TA Instruments

Thermal Analysis & Rheology

RHEOLOGY APPLICATIONS NOTE

RHEOLOGY SOFTWARE MODELS (FLOW)*

Introduction

If there is to be any quantitative comparison of materials using rheology, it is ultimately necessary to fit the experimental data to a model. These models range from the elementary prediction of viscosity as a function of shear stress or shear rate to rigorous constitutive equations which attempt to deal with the material's viscoelastic properties at an infinitesimal level. Indeed, these models hold the key to the successful application of rheology to materials characterization, yet they form the most intimidating obstacle to the inexperienced investigator. Fortunately, in the majority of cases, there is no need to obtain a constitutive model of a material in order to obtain pragmatic information over a limited range. Rather, existing models from the literature with only minor modifications give useful results.

Model fitting forms one of the three supporting legs to the "rheology stool". The other legs of this stool are measurement and prediction. Model fitting lies between these other two fundamentals, and together the three form a loop which can be traveled several times allowing a more complete prediction of sample behavior versus shear, time, and temperature. From an instrumentation point of view, therefore, it is important for a rheology supplier to provide not only quality hardware which generates the best possible data over as wide a range as possible, but also to provide versatile software which evaluates the data generated by applying a suitable range of models to it.

Flow Data Modeling

The use of flow models is the most basic form of data processing in rheology, and indeed, most flow models more properly belong in viscometry because the elastic behavior of the material is not even considered. The emphasis of such models is prediction of the flow behavior over a range of shear rates or shear stresses. Newton's Postulate from the "Principia" is the simplest model for flow and also one of the earliest dating from 1687. This postulate which describes an ideal viscous liquid is based on a linear relationship between stress and shear rate where the proportionality constant is viscosity.

$$\textbf{Stress}[\sigma] = \textbf{Viscosity }[\eta] \bullet \textbf{Strain Rate}[d\gamma/dt]$$

In many ways, this relationship resembles Ohm's Law (V=R•I) where stress is potential difference, strain rate is current, and viscosity [the resistance to flow] is electrical resistance. It is of interest to note that just as there are "ohmic" and "non-ohmic" materials, there are "Newtonian" and "Non-Newtonian" materials. Unfortunately, very few materials are Newtonian. Only simple fluids with small non-interacting molecular components such as oils, water, and sugar solutions behave this way.

Simple Shear Stress vs. Shear Rate Models

Since most fluids are non-Newtonian, non-linear models are needed to describe the change in viscosity with shear rate or shear stress. [These models assume a rheogram plot of shear stress on the ordinate and shear rate on the abscissa.] The simpliest of these non-linear models is a Power Law, where viscosity [either Newtonian or apparent] is replaced by a consistency coefficient [K]. Furthermore, the index of shear rate in the Newtonian model can be considered to be 1, but the Power Law, as its name implies, has a flow behavior index n (where $n \neq 1$), which designates just how non-linear the curve is.

Two examples of the Power Law are shown below. The first describes pseudoplastic [shear thinning] materials which dominate the field of rheology. Most materials are shear thinning because the input shear energy tends to align anisotropic molecules or particles and disaggregate any large clumps of particles, thereby reducing the overall hydrodynamic drag, which in turn reduces the dissipation of energy in the fluid and the viscosity. On the other hand, some materials show an increase in viscosity as shear rate or stress increases. This [shear thickening] is relatively unusual, occurring mainly in dispersions of particles where the volume fraction is relatively high. Shear thickening can sometimes even result in a volumetric expansion as the dispersed solids are forced together, squeezing out the suspending phase. The Power Law can model both situations by simply having a flow behavior index either greater than one [shear thickening] or less than one [shear thinning].

PSEUDOPLASTIC $$\sigma = K \dot{\gamma}^{n} \quad (n) < 1$$

DILATANT $$\sigma = K \dot{\gamma}^{n} \quad (n) > 1$$

An additional level of complexity is introduced if the fluid rheogram [plot of shear stress vs. shear rate] has a non-zero intercept. If the line crosses the shear stress axis at a fixed value, then all stresses below that value are assumed to result in a zero flow situation. The value of the stress where this occurs is called the "Yield" stress and for many years this stress was thought to be a constant for a specific material. With the advent of more sensitive viscometers, however, workers found that the yield stress decreased once lower shear rates could successfully be set. Eventually, controlled stress rheometers showed that the yield stress was an apparent phenomenon whose magnitude depends on the measurement technique used. The majority of materials are thought to exhibit a high but finite viscosity known as the zero shear viscosity, rather than an infinite viscosity below a certain yield stress. Three models include a yield stress term. These models range in complexity from a linear model with an added yield stress [Bingham] to a linear model taken as the square root [Casson] to a Power Law with an added yield stress [Herschel-Bulkley].

