application note

Yield Stress Determination of Complex Fluids

Introduction

Materials that exhibit a ***yield stress*** are ubiquitous in our everyday lives. **Personal care products** such as hand creams, **pharmaceutical and healthcare products** such as gels and ointments, and other products such as **paints and inks** all exhibit this common behaviour. These materials are complex fluids with internal structures that must be broken down before they will flow and in order to break down this structure to initiate and/or maintain flow a minimum stress specific to each material, ***the yield stress***, must be applied.

The yield stress is a particularly important property to be considered when designing and formulating product materials. The yield stress determines how we perceive and use these products. It controls material stability, influences how we remove the material from its container (e.g. squeezing and scooping) and governs how we apply the material (e.g. rubbing, spreading and brushing) to a target area.

It therefore follows that the rheological analysis of yield stress is a vital step in understanding these products and their performance. A good variety of techniques exist for measuring the yield stress when using a rotational rheometer such as the ***Malvern Kinexus Ultra+***. A yield stress value measured by each technique, however, cannot be considered as an absolute value and an understanding of the context under which the data has been generated is crucial. The value obtained from testing will always depend on the identity of the technique employed and the test conditions used. Shear history, timescales of testing and temperature are all key factors that must be considered.

In this paper we will discuss a number of techniques and demonstrate their use in the measurement of yield stress for a variety of everyday products. The results from the measurements will then be collated and the techniques compared.

Yield Stress Methods

A moisturising hand cream, a pain relief gel, an interior wall paint and a screen printing ink were tested using the techniques under investigation.

All experimental data reported was generated using escubed limited's Malvern Kinexus Ultra+ rheometer with appropriate geometries. Each test was performed with a fresh sample preparation, which was loaded onto the rheometer using a standardised loading sequence. Each sample preparation was appropriately pre-sheared and then allowed to rest for 5 minutes before yield stress testing was initiated to ensure a consistent shear history. All tests were performed at 25 °C.

Model Fitting

The simplest method for determining a yield stress is through fitting a suitable model to flow curves (shear stress versus shear rate) and extrapolating to zero shear. A number of models are available (shown in Table 1 and Figure 1) and their suitability depends on whether the sample demonstrates Newtonian or non-Newtonian behaviour after yielding. The correlation coefficient associated with the model fitting should be used as a guide to assess the model suitability.

Bingham Model

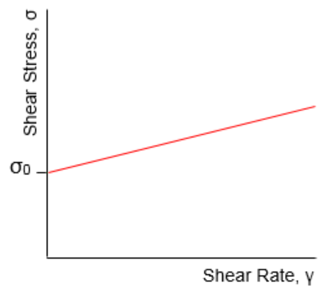

Figure 1a: Example plot of shear stress versus shear rate for a Bingham plastic. The material exhibits a yield stress and after yielding behaves as a Newtonian fluid.

Herschel-Bulkley/ Casson Models

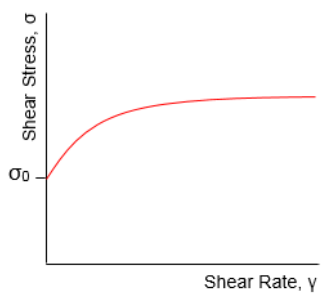

Figure 1b: Example plot of shear stress versus shear rate for a Herschel-Bulkley or Casson material. The material exhibits a yield stress and after yielding is either shear thinning or shear thickening.

Model	Mathematic Representation	Notes
Bingham (Newtonian behaviour after yield)	$\sigma = \sigma_0 + \eta_B \dot{\gamma}$	σ is shear stress, σ_0 is the yield stress, η_B is the plastic viscosity, $\dot{\gamma}$ is the shear rate
Herschel-Bulkley (Non-Newtonian behaviour after yield)	$\sigma = \sigma_0 + K\dot{\gamma}^n$	σ is shear stress, σ_0 is the yield stress, K is the flow consistency index, $\dot{\gamma}$ is the shear rate, n is the flow behaviour index
Casson (Non-Newtonian behaviour after yield)	$\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{\eta_C \dot{\gamma}}$	σ is shear stress, σ_0 is the yield stress, η_C is the Casson viscosity, $\dot{\gamma}$ is the shear rate

Table I: Mathematical representations of models describing materials with yield stresses [1].

