

INTRODUCTION TO THE APPLICATION OF POLYMER RHEOLOGY

Polymers are viscoelastic fluids, which behave viscous or elastic, depending on how fast they flow or are deformed in the process. The silicone putty test is a good demonstration of this phenomenon (Figure 1). If a ball of silicone is subjected to a rapid deformation, for example bouncing on a table, the silicone ball behaves like an elastic body. It is the recoverable elastic deformation, which stores the energy and makes the ball bounce. If the silicone ball is at rest for a longer period of time, the gravity causes the material to flow - thus making it behave like a viscous fluid. Whether a material behaves elastic or viscous depends on the time scale of the deformation, or in other words on the ratio of process time and material time, referred to as Deborah or Weissenberg number. If the material time is short in relation to the process time, the material shows predominantly viscous behavior. If the Weissenberg number equals unity or is larger, the elastic behavior of the fluid increases and becomes dominant.

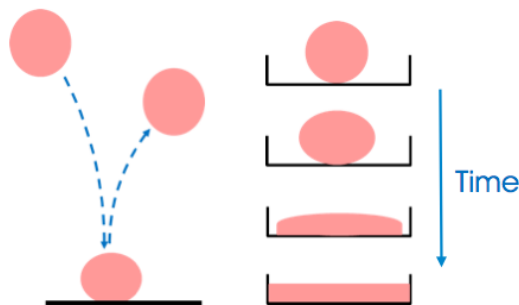


Figure 1: The filled polydimethylsiloxane (PDMS) behaves predominantly elastic if deformed for a short period of time and predominantly viscous if subjected to gravity over a long time period.

The viscosity is the prime material parameter in many processes. A material which did process easily on a film blowing line twenty years ago may not run at all on today's lines, which operate at much higher draw speed. The process time has become much shorter and the material under the new conditions is behaving more elastic, which consequently has negative effects on its processibility. The same is true for the flow in the mold during the injection molding process. Increased elasticity causes more locked in orientation during rapid cooling.

In order to guarantee a smooth operation process it is a must to control the rheology of the material within the specified range. The structure-rheology relationship is a key to the development of polymers for processing. The ultimate goal

of the design engineer is to modify the material structure to give better processing performance without sacrificing the performance of the final product (impact resistance, wrappage, etc.). Due to its sensitivity to material's structure changes, rheology is also the desired technique to control the process. Product quality can be insured and down time of the production line reduced as well as the quantity of off-spec material.

STRUCTURE-RHEOLOGY RELATIONSHIP, THE KEY TO PRODUCT DEVELOPMENT AND PROCESS CONTROL

It is well known that materials of the same grade, but from different batches, may process quite differently. The transformation process reacts very sensitively to small variations of the material, i.e. the rheology of the polymer melt is very sensitive to small changes of the polymer structure. Because of the sensitivity of rheology of the condensed phase to structure, rheology is a most convenient method to characterize polymers. A small amount of a high molecular weight polymer can change the processing behavior dramatically and so does the melt rheology.

The important structure parameters defining the rheology of the polymer melts are molecular weight (MW), molecular weight distribution (MWD) and branching $1/\lambda$. Whereas an increase of the molecular weight causes the viscosity to increase, changing of the molecular weight distribution and branching mainly affects the elasticity of the melt. The time dependence is affected by both. Viscosity measurements are performed with capillary and rotational rheometers. The two methods are the backbone of the polymer rheological characterization (Figures 2a and 2b).

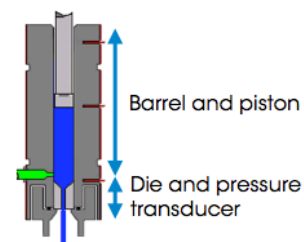


Figure 2a: In a capillary rheometer the material is forced through a slit or round die. From the pressure drop and the volume flow rate, a steady state viscosity as a function of the applied rate (piston speed) or stress (applied pressure) is measured.