BINGHAM $$\sigma = \sigma_y + \eta_p \dot{\gamma}$$

CASSON $$\sigma^{1/2} = \sigma_o^{1/2} + \eta^{1/2} \dot{\gamma}_c^{1/2}$$

HERSCHEL-BULKLEY $$\sigma = \sigma_y + K \dot{\gamma}^{n}$$

Figure 1 shows the curve shapes for stress versus shear rate plots using the different simple flow models. Often the simple exercise of visually comparing the experimental data curve for a material with these "standard" model curve shapes is sufficient to indicate which model is most likely to provide a good fit. For those situations where visual comparison is not able to reduce the choice of potentially acceptable models to one, the potential models must be sequentially fitted to the data and the best one chosen on the basis of standard error. Where two models give an equally good fit, the simpler one is usually chosen. Figures 2-5 illustrate this model fitting process on two toothpastes with similar flow properties.

Rheological flow data can be obtained while linearly increasing or decreasing stress or shear rate, and the models can be fitted to either the resultant "up" or "down" curves. Figure 2 shows that both toothpastes yield flow curves with slight hysteresis between the up and down curves, both are shear thinning, and both seem to have a yield stress. Figure 3 concentrates on a single curve - the "up" curve - of the lower viscosity toothpaste. The "Best Fit" routine has been used and the Herschel-Bulkley (solid line) chosen as the best fit, which is not surprising since this model is the most complex of the shear stress/shear rate models and therefore the most flexible when it comes to fitting data. Visual inspection of the line shows the fit to be acceptable. The results of the fit (shown in Figure 4) support the conclusion that a good fit from a mathematical point of view is achieved. In general terms, a standard error term that is below 10 is indicative of an adequate fit, except when the data are seen to be noisy, in which case more lenient standards should be set [e.g. 10 - 30].