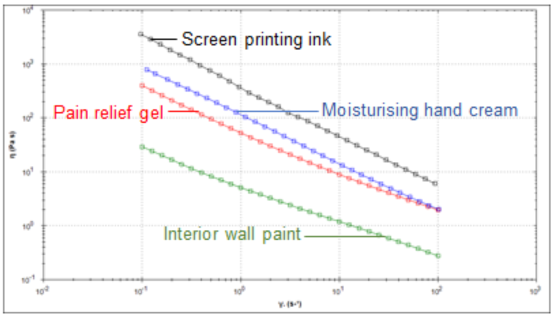

Figure 2: Plots of shear viscosity versus shear rate for the test samples. All samples are shear thinning and a wide range of viscosities is observed. The screen printing ink is approximately 74 times more viscous than the interior wall paint at 1 s^{-1}.

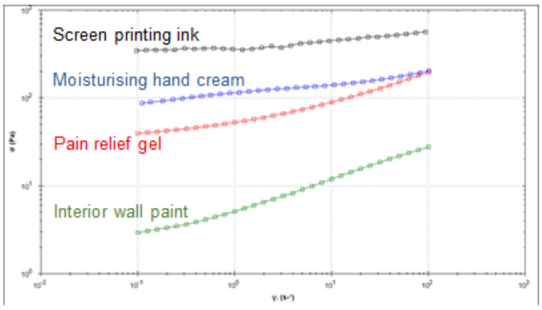

Figure 3: Plots of shear stress versus shear rate for the test samples. The data for all samples is reaching a plateau at low shear rates, which is indicative of the presence of yield stresses.

The result achieved through model fitting is a measure of the dynamic yield stress, which is the minimum required stress to maintain flow. A dynamic yield stress is reported using this technique as data is extrapolated from when the sample is already flowing. The dynamic yield stress is useful when investigations concern the maintenance or stopping of systems already flowing e.g. brushing of paint, rubbing of cream onto skin.

The plots of the shear viscosity versus shear rate obtained for the various test samples (Figure 2) show that they all exhibit shear thinning behaviour i.e. the shear viscosity decreases with increasing shear rate. This indicates that either the Herschel-Bulkley or Casson models are most appropriate. The plots of shear stress versus shear rate (Figure 3) are all approaching non-zero values of shear stress at low shear rates and for each sample the data is best fit to the Herschel-Bulkley model.

Stress Ramps

Another method that is favoured for its quick and simple nature is the stress ramp method. The shear viscosity is measured as the shear stress is increased under controlled stress conditions. The yield stress in this instance can be defined as the stress where a maxima in shear viscosity is observed (Figure 4a). An alternative means of determining the yield stress from a stress ramp experiment is through application of tangent analysis (Figure 4b).

Unlike other methods for determining yield stress, such as model fitting, the result can depend on the rate of increase of shear stress and therefore the test time. As such, when comparing samples using this method it is advisable that the samples are tested using the same conditions.

Furthermore, stress ramps measure the static yield stress of a system, which is the minimum required stress to initiate flow. The static yield stress is typically larger than the dynamic yield stress for thixotropic fluids [2]. The static yield stress is relevant to processes where flow start-up is of interest e.g. squeezing of gel from tube, ink on screen mesh prior to printing.

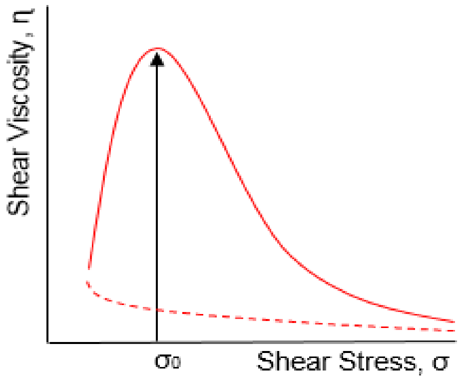

Figure 4a: Determining yield stress, σ_0, from maxima in stress ramp experiment. The solid red line and the dotted red line are examples of the expected response from a material with a yield stress and a material without a yield stress respectively [3].