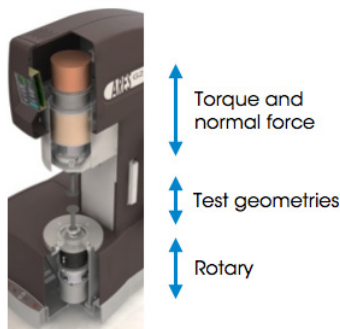


Figure 2b: In a rotational rheometer the sample is sheared between two plates or a cone and plate geometry. The viscosity is calculated as the ratio of the applied stress and the applied deformation rate (rotation speed). The rotational rheometer, in contrast to the capillary rheometer, measures time dependent material behavior also.

The viscosity of a polymer melt varies with the weight average molecular weight M_w to the power of ~ 3.4 . In polymer processing the Melt Flow Rate, or MFR, is used to characterize a polymer melt. Whereas the MFR (Figure 3) is a very common measurement, it is not a pure measurement of viscosity. Off-spec material can be easily blended to make a material with the correct MFR, but the viscosity and the elasticity of the blended material can be quite different, which becomes evident in the processability. Despite this fact, the MFR is the preferred parameter to characterize and specify polymer grades. The on-line measurement of the MFR has become an important issue in polymer manufacturing and complete QA concepts are built around the MFR measurement (Figure 4). Most of the polyolefin production lines use on-line rheometers to continuously measure the MFR, typically at the end of the extruder before the pelletizer.

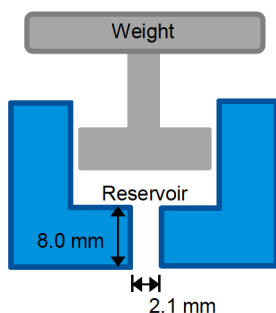


Figure 3: The MFR is a standardized die with a barrel to preheat the sample (ASTM D1238 and DIN 53735). The material is forced through the die by applying a weight of 2.14 or 21.4 kg. The measured quantity is the weight of the material flowing through the die within a given time period. The MFR is not only a measurement of the viscous effects in the die, but includes also contributions of the die inlet and exit effects.

On-line measurements are also used to control the process itself. Closed loop control is very successfully applied to the peroxide degradation of polypropylene, in order to produce different grades of material with different MFR. The degradation process narrows the MWD, which is an additionally desired feature [2]. The real advantages of the on-line technique however are: 1) automatic and continuous real time display of the material quality, thus allowing a reduction of the expensive, time consuming and often too late laboratory testing and the ability to take immediate corrective

actions based on the trend analysis of the continuous MFR measurement; 2) the reduction of off-spec material during transitions, as they can be easily optimized with an on-line real-time control of the material during the material change.

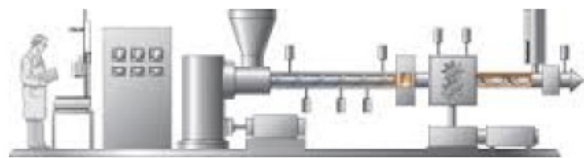


Figure 4: On-line rheometers are sensors inserted into the process line to monitor key parameters in order to allow controlling product uniformity and adherence to the desired specifications. On-line rheometers operate as return to stream or return to waste sensors. Depending on the die geometry, on-line rheometers can provide a real time measurement of MFR or shear viscosity as a function of rate. Equipped with an optical window to do NIR, UV etc. measurements the on-line rheometer can measure also additive levels, degradation, color, etc.

In order to develop materials with the correct processing behavior, it is not just sufficient to take into account the viscosity. Elasticity and time dependence of a polymer are equally important to control the processability of a polymer melt. A method to look at the complete rheological response of a material quickly is the dynamic mechanical analysis (DMA) of polymer melts. This technology has become a widely used tool for the product development engineer in the course of the last 20 years (Figure 5). Note: Dynamic mechanical analysis also refers to the testing of polymer solids. However, in the solid state, the DMA provides information on the polymer morphology and secondary transitions. The solid's behavior is independent of the polymer structure (MW and MWD, etc.).

