion profiling, fibre spinning and high speed mixing.

To explore these high shear rate regions capillary extrusion rheometers must be used. They overlap the range covered by the couette and cone-and-plate rheometers. The bottom of the range can be less than 1s^{-1} to many thousands of reciprocal seconds. The more powerful machines can reach values greater than $200,000\text{s}^{-1}$.

A diagram of the rheometer is given in **Figure 4**. The sample is loaded into the heated cylinder. When it has melted and/or reached thermal equilibrium, a close fitting ram is driven down onto the material at a constant controlled rate. This forces the material to extrude through a capillary die of known dimensions. A pressure transducer close to the entrance of the die measures the pressure rise. When the pressure reaches a steady value, the fluid has attained a constant laminar flow through the die; then the pressure and rate of descent of the ram is logged. The ram rate is increased the experiment repeated till the cylinder is empty. In this manner a series of rheological readings is obtained, so that a flow curve of the material can be plotted.

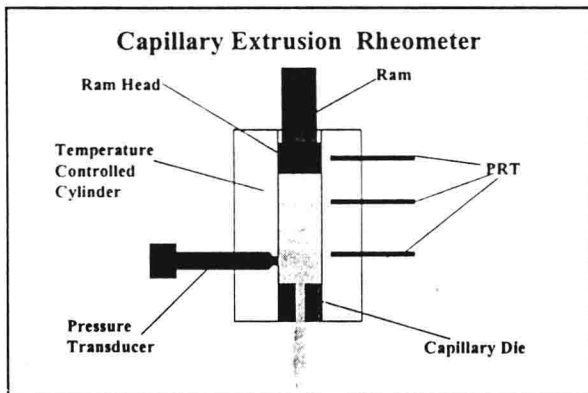


Figure 4
Capillary Extrusion Rheometer

The equations used to calculate the viscosity of the test materials for the cone and plate and capillary extrusion rheometers are shown in **Figure 5**.

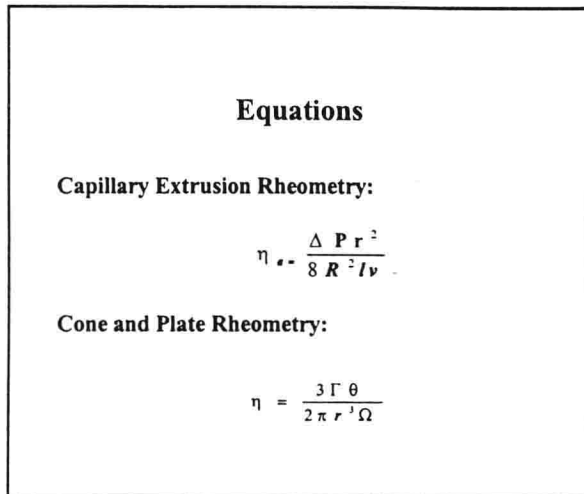


Figure 5
Equations

For the capillary extrusion rheometer η_a is the apparent viscosity, r , is the internal radius of the die (the capillary), R is the radius of the cylinder, ΔP the pressure drop across the die, v the velocity of the ram.

This formula is accurate for a Newtonian fluid, in which case η_a is the true viscosity. Entrance pressure and shear rate corrections must be applied to obtain the true viscosity of a non-Newtonian material ^(1,2,8). Where comparisons between samples is being made it is not always necessary to make these corrections and the apparent viscosity calculated from the Newtonian form of the equation will suffice. It is necessary to apply the corrections if the data derived from the experiment is to be loaded into a finite element modelling program such as Polyflow, Fillcalc or Moldflow.

For the cone-and-plate rheometer, η is the viscosity, Γ is the torque required to rotate the cone at an angular velocity of Ω , r is the radius of the plate and θ is the angle the cone makes to the horizontal.

Both instruments can be operated under constant stress conditions, by applying a steady pressure to the sample in the case of the capillary rheometer, or a constant torque in the case of the cone-and-plate rheometer. The latter is very useful for ascertaining the yield stress of a material.

TYPES OF FLOW

A plot showing the different types of behaviour for time independent fluids is shown in **Figure 6**.

A Newtonian fluid is one in which the shear stress is directly proportional to the shear rate. The constant of proportionality is the viscosity of the material. It is *only for Newtonian liquids that a value for viscosity can be given without stating the shear rate at which the measurement was made*. Simple liquids containing small molecules, e.g. water, exhibit Newtonian behaviour.

A pseudoplastic or shear thinning material is one in which the viscosity decreases with increasing shear rate. Many thermoplastic polymer melts behave in this manner.

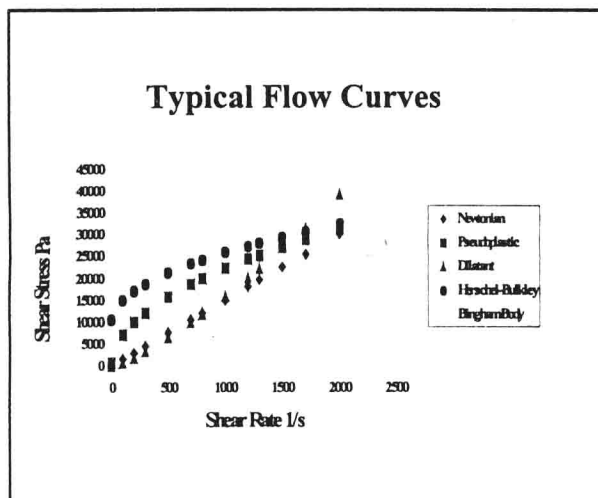


Figure 6
Typical Flow Curves

A dilatant fluid is one in which the viscosity increases with shear rate. This behaviour tends to occur for highly concentrated suspensions, like PVC pastes and certain sludges. It seems to most common for those materials which consist of suspensions containing irregularly shaped particles⁽¹⁾.

A Bingham Body or Plastic material begins to flow once a certain initial shear stress (the yield stress) has been overcome, after which it behaves as a newtonian fluid. Some slurries and suspensions behave in this manner.

A Herschel-Bulkley fluid is one in which a yield stress has to be overcome before it flows as a liquid exhibiting pseudoplastic behaviour. Highly filled polymer systems can behave in this way.

There are time dependent analogues of some of these systems. A thixotropic material is one in which the viscosity steadily decrease as the liquid is sheared at a given rate. Modern paints are constructed to have this property. At rest they can be very viscous, thus ensuring that they do not drip; but on application of shear forces by brushing the viscosity drops sufficiently to allow the paint to flow and spread over the surface being covered.

APPLICATIONS

Pseudoplastic Fluid

Consider the flow curves for the two polymers A and B shown in **Figure 7**.