Figure 1 - Simple Flow Models

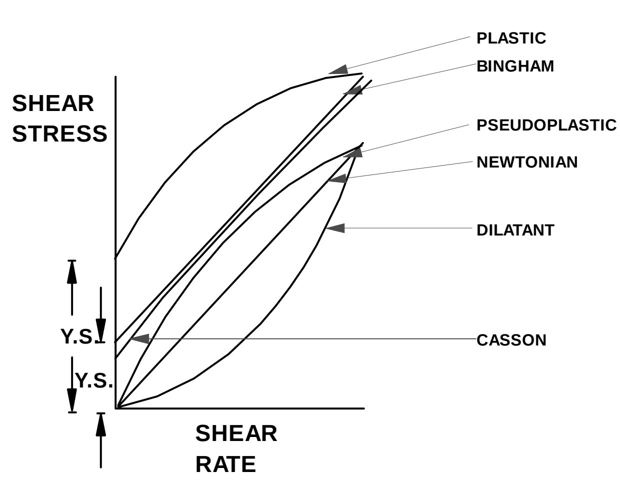


Figure 2 - Comparison of Toothpastes

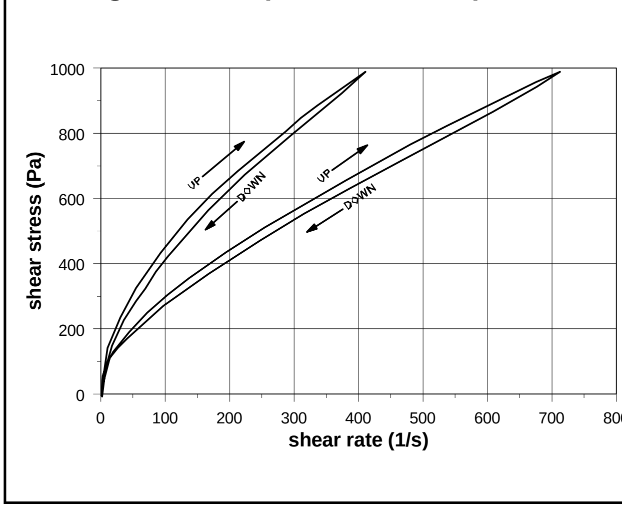


Figure 3 - Model Fit to Toothpaste Data

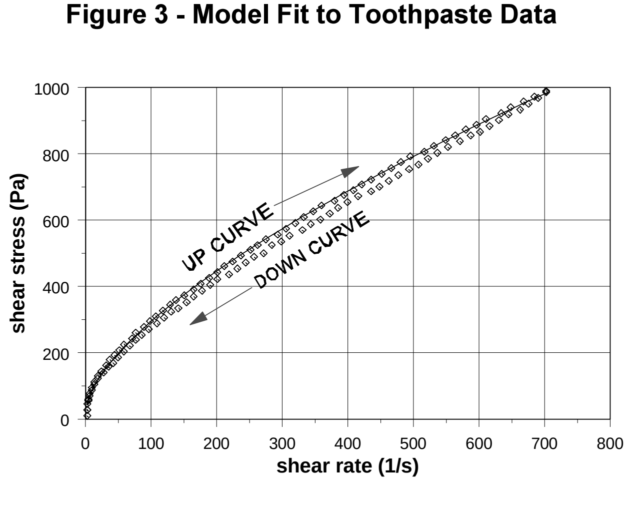


Figure 4 - Comparison of Flow Models

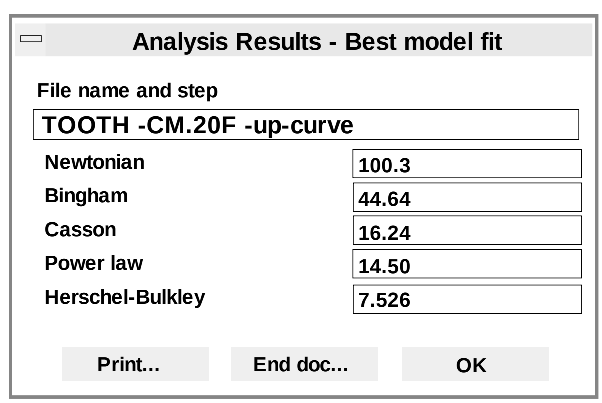


Figure 5 shows a typical results menu after a model fit is completed . The model type is put as a heading, and the appropriate parameters of the model are listed together with their calculated values.

Figure 5 - Model Fit Results

Analysis Results - Herschel-Bulkley

File name and step

TOOTH -CM.20F -up-curve

a: yield stress	41.18
b: consistency	11.91 (Pa·s)^C
c: rate index	0.6665
thixotropy	0 Pa/s
normalized thixotropy	0 1/s
regression	0.99249
standard error	7.526
Variable 1	1.0 Units 1
Variable 2	1.0 Units 2

Print... End doc... OK

In this instance the three most important parameters are the calculated yield stress [41.18 Pa], the consistency coefficient [11.91 $(Pa.s)^C$] and the flow behavior index itself [0.666]. The results are consistent with the observed plot, i.e. a shear thinning line that has a decreasing gradient. Although some slight hysteresis can be seen in the original plot, this is not significant, as can be seen from the two terms, thixotropy and normalized thixotropy. Both are calculated from the area between the two lines [“up” & “down”]. The latter term is designed to help when comparing graphs done with different ramp ranges and ramp rates. These graphs would normally give meaningless data, but by compensating for the difference in stress range, the values may be compared. Two statistical parameters from the regression analysis used on the data follow. The regression coefficient [r] which should be as close to 1 as possible, and the standard error which should be < 10 as previously mentioned. Finally, two user-defined variables (e.g. batch number, molecular weight or molecular weight distribution, mean particle size, pH etc.) are shown. These variables allow a series of curves fitted with the same model to be compared in a data base (eg. yield stress might be plotted as a function of molecular weight for a Herschel-Bulkley fit). In this toothpaste example, these variables were not used.

Figure 6 shows an enlarged view of Figure 3 in the region of the origin. From this expanded view, it is easily observed that the model fit is less appealing at low shear rates, and the calculated yield stress of ~ 41 Pa is clearly higher than it should be from the initial 10 data points. Figure 7 shows the use of limits in the TA Instruments *Rheology Solutions* software. [When the “full scale” icon is clicked on, the user can define limits on the x axis for fitting purposes.]