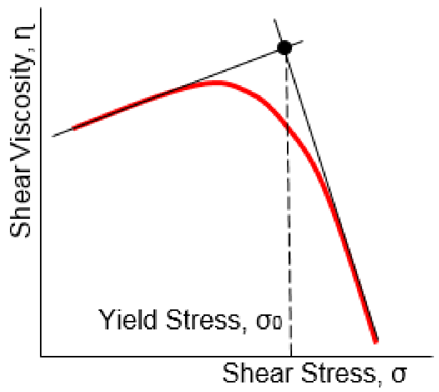

Figure 4b: Determining yield stress from tangent analysis in stress ramp experiment. A tangent is applied to each portion of the curve where viscosity is increasing and decreasing. The yield stress is the shear stress for the point where the two tangents intersect.

The plots of shear viscosity versus shear stress for the test samples (Figure 5) demonstrates that the samples behave as would be expected for yield stress materials. The samples demonstrate elastic behaviour and strain hardening below the yield stress, with increases in viscosity with increasing shear stress observed. A significant reduction in viscosity (at least two orders of magnitude) is observed after yielding for all samples.

Use of the shear stress where a maxima in viscosity occurs as a measure of yield stress is not appropriate for these samples. There is no considerable change in viscosity occurring either side of the peaks in viscosity and the very low shear rates achieved at these peaks in viscosity indicate very limited flow. The points where the applied tangents intersect better represent the stage in the experiment at which flow is initiated as this directly precedes the significant reduction in viscosity observed.

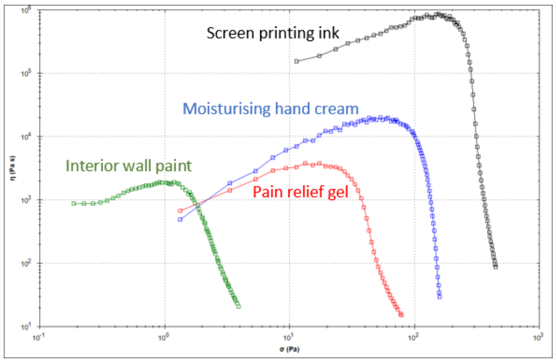

Figure 5: Plots of shear viscosity versus shear stress for test samples.

Oscillation Amplitude Sweeps

Dynamic oscillatory rheological measurements are a standard means of characterising the rigidity and strength of a viscoelastic material's internal structure. A sinusoidal stress or strain is induced in the sample through small oscillations of an upper plate. The amplitude of these oscillations is increased and the resulting responses in the complex shear modulus G* and its components, the storage modulus (G') and the loss modulus (G''), are monitored. G' is a measure of the amount of energy stored by the material (i.e. the solid-like, elastic response) during deformation, whilst G'' is a measure of the amount of energy lost by the material (i.e. the liquid-like, viscous response) during deformation. A typical plot of G' and G'' for a complex fluid is provided in Figure 6.

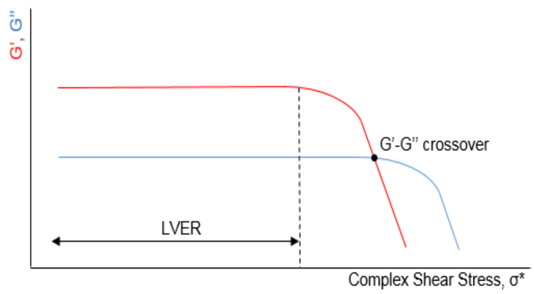

Figure 6: Example of plot of G' and G'' versus complex shear stress. The yield stress can be measured from assessment of the LVER or the G'-G'' crossover point.

Under the action of small deformations, material structure remains intact and both G' and G'' are amplitude dependent. This region is called the Linear Viscoelastic Region (LVER). G' is greater than G'' within the LVER in the case of a structured fluid and elastic behaviour dominates. With even larger deformations applied, just outside of the LVER, G' begins to drop as the material structure begins to be disrupted and break down. G' is still larger than G'' as material structure is still pervasive enough that elastic behaviour continues to dominate. The upper limit of the LVER demarcated by this initial drop in G' is one measure of the yield stress. At even greater complex shear stresses still, G'' becomes greater than G' and a transition from solid to liquid like behaviour occurs as structure is extensively broken down and flow begins. The cross-over is regarded by some as another measure of the yield stress.