Let us imagine that they are polymers of the same type, and that both had properties to suit the characteristics required for the final product. By looking at the flow curve the process engineer can see that since throughput is directly related to shear rate, which in turn is related to the screw speed of the extruder, it would be more economic to select polymer B since it will not require such a high torque to give the same volume output. Shear stress multiplied by shear rate is power.

Now let us imagine that these two polymers although of the same type are sufficiently different in molecular weight and molecular weight distribution to give a product that behaves as designed (polymer A) and one that does not (polymer B). The flow curves tell him that if he is supplied with a polymer

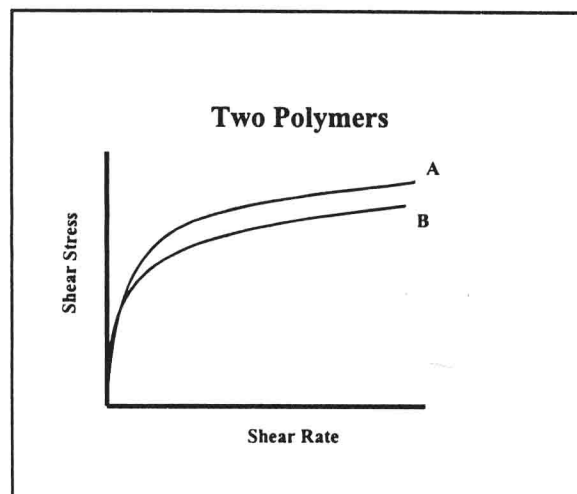


Figure 7
Two Polymers

of the same type that closely matches curve A he will make a product within specification. If his supplier presents him with one that closely follows the flow curve for polymer B, then the product will be out of specification. The engineer can set acceptance limits on the flow curve, and if the supplied polymer does not fall within these tolerances, the polymer can be rejected.

Either a QC lab can supply the data or a process control rheometer mounted on the line can be used to warn that poor polymer is coming through, and corrective action to be taken.

Herschel-Bulkley Fluid

The graph in **Figure 8** shows the behaviour of a Herschel-Bulkley fluid compared with a pseudoplastic material. In a log stress against a log strain rate plot it can be seen that the pseudoplastic material which behaves as a power law liquid gives a straight line the gradient of which is the power law index. The Herschel-Bulkley fluid deviates from the straight line at low shear rates moving to higher stresses. As the shear rate is further decreased the viscosity rise rapidly to very high values as the yield stress is approached

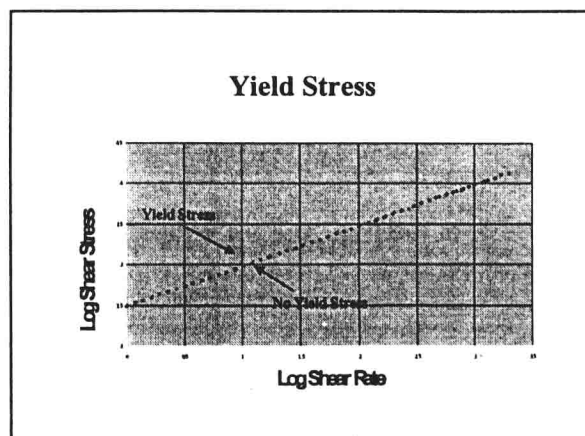


Figure 8
Yield Stress

The yield stress is an important parameter. In a mixing operation if the shear field within the mixer should fall below the yield stress then at those points the material will not flow and mixing will not be complete.

In some cases it is important to have a yield stress to preserve the geometric integrity of the extruded product such as propellants and high explosives ⁽³⁾. Should a sufficiently large yield stress not be present in the extruded products then the material would collapse and alter its geometry. Such a product would not behave ballistically as intended, possibly with disastrous consequences.

Waxy crude oil ⁽⁴⁾ cements ⁽⁵⁾ and ceramic pastes exhibit yield stress and indeed can behave thixotropically. That is why vibrators are used to ensure an even spreading of the concrete over the site.

The effect of temperature on the yield stress of highly filled polymers can give rise to some interesting phenomena. It was found for a particular explosive that extrusion of the material could not be accomplished at an elevated temperature. Extrusion was possible only at room temperature, even though it would be expected that the viscosity would be lower at the higher temperature. The throughput at ambient temperature was at a very low uneconomical rate. The material was tested in a capillary extrusion rheometer over a range of temperatures. It was found that although the viscosity of this pseudoplastic material decreased with temperature for any given shear rate, the yield stress increased with temperature. In fact once the yield stress was overcome high shear rates and hence high volume throughputs were possible. A few simple calculations showed that the press used was not powerful enough to overcome this high initial stress.

Bingham Body

Bentonite muds used in oil-well "down-hole" operations behave as Bingham bodies ⁽⁶⁾. A knowledge of how the material flows under the high temperatures and pressures existing in an oil-well helps the engineers to decide whether a particular mud will operate efficiently for the job in hand. For instance can it be pumped to the required depth, will it flow as expected?

Dilatant Fluid

As mentioned earlier, some sludges and suspensions ⁽⁷⁾ exhibit dilatant behaviour. It is important for a process engineer to know how the viscosity increases with shear rate, so that he/she can correctly size a pump capable of pumping the material at the desired volume throughput for the process.

Shear Heating

All materials if subjected to a high enough shear rate will become warm. This is well known in the thermoplastics trade where polymers are passed through screw extruders. What might not be appreciated is that the shear heating effects can occur in the die. This is particularly true with highly filled polymers (w/w 40%), **Figure 9**. ΔT represents the rise in temperature as the material is being extruded ⁽⁸⁾. As the material travels through the die the maximum temperature rise in the extrudate occurs some 10% in from the wall of the die ^(9,10). If the temperature rise at a given shear rate is sufficiently high then monomers or volatile plasticisers in then these will be evaporated leaving a skin of material round the extrudate with a different composition than the bulk. This

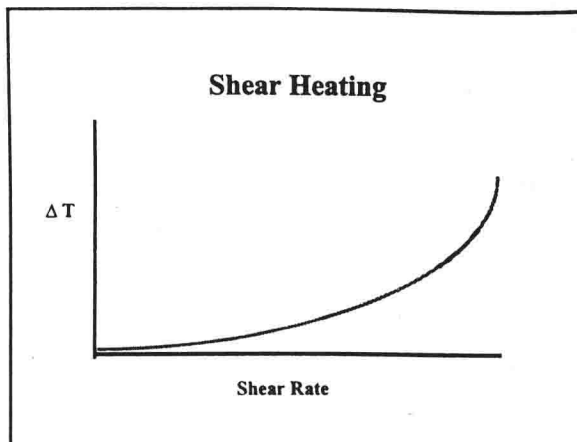


Figure 9
Shear Heating

can effect the physical properties of the final product. In the case of propellant manufacture, the temperature rise could be high enough to flash off solvent causing severe blistering of the extrudate, hence rendering it useless.