Figure 6 - Toothpaste - Low Shear Region

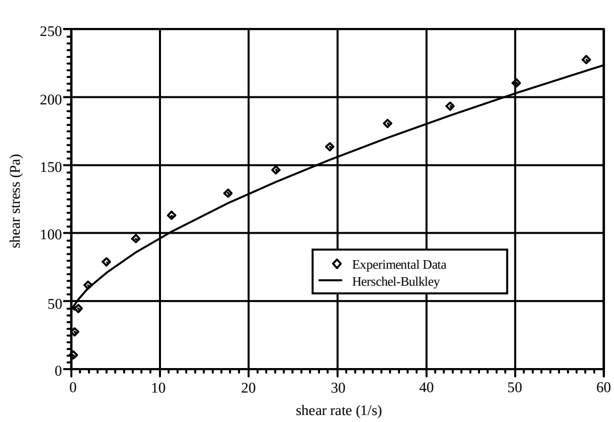
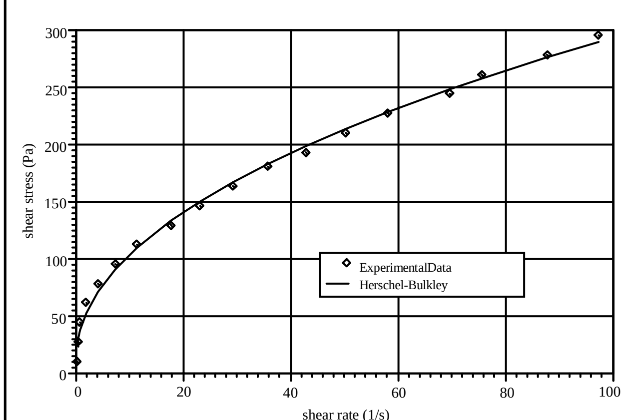


Figure 7 - Toothpaste Data Refitted



In this case, limits of 0 - 100 were selected and the Herschel-Bulkley model refitted. Zooming in on the area defined by the limits shows an improved fit over the previous attempt, albeit the standard error jumps from ~ 7 to ~ 20. Most of that can be accounted for by the reduced number of points. The calculated yield stress is now only ~ 11 Pa, which is far closer to the first data point [~ 10.4 Pa]. It is important to realize that a constant concern in model fitting is matching the model to the appropriate data, that is data *type* and data *range*. These relatively simple models are not useful for more than 2-3 orders of magnitude of data.

Logarithmic Viscosity vs. Shear Rate Models

To explore the low shear rate area of interest to most workers (the zero shear plateau), 3 - 4 decades of stress should be covered, typically generating 5 - 6 decades of shear rate as described in the previous section. One approach for obtaining data is to ramp stress in a logarithmic fashion so that a far higher proportion of the data points is generated in the first 1/3 of the ramped stress. However, the use of simple models is then unwarranted, and anomalously good fits will result because the data is skewed. Another problem with ramped measurement techniques is that any degree of time dependence in the sample will result in some degree of hysteresis in the generated curves. Since this hysteresis is likely to be irreproducible and strongly shear history dependent, it is wise to try to eliminate the effects of time-dependence using an equilibrium flow technique.

Furthermore, as low shear rates are to be probed, the displacement/speed sensor in controlled stress devices will start to encounter its lower limit for “instantaneous” measurement and hence the detection of initial movement will be difficult. To avoid this problem, the applied stress is held constant and the strain is measured as a function of time. This technique generates a creep curve which eventually reaches steady state as a constant rate of change of strain with time. The slope of this linear portion of the creep curve gives a steady state strain rate, which can be used with the known applied stress to calculate the viscosity. If sufficient time is allowed for each step, the effects of time-dependence vanish from the data. Since the displacement/speed sensor is allowed to collect data over minutes not seconds, shear rates of 10^{-6} s^{-1} can be reached.

This “equilibrium” flow process can be automated by the software to generate a series of stress steps which are ended when certain user-defined criteria for steady state are satisfied. In such a procedure the stress range [logarithmic] is set, along with the number of data points. A maximum time for each point is set [e.g. 2 - 60 minutes] and a sample period [e.g. 5 seconds - 1 minute], which is the time over which strain data is accrued before comparison with the accrued data from the previous sample period. If this data average is within a certain user-defined %, then a count is made of that period. If the data remains within the same % or less, 2 - 5 times [user-defined] in succession a data point is taken and the next stress applied. Otherwise data is gathered until the maximum point time is exceeded. In that case, the best fit from the last period is used. Many rheologists contend that "equilibrium" flow is the only “acceptable” way to gather flow data.