An overlay of G' (square symbols, □) and G'' (circle symbols, ○) versus complex shear stress for the test samples is provided in Figure 7. The test samples are all structured fluids, which are elastically dominated and so G' exceeds G'' within the LVER. There appears to be a common trend amongst these samples, whereby yield stress (measured either from the extent of the LVER or G'-G'' crossover) increases with sample rigidity (combination of G' and G''). The soft and delicate nature of the interior wall paint is in stark contrast to the rigid and robust structure of the screen printing ink.

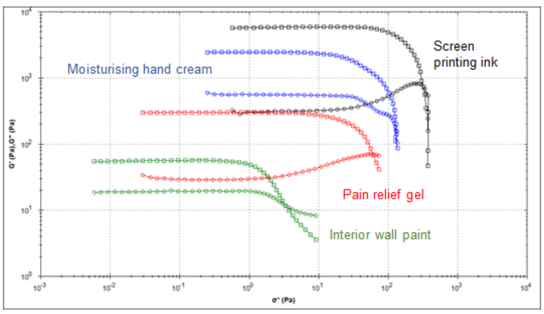

Figure 7: Overlay of plots of G' (square symbols, □) and G'' (circle symbols, ○) versus complex shear stress for the test samples. The yield stress can be determined using small oscillation amplitude sweep testing, but this technique has many other uses. Similarly important information relating to sample rigidity and the balance of elastic and viscous behaviour can also be ascertained.

Stress Growth

The sample is sheared at a constant low shear rate (typically 0.01 s^{-1}), so that a constantly increasing strain is created within the sample. The resulting stress build up is monitored by plotting shear stress versus time. A typical response from a yield stress material is shown in Figure 8.

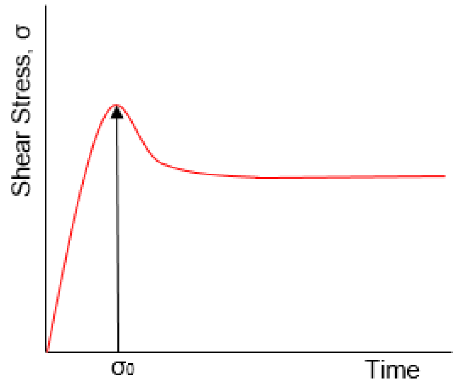

Figure 8: Example plot of shear stress versus time for a stress growth experiment. The maximum shear stress (exaggerated here for illustrative purposes) coincides with the yield stress [3].

The stress initially increases as elastic components of sample structure are stretched. When the strain created within the sample approaches the critical strain, these elastic elements start to break down and the sample will begin to flow. At this point, the shear stress reaches a maximum and this is equal to the yield stress. The shear stress then plateaus at its equilibrium value ($\sigma = \eta\gamma$)

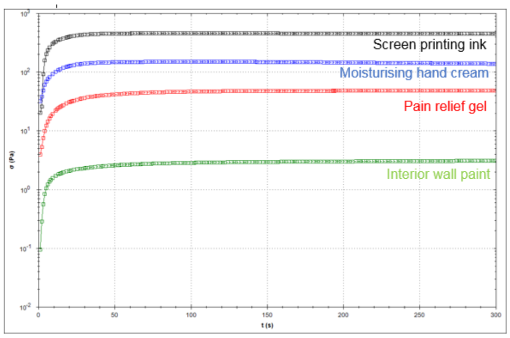

Figure 9: Overlay of plots of shear stress versus time for the test samples.

Multiple Creep

Creep testing involves applying a constant stress to the sample under test and monitoring the deformation over time. Viscoelastic materials, such as the test samples presented here, initially deform by elastic and viscous processes and it is the elastic processes that dominate early on. As the test progresses, the sample eventually reaches an elastic equilibrium and the deformation is then dominated by viscous processes. The strain response of the sample depends on the applied stress, so it is convention that deformation is reported through use of compliance, which is the shear strain divided by shear stress [1].