A knowledge of the expected temperature rise for a given shear rate will allow, the process engineer to tailor his process to avoid any problems that might arise from this effect.

Die-swell

Since polymer systems are visco-elastic, they exhibit die-swell (the Barus effect). This is seen as a swelling of the polymer as it exits the die, i.e. the geometric cross-section of the extrudate is larger than the die from which it was extruded. The effect is shown in **Figure 10**. It will be noticed that the ratio of the extrudate diameter "D" to the die diameter " D_0 " rises to a maximum as the shear rate is increased ⁽¹⁾.

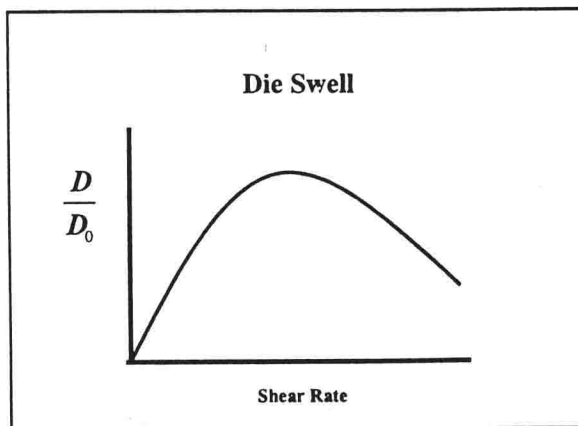


Figure 10
Die Swell

This is an important parameter and must be taken into account to produce an extrudate of the correct geometry ⁽⁸⁾. Volume throughput is a function of shear rate, so in designing the correct diameter for extruding a rod or pipe for example, it would be helpful for the engineer to know how much swelling will occur for a given throughput of product.

If the product consists of a more complex shape, e.g. square or T cross-section then the die must be made in such a manner that the swelling is uniform. The die must be designed such that as far as possible the shear rate experienced by the material is as uniform as possible across the die.

Nowadays there are powerful finite element software packages, which when loaded with the correct rheological parameters can help the engineer to arrive at a satisfactory die design.

Effect of Hydrostatic Pressure

The viscosity of a polymer is a function of hydrostatic pressure. Some excellent work has been carried out at RAPRA, using a special attachment to the capillary extrusion rheometer^(11,12). The graph in **Figure 11** shows that the change in viscosity with hydrostatic pressure is not only a function of the pressure; but also a function of the shear rate. The effect of hydrostatic pressure on viscosity is important in injection moulding. The results discovered at RAPRA have been incorporated into their Fillcalc software to design more efficient gates⁽¹²⁾.

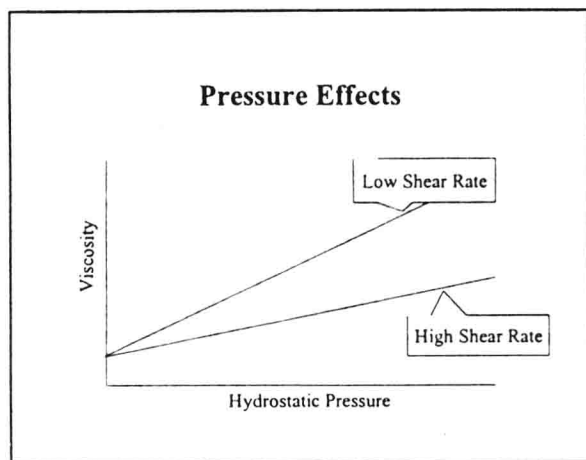


Figure 11
Pressure Effects

Elongational Viscosity

Blow-moulding, film forming and fibre spinning all involve stretching the polymer melt. Rather than shear viscosity, elongational viscosity is the more sensitive parameter for controlling these processes. There are many methods for measuring the elongational viscosity^(1,2), but perhaps the most exciting development is that devised by J. Collier and co-workers at Louisiana State University. They have developed a hyperbolic die that can fitted to a capillary extrusion rheometer⁽¹³⁾. The shape of the die causes the melt to be stretched with little shearing forces. The Henky strain that can be imposed on the melt is governed by the geometry of the die. Unlike nearly all the current methods, the elongational viscosity can be measured directly at stretching rates compatible with those experienced in the production environment⁽¹⁴⁾. Other methods using capillary extrusion rheometers to approach industrial stretching rates have to separate the shear viscosity from the elongational by using various models^(14,15).

The elongational viscosity can either decrease (strain thinning) with extension rate or increase (strain hardening).

For stable fibre spinning it is important to have a material that strain hardens rather than a strain thins. A polymer with the latter properties will exacerbate any non-uniformity in the fibre leading to instability and fibre breakage.

Knowing the rheological properties of the polymer can help the process engineer to set the spinning rate at the correct value and to take corrective action for lots slightly out of specification.

During blow moulding the parison is inflated to fill the mould. The polymer experiences stretching forces and hence a strain thinning material will tend to give thin walls at corners as extra gas pressure is required to push it into the corners of the mould. A strain hardening material will maintain a more uniform thickness.

Oscillatory Measurements

By using either couette or parallel plate type rheometers the visco-elasticity of a polymer can be explored in more detail⁽²⁾.

The sample in the rheometer is subjected to a small oscillatory strain or stress. The resultant torque is measured and separated into that component that is in phase with the imposed oscillation and that which is 90° out of phase. From these measurements complex shear modulus G^* is derived and separated into the elastic modulus G' and the loss or inelastic modulus G'' . The measurements are made over a range of frequencies. A typical plot for a polymer melt is shown in **Figure 12**.

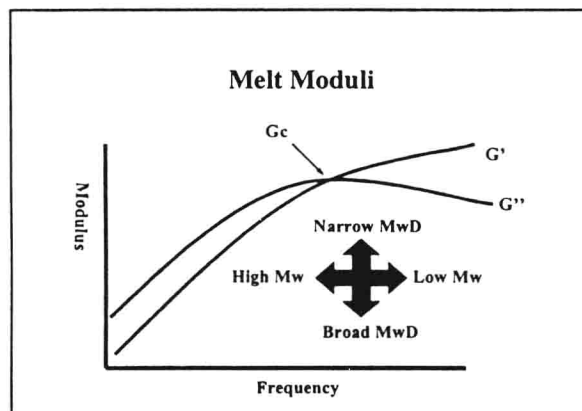


Figure 12
Melt Moduli

The graph shows that G' and G'' cross-over at G_c . The position of G_c is governed by the molecular weight and the molecular weight distribution. This can be and indeed is used as a Quality Assurance tool to assess the consistency of polymer pellets produced by the resin manufacturer. An automatic instrument has been developed by Rheometric Scientific for assessing PE and PP pellets and is used by several manufacturers as part of their QA protocol.