Figure 8 depicts equilibrium flow data on toothpaste, plotted as a conventional rheogram. The data points obtained are fewer than with conventional ramped flow, and concentrated around the origin. Clearly, even the Herschel-Bulkley model would give an unsatisfactory fit, based on this limited data. Figure 9 shows the more common plot for a flow curve, namely viscosity vs. shear rate on log axes. The model fitted to the data is called the Cross model. It is an empirical model and is designed to fit a straight line portion between two plateaus [zero shear and infinite shear viscosities].

Figure 8 - Toothpaste - Equilibrium Flow Data

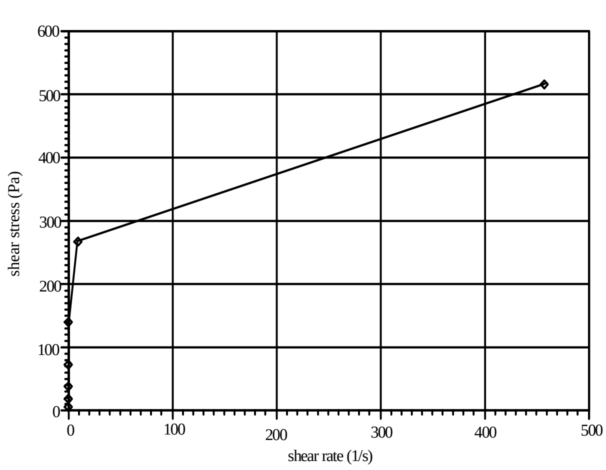
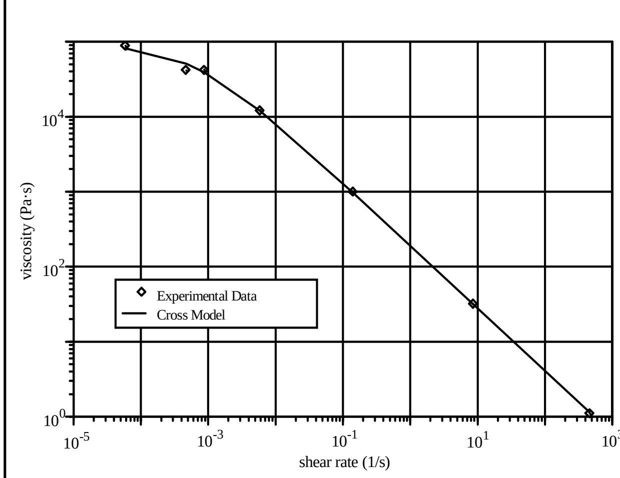


Figure 9 - Toothpaste Fitted to Cross Model



In this case, the data does not extend into a sufficiently high shear rate region for the infinite shear plateau to be attained, but the model is still able to cope with this deficiency. The equation for the Cross model is shown in Figure 10. This model can be broken down into two components - a model known as the Sisko model that includes the infinite shear plateau and the Power Law region, and the Williamson model covering the zero shear plateau and Power Law region.

Figure 10 - Complex Flow Models

CROSS

$$\frac{\eta_0 - \eta}{\eta - \eta_\infty} = (K[d\dot{\gamma} / dt])^m$$

Power Law $\eta = K_1 \, [d\dot{\gamma}/dt]^{n-1}$

Sisko $\eta = \eta_\infty + K_1 \, [d\dot{\gamma}/dt]^{n-1}$

Williamson $\eta = \eta_o - K_1 \, [d\dot{\gamma}/dt]^{n-1}$

CARREAU

$$\frac{\eta - \eta_\infty}{\eta_o - \eta_\infty} = \frac{1}{\left[1 + (K_{1\dot{\gamma}})^2\right]^{m^{1/2}}}$$

Other models of a similar form to the Cross have been developed, such as the Carreau model. Trial and error will tell which model is more suitable for specific experimental results. The models are empirical, so there is little theoretical precedent to decide which to use. Figures 11 and 12 show the toothpaste results fitted to the Carreau and Williamson models respectively.