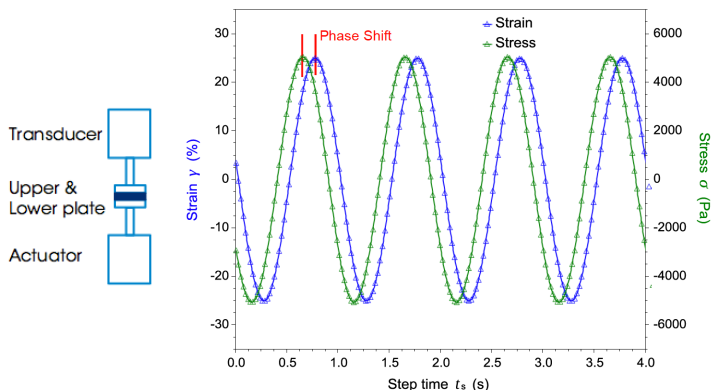


Figure 5: Dynamic mechanical testing involves the application of an oscillatory strain (or stress) to a material and to measure the resultant stress (or strain). The phase shift and the ratio of stress amplitude and strain amplitude allow the calculation of the dynamic moduli, the storage and loss modulus as well as the complex viscosity as a function of frequency.

The DMA measurement provides a kind of fingerprint of the material and allows calculating viscosity, elasticity and the material's time dependence at melt temperatures.

Whereas the viscosity correlates with the weight average molecular weight M_w , the elasticity however, is strongly dependent on the molecular weight distribution ($\sim M_w/M_z, M_z$ being the Z average molecular weight). In an oscillatory test, the material is mechanically probed at different frequencies

and the polymeric chains and chain segments relax to these external stimuli. The dynamic mechanical analysis is therefore also referred to as mechanical spectroscopy. A typical frequency sweep is shown in Figure 6.

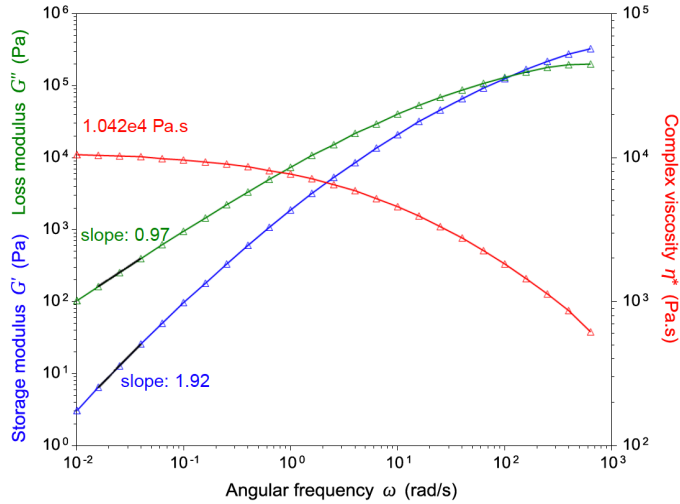


Figure 6: The frequency sweep provides a characteristic fingerprint of the material. At higher frequency, G' shows a plateau value referred to as plateau modulus. The plateau value relates to the average molecular weight between entanglements M_e . At low frequency, the loss modulus is a measure of the materials viscosity (G''/ω) and the ratio G'/G''^2 of the elasticity.

DMA is a very sensitive method to fully characterize linear polymers in terms of MW and MWD. Commercial software packages are available to calculate MW and MWD directly from the oscillatory data [3,4].

HOW RHEOLOGY CAN MAKE THE FINAL PRODUCT BETTER

Application examples are many fold for typical processes like injection molding, film blowing, extrusion, etc. In processes which involve free surface deformations of the material (film blowing and fiber spinning), the elongation viscosity, and not the shear viscosity is important (Figure 7).