A similar oscillatory technique can be used on solids. The sample is held within grips which can apply oscillatory bending, shearing or tensile stress to the sample. These instruments are known as Dynamic Mechanical Analysers. The technique is very good for measuring the glass to rubber transition (T_g) of polymeric systems. The $T_g(\alpha)$ transition is shown in **Figure 13**. At this point the modulus of the material usually drops by several decades, and hence is an important

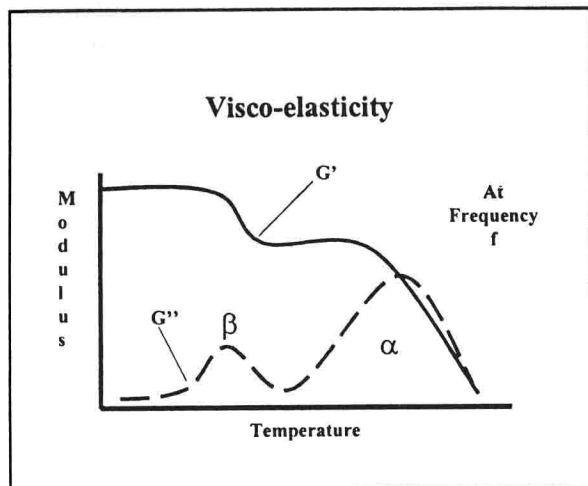


Figure 13
Visco-elasticity

engineering quantity. It is no good designing a polymer spring, or snap lid if the article will be operating above its T_g , since it will have lost all its stiffness.

Since it is not always possible to cover a wide frequency range with these instruments, the samples are often run at a fixed frequency and subjected to a slow temperature ramp.

By making measurements at different frequencies over the same temperature range, the performance of the polymer over a much wider frequency range than covered by the instrument can be estimated from the WLF temperature superposition equation or the Arrhenius equation.

Relaxation peaks⁽¹⁷⁾ occurring at low temperatures are due to movement of moieties within the polymer that have short relaxation times such as side chain groups and the high temperature relaxation are due to events such as main chain movement at the T_g .

Thus for a polymer to have high impact absorption properties it must possess a large high frequency (low temperature) loss peak, i.e. a broad low temperature relaxation peak.

CONCLUSION

This paper was written to bring to the reader's attention the importance of rheological measurements for processing and which rheological properties are important for different production techniques. In such a short paper it is impossible to cover all aspects of this important science and its application to industrial problems. There are many good books on the subject, and have been referenced as 1, 2, 9, 14 and 17 for polymer relaxation phenomena.

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Rheology Conference

A Practical Approach to Quality Control

Thursday 1st and Friday 2nd October 1998

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A New Approach to Polymer Rheology for Process and Quality Control

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DYNISCO Measurements and Control Group, UK

INTRODUCTION

Measurement of flow in the melt state is important to the polymer industry for several reasons. First, and most importantly, it gives us a measure of whether a thermoplastic material can be extruded, molded or formed into useable objects, by the common plastics conversion processes. In all of these processes, the plastic is first melted and then forced to flow through a die or into a mold, which gives it a final shape. If the melt flow is not matched to the process the material may not completely fill a mold or cause flash, distort an extrudate, cause uneven sheet or profile, or produce parts that fail under normal stresses or impacts. Secondly, the flow of a plastic material is also used as an indication of the whether it's final properties will be consistent with those required by an application. An increase in the melt flow from the specification may indicate a degradation of the polymer molecules, while a decrease may be the result of reaction between the molecules, or cross-linking. Errors in compounding may result in changes in either direction. These molecular changes may result in a loss of mechanical strength, impact, or chemical resistance sufficient to affect the final properties of a finished part.

SO, HOW DO WE MEASURE THE MELT FLOW OF A PLASTIC MATERIAL?

The major method used in the plastics industry today is the Melt Flow Rate Test (MFR) sometimes referred to as the Melt Flow Index (MFI). In this test the weight of polymer extruded in 10 minutes is measured under standard conditions of temperature, geometry, and force. Standard test procedures, which have been established for most polymers, can be found in ASTM D1238-95 or ISO 1133. The almost universal acceptance of this test has arisen from the fact that it gives an indication of quality while being simple, easy to operate, fast and, most importantly, inexpensive. These single point data are plotted versus time on control charts to establish the variability of the process and the consequential product quality. The test does, however, suffer from some shortcomings which make it less appealing for quality or process control. The short length of the die precludes fully developed flow, while its small length to diameter ratio leads to a mix of shear and extensional deformations. The large die diameter, relative to that of the barrel, causes the barrel pressure drop to become significant. Thus, the resulting flow of a material reflects many different aspects of a polymer's structure. The fact that all of these qualities are included in a single number, attractive though it may be,

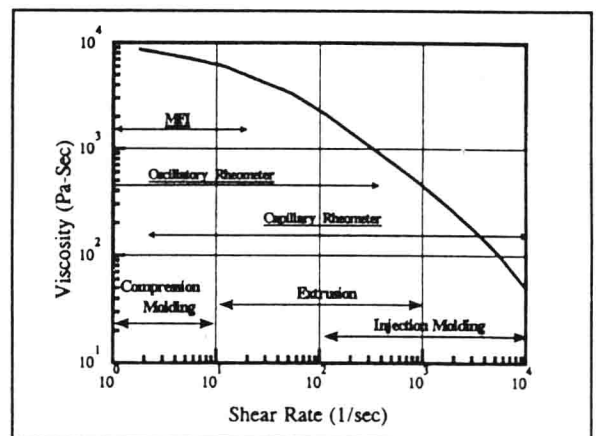


Figure 1
Rheology of Polymer Processing

frequently causes problems when we try to predict processability from it.

And processability is what the customer is interested in! **Figure 1** shows a plot of viscosity (resistance to flow) versus shear rate (rate of flow) covering the range of flow rates seen in several polymer conversion processes. The range in which the single point MFR values are generally found is also shown. From this figure we can see that, in general, the MFR test conditions are far removed from those seen in most conversion processes. A result of this is seen in **Figure 2a** which shows the rheology curve for a typical linear low density polyethylene (Resin A) and one of the more homogeneous metallocene catalyzed octene copolymers (Resin B). In this case standard MFR measurements on the two polyolefin polymers show that they both have the same melt flow rate of 1 gram/10 minutes. However, as we can see from the rheological comparison, the materials have much different viscosities at the deformation rates under which they may be processed. The reason for this can be seen in **Figure 2b**, a comparison of the polymer's calculated average molecular weights, determined from size exclusion chromatography. It shows that, although they have similar average molecular weights (as reflected in the MFR), they have significantly different molecular weight distributions (MWDs). And this difference in the MWDs results in significantly different flow under typical processing conditions. Thus, for example, although Resin A may successfully produce injection molded parts, under the same molding conditions Resin B may produce flash.