The use of compliance allows for direct comparison of data generated at different shear stresses and it is on this basis that the yield stress can be determined with multiple creep testing. Below the yield stress, the plots of compliance versus time will overlay. When the shear stress exceeds the yield stress, the plots compliance versus time begin to deviate from each other and higher values of compliance are achieved. An overlay showing compliance curves for the test interior wall paint before and after yielding is shown in Figure 10.

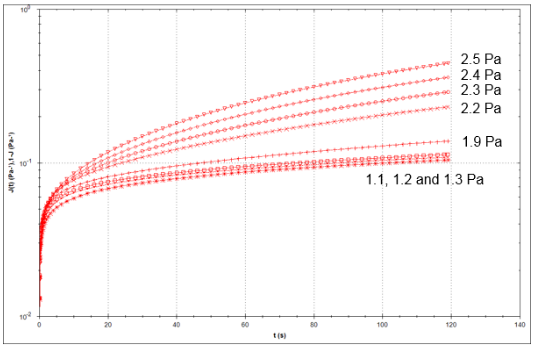

Figure 10: Compliance curves for the interior wall paint recorded at a variety of shear stresses. The compliance curves overlay until a shear stress of 1.9 Pa is achieved, at which point the sample is observed to yield.

If the value of compliance achieved at the end of each test is plotted against shear stress, it is possible to determine the yield stress as the point where a clear discontinuity is observed. The plots of compliance (at the end of each creep test) versus shear stress for the moisturising hand cream, the pain relief gel and the interior wall paint are overlaid in Figure 11. This methodology is lengthy and is particularly unsuitable for samples that dry quickly as was the case with the screen printing ink. As such, a yield stress value for the screen printing ink has not been reported.

Figure 11: Plots of compliance versus shear stress for test samples. The yield stress is given by a clear discontinuity and sharp increase in the gradient of the plots. This discontinuity is readily observed for the moisturising hand cream and the interior wall paint, and whilst it is less pronounced for the pain relief gel, a discontinuity can also be observed for this sample.

Comparison of Yield Stress Results

The yield stress results for the four test samples are reported in Table II and summarised graphically in Figure 12. The yield stress results are dependent on the method adopted with a wide range of values recorded for each sample. In general, the methods all agree with expectation that the relative order of yield stress values for the four samples is as follows: screen printing ink > moisturising hand cream > pain relief gel > interior wall paint. The results from Herschel-Bulkley model fitting, stress ramps (peak or tangent analysis) and multiple creep testing were mostly similar.

The results from LVER determination in small oscillation amplitude sweeps consistently provides the lowest value for the yield stress. This is likely due to the fact that the LVER denotes the commencement of structural disruption rather than the initiation of material flow. Similarly, the results from the G'-G'' crossover in small oscillation amplitude sweeps tend to over report the yield stress. The G'-G'' denotes the transition from elastic to viscous behaviour, which occurs typically after material flow has already started.

	Moisturising hand cream	Pain relief gel	Interior wall paint	Screen printing ink
Model Fitting – Herschel Bulkley	62.88	33.25	0.73	313.70
Stress Ramp - Peak	52.98	17.33	1.23	155.30
Stress Ramp - Tangents	99.34	31.33	1.31	221.30
SOAS - LVER	9.61	2.38	0.19	36.92
SOAS - Crossover	131.7	61.39	3.34	320.00
Stress Growth	151.1	48.49	3.23	459.40
Multiple Creep	115.00	34.00	1.90	Not reported