Figure 11 - Toothpaste - Fitted to Carreau Model

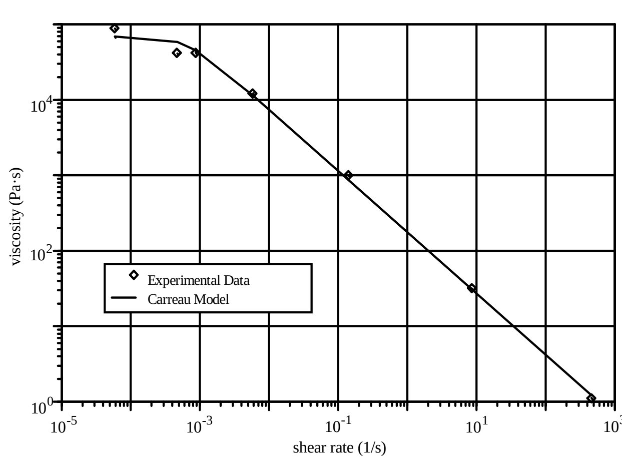
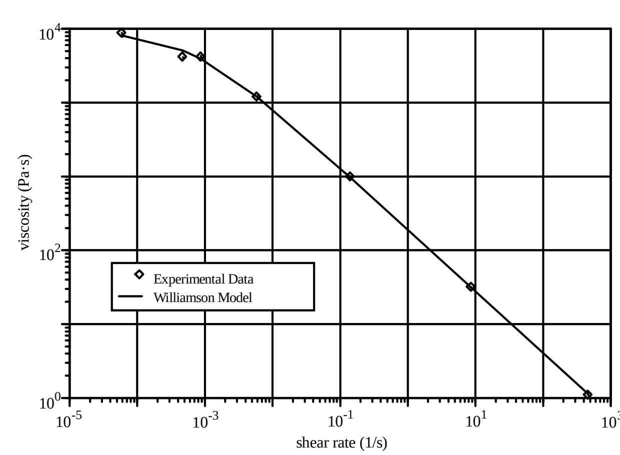


Figure 12 - Toothpaste - Fitted to Williamson Model



The historical dominance of controlled rate rheometers has lead to the acceptance of viscosity versus shear rate plots as the standard display of results. However, as shown in Figures 13 and 14, the display of viscosity versus shear stress can also be valuable. In this case, an automotive sealant displaying effectively a "full" flow curve covering all types of shear within the constraints of laminar flow at a single temperature is evaluated. Plotting the data versus shear stress shows an interesting "z" slope which more clearly reflects the range over which the largest structure breakdown occurs in the sealant.

Figure 13 - Equilibrium Flow Curve on Sealant

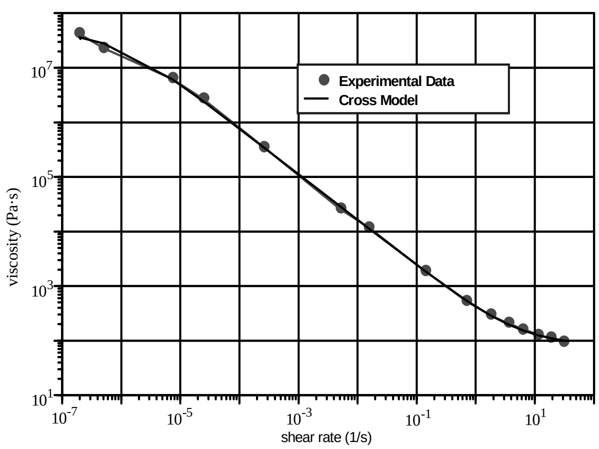
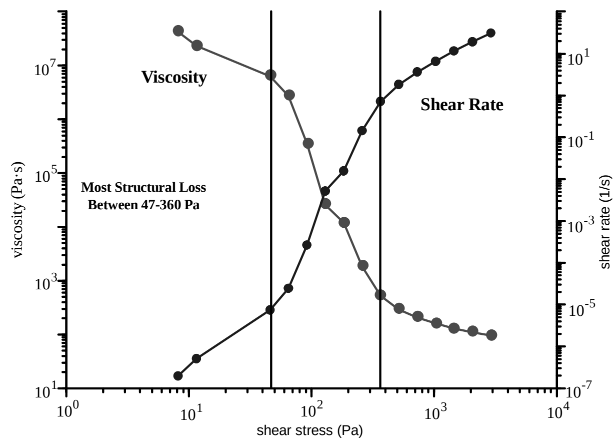


Figure 14 - Equilibrium Flow Curve on Sealant



Conclusions

This article attempts to provide some guidelines for model fitting flow data, as well as describing some of the available models. In general terms, the experiment type determines the sort of model used. For a simple linear flow curve, the simple models, Newtonian to Herschel-Buckley, should be used. Furthermore if an apparent yield stress must be found, the ramp rate should be kept constant. For a logarithmic data set, use the Cross, [Sisko / Williamson] or Carreau models. The real judge of the model though is mathematical, in the form of regression coefficients and standard errors.

*TA Instruments *Rheology Solutions* Software allows materials to be evaluated in flow, creep, and oscillation. This note describes the models available for analyzing results from flow experiments.