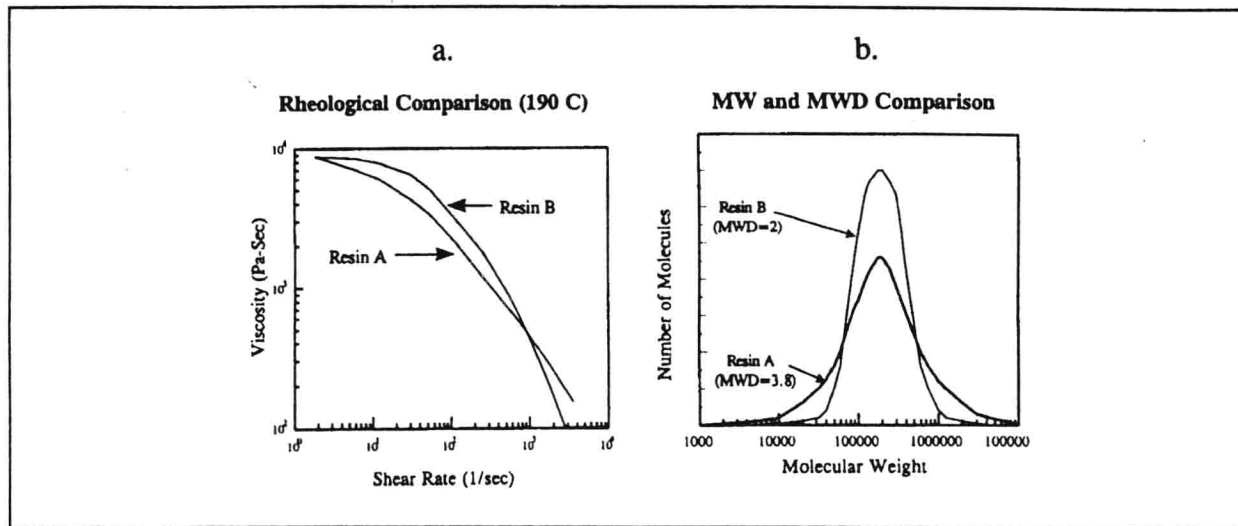


Figure 2
Comparison of Two Resins with MFI = 1.0

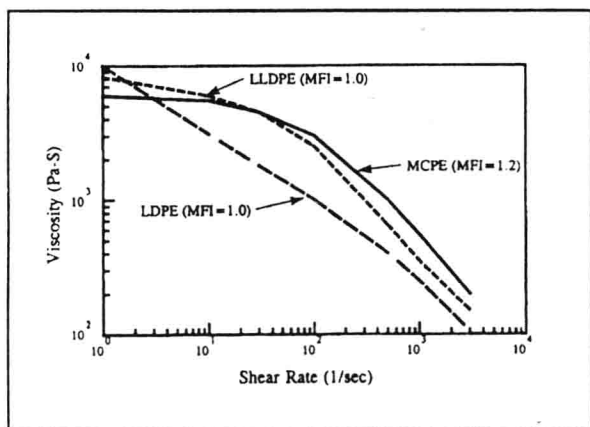


Figure 3
Rheological Comparisons (190°C)

Figure 3 shows another comparison, of three resins Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE) and Metallocene Catalyzed Polyethylene (MCPE) or "plastomer", which have similar melt flow rates. Melt flow index would predict that all of these resins with different polymer structures would require similar processing conditions. However, we can see from the curves that at the higher shear rates seen in extrusion or injection molding, their flow behaviors, which dictate their processing parameters, are quite different.

One way to determine the processability of a material would be to test each batch on actual plastics conversion equipment. This method, however, is slow, costly in machine time and in material. Another approach is to use the capillary rheometer (see Figure 4), which has many of the elements necessary to simulate the operation of the machines used in these processes. It is similar to the MFR instrument, with a temperature controlled barrel containing a piston that forces molten polymer through a capillary of fixed dimensions. In the capillary rheometer, however, the force used to extrude the polymer is generated by a motor and screw or servo-hydraulic system with the capability of producing a variable force and rate of extrusion. The force is measured, either by a load cell on the piston or a pressure transducer in

the rheometer barrel. The force necessary to produce flow (Shear Stress) and the rate of flow (Shear Rate) are then used to calculate the Viscosity or resistance to flow -

$$\text{Viscosity (h)} = \text{Shear Stress/Shear Rate.}$$

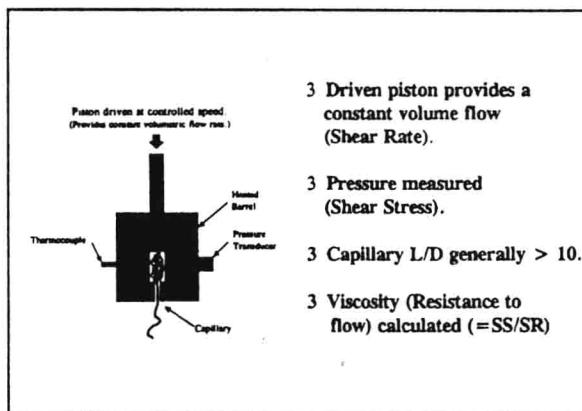


Figure 4
The Capillary Rheometer

Since this rheometer is able to reproduce the deformation rates at which polymer is actually processed (and that many of the early extruders and injection molding machines used a ram instead of a screw) it can actually simulate the conditions seen in a conversion process.

As we have seen, the processability or true consistency of a resin cannot be predicted from the single point produced in the MFR test. And the capillary rheometer can produce the function or curve that describes its behavior in an actual conversion process. So, why don't we use the entire curve to assure a resin's consistency and suitability for a conversion process, simultaneously? To accomplish this we must establish the variability of the viscosities, due to machine, material, methodology, environment and man, with time, over the entire range of shear rates measured. 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 twenty or more viscosity versus shear rate curves over the shear rates estimated to be seen in your 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 and $\pm 3s$ values of viscosity at each shear rate.
4. Plot all the data on a normal viscosity versus shear rate graph. The $\pm 3s$ values about the mean viscosity values produce what we call a "tube". (see Figure 5)