Table II: Summary of yield stress results for test samples

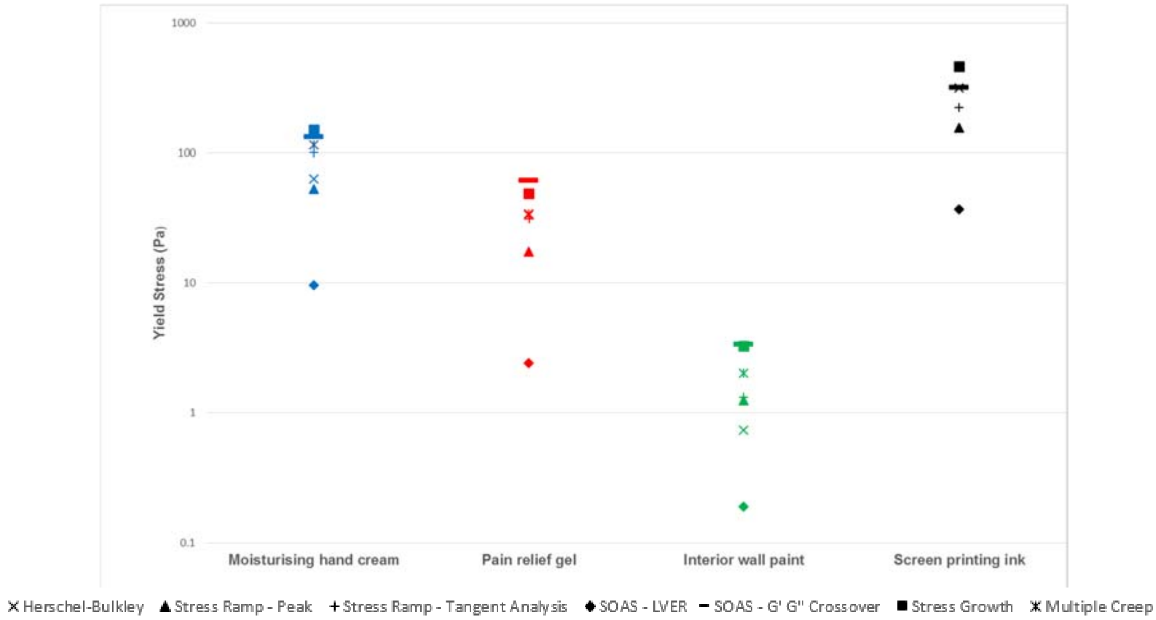

Figure 12: Graphical summary of yield stress results for test samples

application note

Conclusions

To conclude, the results presented demonstrate the clear need to assess the suitability of the test methodology for each particular material and that materials' application. The test methodologies report different yield stress values as they relate to different yielding behaviours and processes, and considerations must be made to ensure the chosen test method replicates the yielding behaviour or process of interest. Each technique has its own advantages and disadvantages, which must also be taken into account when making a selection - these are summarised in Table III. Once a technique has been selected, it is important that the test conditions are investigated and optimised. Shear history, temperature and time/rate dependences can all affect the result.

Test	Advantages	Disadvantages
Model Fitting (Herschel-Bulkley)	• Result is unambiguous • Additional information relating to flow behaviour and consistency achieved	• Low shear rate must be achieved; steady state not always achieved
Stress Ramp	• Quick and simple methodology • Significant drop in viscosity is clear sign of yielding.	• Result is ambiguous – should peak or tangent analysis be used? • Only provides a yield stress result • Result can be dependent on the rate of increase of shear stress
Small Oscillation Amplitiude Sweeps	• Additional information relating to sample rigidity and viscoelasticity.	• Result is ambiguous – should limit of LVER or G'-G'' crossover be used? • Limit of LVER needs to be defined. LVER can give underestimate of the yield stress as it relates to break up of internal structure and not necessarily commencement of flow. • Crossover point is well defined but it can overestimate the yield stress as yielding is likely to have occurred before G' = G''.
Stress Growth	• Quick and simple methodology	• Result can be dependent on the shear rate chosen • Only provides a yield stress result
Multiple Creep	• Can be a highly accurate methodology • Additional information relating to viscoelasticity	• Lengthy and labour intensive as methodology consists of a series of tests. • Relies on knowledge of an approximate range of shear stresses to use as starting point. • Accuracy of result achieved depends on number tests performed.

Table III: Advantages and disadvantages of using the various techniques for determining yield stress [4]. No one technique can be used reliably to measure the yield stress of all materials. The technique must be selected with the material and its' application in mind

References

[1] Howard A. Barnes, *A Handbook of Elementary Rheology (*Aberystwyth: Cambrian Printers, 2000*)*, p. 75.

[2] Cheng, D. C-H., Yield stress: A time-dependent

[3] Duffy, J., Understanding yield stress measurements, Malvern White Paper MRK1782-01, 2012.

[4] *M. Dinkgreve et al. / Journal of Non-Newtonian Fluid Mechanics 238 (2016) 233–241*

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