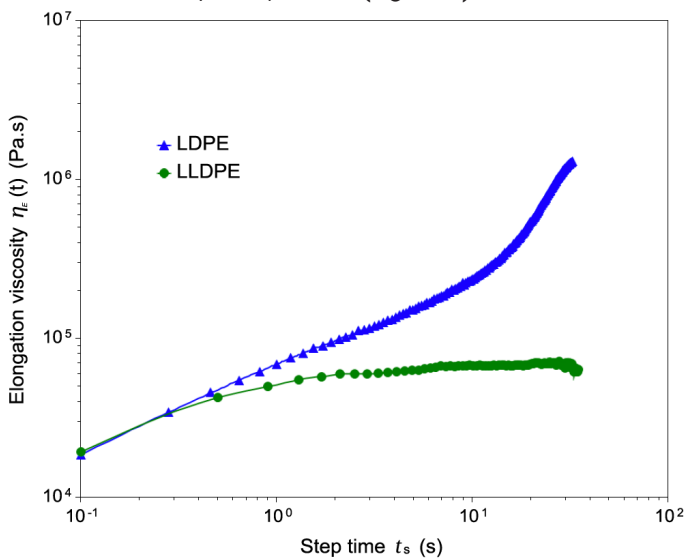


Figure 7: The elongation viscosity is determined by stretching a thin polymer bar and recording the force. The extensional viscosity fixture can be used to perform elongations of a Hencky strain of 4 [5]. The LDPE sample shows the typical strain hardening effect above $e^H = 3$.

The strain hardening behavior of polymers (elongation viscosity increase at large deformations) is essential for the processability during the film blowing and fiber spinning process. In order to insure film and fiber thickness tolerances, it is important to control the strain hardening effect stabilizing the filament and the bubble during the elongation process.

Pressure sensitive adhesives (PSA) are polymer blends, rheology-optimized to have a viscosity (or modulus) high enough to prevent flow under application temperatures, but low enough to flow into the substrate under the pressure applied (Figure 8). At elevated temperature the material must show low enough viscosity for easy coating of the film during the tape manufacturing process.

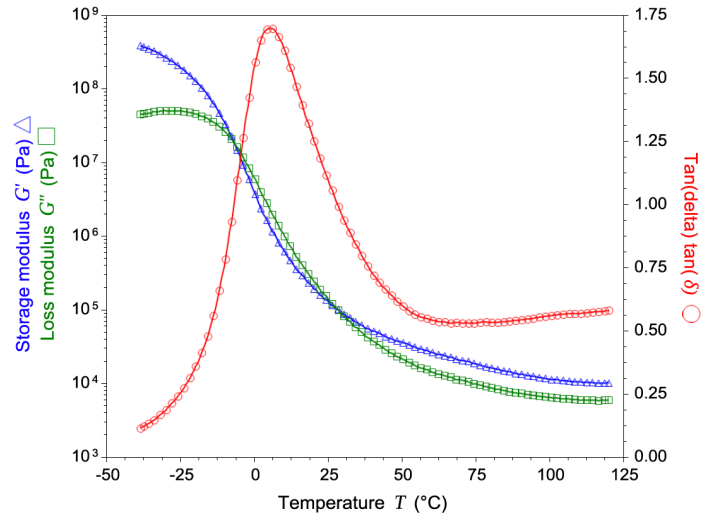


Figure 8: The DMA trace of a PSA adhesive as a function of temperature allows determining the critical application parameters. 1) The modulus at application temperature ($G'=2 \times 10^4 \text{ N/m}^2$) [6]; 2) the lowest application temperature limited by the low temperature transition ($T=10^\circ\text{C}$); 3) the lowest processing temperature defined by the cross over point of G' and G'' [7].

Reactive materials evolve from a low viscosity fluid to a solid material during processing. Rheology is an ideal technique to follow the evolution of the viscosity during cure. Today's rheometers can easily be programmed to simulate cure cycles and to optimize the temperature and pressure profiles in the mold. Changes in material (advancement as a result of storage or moisture effects) can easily be detected and the process parameters adjusted for the given batch of material [8]. Dynamic mechanical testing however, can provide more than just a viscosity. The gel point (Figure 9) can be determined from dynamic mechanical data easily.