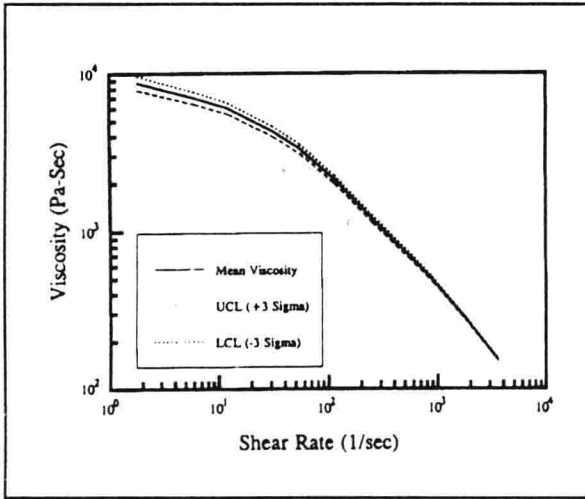


Figure 5
The "Rheology Tube"

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. (See Reilly, J.F., "A Practical Method for Improved Rheological Analysis", Technical Papers Vol XLII, p. 2370, SPE ANTEC (1996).)] Then, if the rheology curve for a test resin fits in the "tube" it is within the established specification 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 out of specification. And the way in which it moves out of the "tube", its direction, slope, or shape, will provide an indication of what change has taken place in the product. For example, if there is a change in average molecular weight, perhaps from degradation or cross-linking, the entire curve will tend to move up or down (see Figure 6).

As seen in Figure 7, a change in the molecular weight distribution (MWD) will cause a shift of the central part of the curve. A narrowing of the MWD will result in the appearance of a "knee" or a sharp change in the slope, whereas a broadening will cause the curve to flatten.

The effect of an increase in branching is shown in Figure 8. In this case we see that the whole curve is rotated to produce an increase in the slope. Similar changes in the rheology

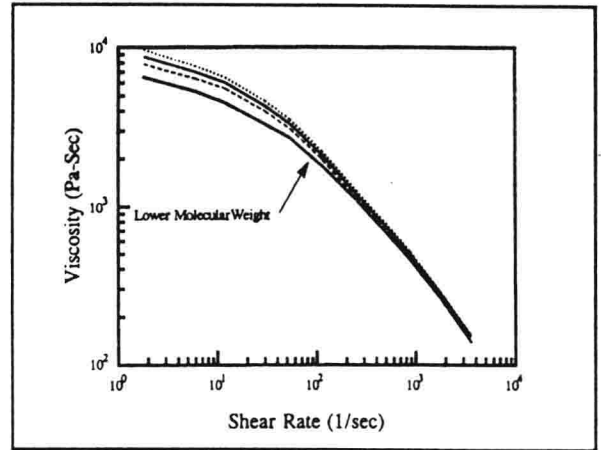


Figure 6
Effect of a Change in Average Molecular Weight

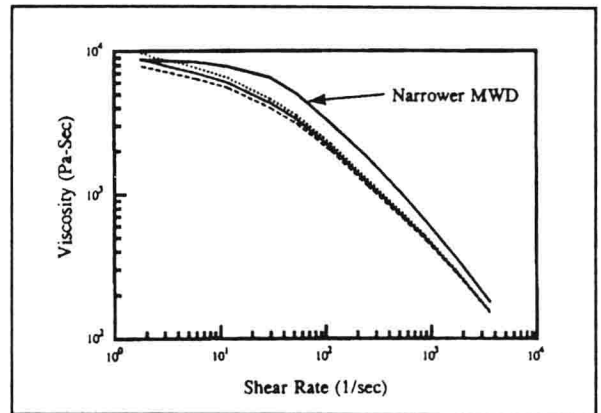


Figure 7
Effect of a Change in Molecular Weight Distribution

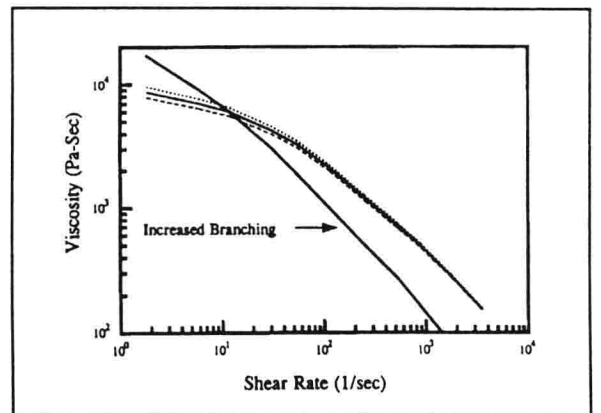


Figure 8
Effect of a Change in Branching

curve may be correlated to changes in, for example, blend composition or modifier level.

"Sure, that's real interesting", you may be saying, "but, how can I use it? I don't have the trained people to run the capillary rheometer, much less a rheologist to interpret the results. And I can't sit around and wait for the lab to produce results. I need to get product out the door!"

There are, however, practical methods for application of the rheology "tube" to process control and/or quality assurance. The first step in applying this concept in manufacturing might be to use a measure of the average goodness of fit for the rheology curve to alarm a change in the product. Then the value of the slope of the data could be used for a preliminary diagnosis. Finally, examination of the entire curve, by experienced personnel, would be used for trouble shooting. Eventually, variability seen in the product rheology could be related to the process variables causing the change. These relationships could then be used, with experience based software, to automatically diagnose and, perhaps, correct faults in the process to continually improve the product.

Timely production of data, for the software discussed above, will be required to provide inputs for process control. It will be labor intensive and the laboratory will not be fast enough. At best, it might produce a result every half hour. A new approach to providing these data is provided by the "Rheo-Truder", an automated capillary rheometer system. It consists of a laboratory type capillary rheometer interfaced to a small single screw extruder, (see Figure 9). The system, which may be located in a laboratory or on the manufacturing floor near the process, uses a pneumatic system to sample pellets or powder and transfer them to the extruder. (The rate of sampling is triggered by a detector in the extruder throat.) The extruder, set at the test temperature, then melts the polymer and transports it into the rheometer. Polymer entering the rheometer barrel forces the piston upwards until it strikes the load cell and initiates a test. As the piston is driven downwards increasing pressure closes a check valve, located between the extruder and rheometer, to prevent back flow. The rheometer then proceeds with a pre-set program of shear rates to produce the specified rheology curve. At the end of the test, piston travel stops and the resulting drop in pressure signals the rheometer to return its screw drive system to the "up" position. Low pressure in the barrel now allows the check valve to open admitting molten polymer, which pushes the piston up and starts a new test cycle. The total cycle time for the system depends on;

- 1) the pellet transfer time through the sampling system (seconds)
- 2) the extruder dwell time (minutes - depends on screw speed)
- 3) the barrel fill time (~30 seconds), the rheometer test time (depends on number and magnitude of shear rates used).
- 4) the rheometer test time

Hundreds of tests with the Rheo-Truder have shown that it produces very reproducible results that are in excellent agreement with laboratory measurements (see Figure 10.) In fact, the precision of measurement is much better than that obtained in the laboratory. Figure 11a shows the "tube" generated with our Dowlex 2045 LLDPE standard, while Figure 11b shows results on the same resin from laboratory tests. The improvement in precision probably arises from the

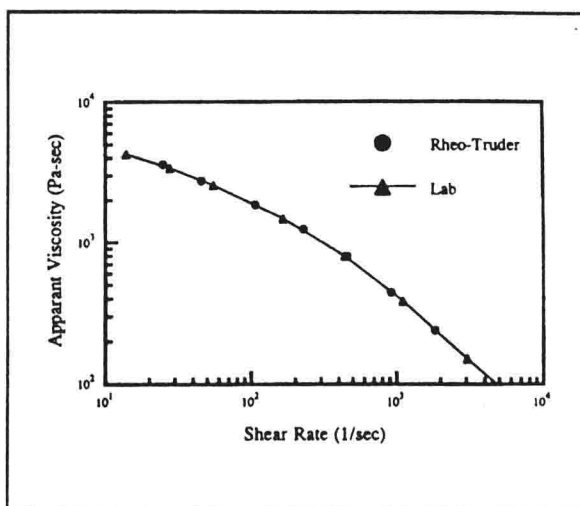


Figure 10
Results: Dowlex 2045 LLDPE (Accuracy)

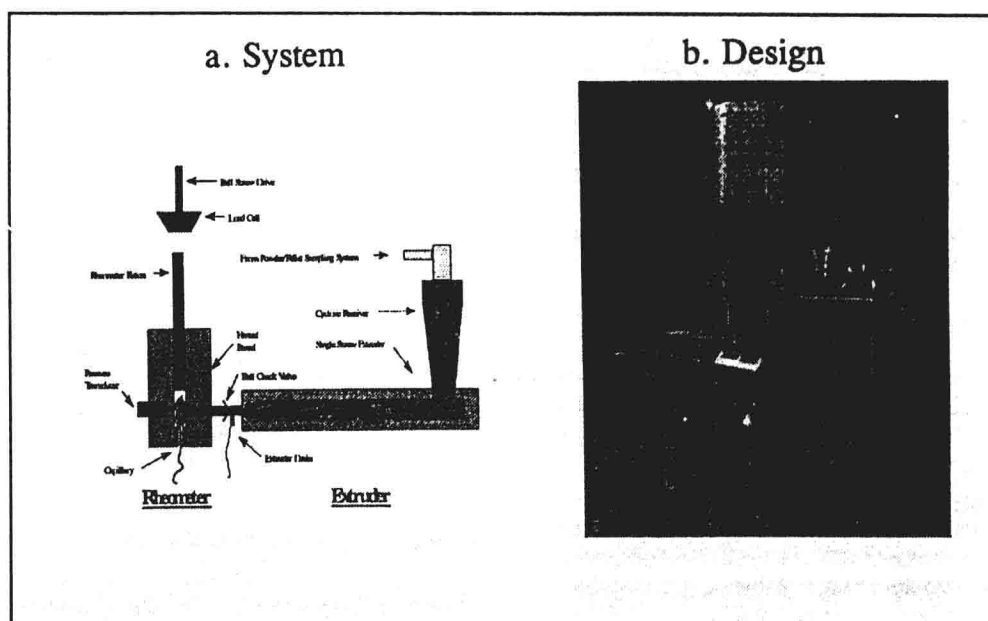


Figure 9
The Rheo-Truder

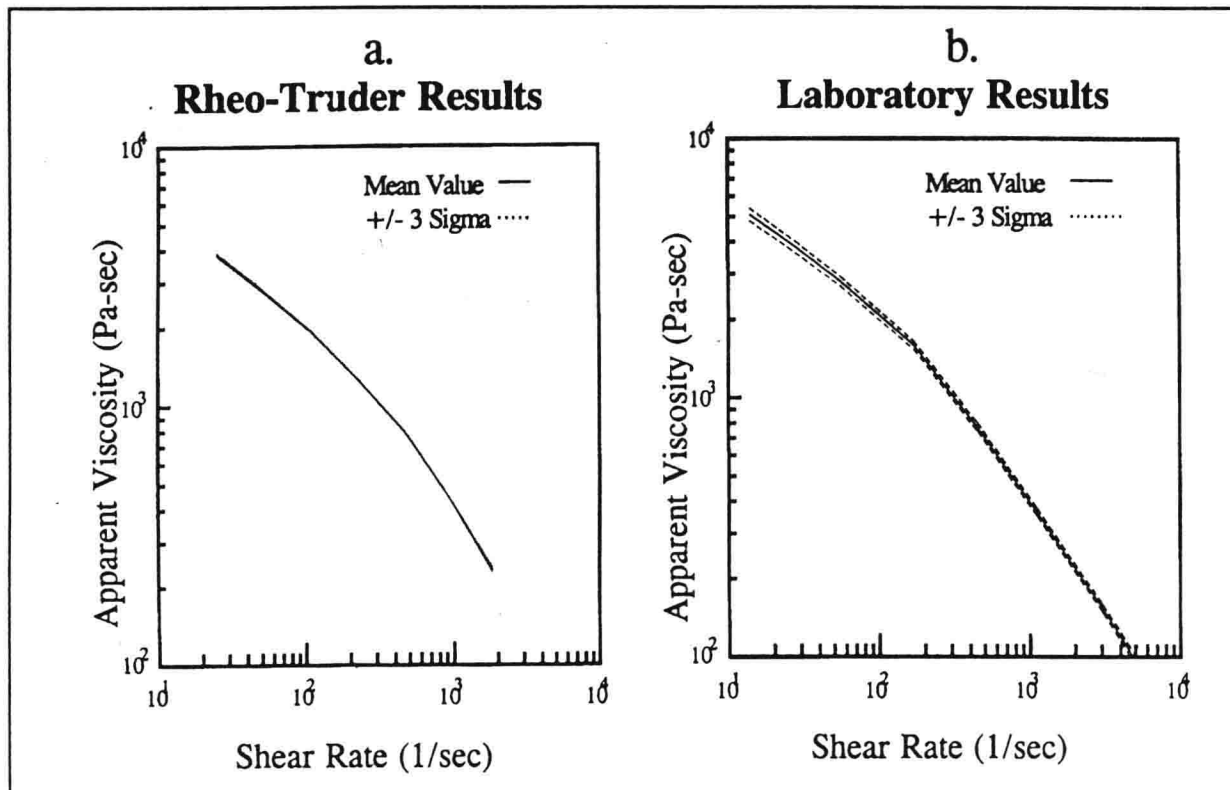


Figure 11

Results: Dowlex 2045 LLDPE (Precision)

complete melting, fast and uniform temperature equilibration, and consistent packing of the resin. **Figure 12** shows results obtained using the Rheo-Truder with resins having a wide range of melt flow rates.