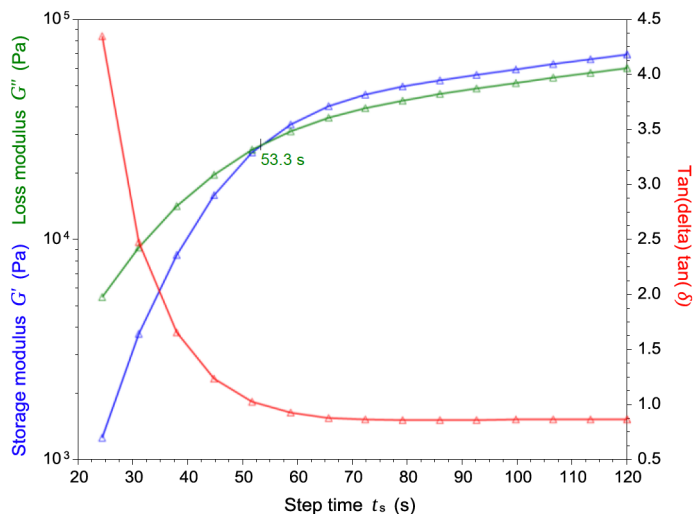


Figure 9: The Gel point of a resin (epoxy resin shown here) can be measured using the DMA technique. The curing is followed in time by applying a small amplitude deformation to the sample and recording the dynamic moduli. The gel point can be defined as the time when G' and G'' cross over.

How rheology is involved in solving material, processing and performance problems falls always into the same scheme and is illustrated in Figure 10. The rheology-polymer structure relation makes rheology the ideal tool to design materials with specific processing and end-use performance. Whereas the rheology of the melt provides direct information on the processability, the rheology of the solid and melt phase can be related to the performance of the end product. Also, due to the viscoelastic nature of the melt which may cause wanted and unwanted anisotropy during flow, the final product also depends on how the material is being processed.

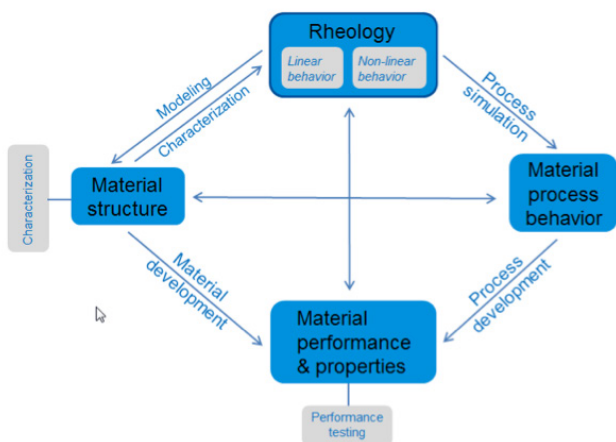


Figure 10: This diagram shows how rheology can be used to correlate end-use and processing performance to the polymer structure. Rheology is a key characterization technique for developing materials with the desired physical properties and for controlling the manufacturing process in order to ensure product quality.

CONCLUSION

Rheology is very sensitive to small changes in polymer structure – thus ideal for characterization of polymers. The rheology-structure relationship is the key to the development of new materials.

Because of the sensitivity of the process to the polymer structure, the material needs to be controlled within tight tolerances in order to guarantee good processability. Rheology is a most suitable tool for process and quality control.

For complex materials (multi-phase systems), the structure-rheology relationship is ambiguous, because the rheological behavior is not a unique representation of the polymer structure. Additional test methods have to be used in conjunction with the rheological measurement to be able to isolate the contributions of different structure elements. Optical, thermal, dielectric, etc. methods are potential candidates to be used simultaneously with the rheological measurement.

Nevertheless, today rheology is a standard in the polymer industry to characterize materials with the goal to develop new and better materials with the desired processing and end-use properties.

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Revised by A. Franck.

For solid polymer characterization consider the torsion fixture available for a rheometer or a separate dynamic mechanical analyzer (DMA).

For more instrument specific information, get in contact with your local technical sales representative, or to place an order, please go to <http://www.tainstruments.com>.