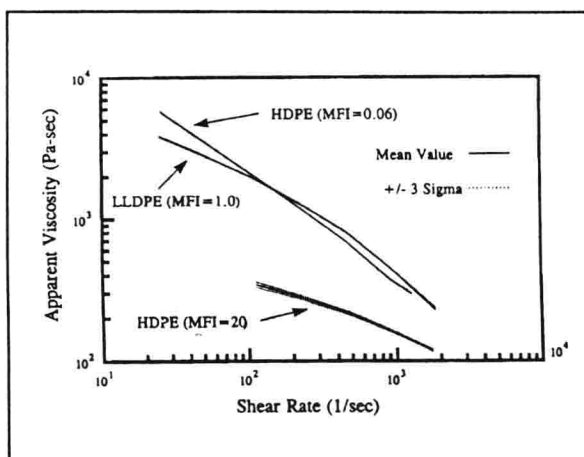


Figure 12

Rheo-Truder Results for Three Polyethylenes

An additional feature of this system is that it may be used for process or quality control in the production of filled (e.g., glass fiber) resins. Presently available on-line rheometer systems cannot be used since wear on the melt pumps results in the production of inaccurate measurements. Wear in the Rheo-Truder, however, is mainly confined to the extruder

screw, which is not involved in the measurement. Some wear may be expected take place in the capillary, however, the very hard tungsten carbide used for these dies should prove to be very resistant. (Preliminary experiments with glass filled PET have shown no measurable wear after running continuously for a week.)

Generation of curves, similar to those above, covering several decades of shear rates, generally takes about six minutes. Thus 8-10 curves can be generated per hour, compared to 2-3 per hour from the laboratory. (If only one or two shear rates are measured, up to 20 runs per hour can be achieved.) This will be enough to provide sufficiently timely results for use in process control. Thus application of the rheology "tube" becomes practical for use in QA and process control.

SUMMARY

It has been shown that rheological data obtained under the conditions existing in conversion processes are required to predict and assure the performance of resins in those processes. The rheology "tube", produced by the $\pm 3s$ variation of polymer viscosity over the range of shear rates seen in a process, provides a tool for assuring the processability and consistency of a polymer resin or blend. Practical application of the rheology "tube" is made possible by the "Rheo-Truder" automated capillary rheometer system, which provides the timely measurement of rheological functions required for process control.

BIOGRAPHICAL NOTES

D. E. De Laney

Don De Laney is the Vice President of Technology for DYNISCO Polymer Test, Inc., a manufacturer of laboratory and on-line testing instruments for the plastics industry. In this position, he is responsible for the innovation, development, and implementation of new instrumentation and methodologies in response to customer needs. These include instruments and software for the measurement and analysis of polymer melt rheology, both in the lab and on-line, and proprietary systems for on-line composition and particulate analysis in molten polymers. Prior to joining DYNISCO Polymer Test Inc., Dr. De Laney spent 17 years with GE Plastics, holding several positions including Manager of ABS Analytical Technology and Manager of Polymer Systems Technology. The latter was a laboratory focused on the development of novel processes, instrumentation, and process control for use in resin production, compounding, and QA. He holds a BS degree in chemistry from Dickinson College, an MS in chemistry from the University of Delaware, and a Ph.D. in physical chemistry from Rensselaer Polytechnic Institute.

The Use of Maximum Information Procedures in Quality Control and Assurance

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ABSTRACT

The commercial availability of computer controlled instrumentation has led to a revolution in the quality control testing of industrial materials. The relatively unsophisticated single point procedures which were standard until the last ten or fifteen years, have been supplemented or replaced by instrumental methods which provide more meaningful and reliable measurements. But the instruments concerned are usually only used to their full capacity in the research and development environment. For quality control, the tests used are designed to be simple to run, and easily understood by staff who are often not highly trained.

But a second revolution is in progress, driven by instruments which are not just computer controlled, but are also programmable. Now tests can be developed which can be carried out alongside the standard quality control tests, but which provide far more information for the works chemist in the event of adjustment being needed to a batch of material which is being processed. The term 'maximum information' might be applied to such procedures.

INTRODUCTION

In the last ten or fifteen years, there has been a revolution in the quality control testing of industrial materials, driven mainly by the commercial availability of computer controlled instrumentation. The revolution is still in progress; in fact, a second, and even more fundamental, revolution is on its way.

Before the first revolution began, the procedures used in process and quality control in many industries were not usually very sophisticated. The hard resin industry, for example, used acid value, viscosity index, melting point and cloud point tests, amongst others. Most of these did not relate directly to the final application of the material, as the binder in a printing ink vehicle, but they were (and are) valuable because they were quick and easy to perform, and provided single point values which could be readily used as quality control criteria

The properties measured by these simple tests are not, of course, completely unrelated to a resin's performance. Acid value is partly indicative of chemical composition. Viscosity index and cloud point depend on solubility and molecular weight, amongst other things. But as materials science progresses, the single point values produced become less and less useful. In general, the higher the specification of materials, the more sophisticated the methods for testing

them need to be. It is surprising how often it is overlooked that advanced materials require advanced techniques for their characterisation.

As part of the materials testing revolution, computer controlled rheometers have largely replaced the older methods of measuring viscosity. But many rheometers in industrial quality control laboratories are not put to full use. Typically, an industrial chemist with a good knowledge of rheology will use his or her instrument to its full capability for product development, and perhaps final product testing, but will be reluctant to impose anything other than very simple quality control procedures on the shop floor. More sophisticated procedures are time-consuming and vulnerable to operator error, and present difficulties in data interpretation to unskilled staff.

In an ideal world every batch of material would stay within specification at each stage in the manufacturing process, no adjustments would be necessary, and the final product would perform to the customer's satisfaction. In the real world, our materials are infuriatingly (or perhaps interestingly) recalcitrant. They run out of spec. during processing; they need constant adjustment; they stay in spec. until final testing, then test out of spec; they are in spec on four criteria but out on a fifth, and so on. None of this would be too bad, if bringing the batch back into specification were straightforward. Unfortunately this is not always so. Sometimes (we hope rarely), things go wrong, or adjustments are necessary.

MAXIMUM INFORMATION PROCEDURES

For a complex formulation, the more information a works chemist has, the better able he or she is to keep the batch of product in specification, or to make the necessary adjustments to it bring it back in should it run out. But the nature of the quality control procedures referred to earlier is such that, although they may be perfectly adequate when all is going well, they are often of little use when things go wrong. There is a dilemma: if the tests are too sophisticated they will be unworkable, if they are too simple they will provide inadequate information. The second quality control revolution is beginning to solve this problem.

This revolution is being driven by instruments which are not just computer controlled, but are programmable. An experienced person can then program the instrument to perform any operation or series of operations, to which the untrained staff need make no reference, or even know about.