CaBER® Tests on Yield Stress Fluids

The CaBER®, or Capillary Breakup Extensional Rheometer, is a simple-to-use rheometer used to measure the extensional properties of polymeric fluids.[i] By monitoring the dynamics of capillary thinning and breakup of a fluid filament following a short, rapid extensional deformation, the CaBER® allows one to obtain information about the constitutive properties of a fluid, and the time to breakup for the thread under the action of surface tension. The latter parameter is of particular value to batch filling applications and also to continuous processes involving free surfaces such as spraying/atomization, inkjet printing and coating flows. Fitting the measured radius data requires the selection of an appropriate constitutive model to characterize the fluid.

This note focuses on the analysis for fluids that exhibit a yield stress (denoted τ_y) and which can be described by the Bingham Plastic constitutive model (Bird et al. 1983; 1987).

The existence of a Critical Radius and Critical Stress

The single most important difference between a fluid exhibiting a yield stress and other fluids tested in the CABER® is the existence of a critical sample radius (at the 'neck' or midpoint). The capillary pressure in a thread of fluid is, in general, given by σ/R and it is this that drives the fluid flow in the thread. If the yield stress exceeds this value, then capillary pressure is insufficient to generate a flow. The exact value for this critical radius has to be determined from the full solution to the problem; however, an *a priori* scaling estimate for the critical radius can be deduced on dimensional grounds to be given by the stress balance:

$$\tau_y \approx \frac{\sigma}{R_y} = \frac{\text{surface tension}}{\text{critical radius for fluid to yield}} \qquad (1)$$

If the sample radius is bigger than R_y then the thread or 'liquid bridge' formed in a CABER® test will simply sit in static equilibrium and not evolve in time. This has been observed in careful experiments with liquid bridges of liquid crystalline materials which exhibit a yield stress (Mahajan et al. 1999). Note that as the radius of the thread decreases, the pressure inside the fluid increases and will eventually exceed the value of the yield stress. This is why you can observe stable 'liquid bridges' (i.e. static fluid threads) of yield-stress fluids such as mayonnaise or ketchup connecting two solid surfaces (e.g. your thumb and forefinger) when the radius is large, however these threads suddenly break when you slowly pull your fingers apart – and you never see thin "stringy" threads (unless high mol. weight additives are added).

In the CaBER®, the midpoint radius of the sample immediately following the axial stretching imposed by the endplate can be varied systematically by changing the 'strike' distance. For small strikes, no flow will be observed after the top endplate stops moving; however for a large enough strike distance, the neck is reduced below the critical value, the capillary pressure exceeds the yield stress and the sample starts to neck down towards break-up.

[i] The CaBER® is distributed by ThermoHaake.

A final point to note is that many complex fluids are very sensitive to deformation history. The act of loading a sample into the CaBER® and then forming a thread by separating the plates, means that the relevant yield stress is the 'dynamic yield stress' (which can be significantly different than the equilibrium yield stress determined from, say torsional creep experiments (Larson, 1999).

Necking of a Fluid Thread Below the Critical Radius

The analysis considers a long thin cylindrical thread of fluid that is described by the Bingham plastic constitutive model. For a general flow field, the apparent viscosity for this model is given by

$$\begin{aligned} &\eta \to \infty && for\,|\boldsymbol{\tau}| \le \tau_y \\ &\eta = \frac{\tau_y}{|\dot{\gamma}|} + \mu && for\,|\boldsymbol{\tau}| < \tau_y \end{aligned} \qquad (2)$$

where $|\mathbf{A}| = \sqrt{\tfrac{1}{2} A_{ij} A_{ji}}$ is the magnitude of the indicated second rank tensor, ***A*** (Bird et al. 1987).

If the thread radius is $R_1 \ge R_y \approx \sigma/\tau_y$ then there is no flow. However if $R_1 \le R_y$ then a one-dimensional theory gives the following force balance on the thread (McKinley & Tripathi, 2000)

$$3\eta_{app}(\dot{\gamma})\,\dot{\varepsilon}_{mid}(t) = 3\left[\frac{\tau_y}{\sqrt{3}\,\dot{\varepsilon}_{mid}(t)} + \mu\right]\dot{\varepsilon}_{mid}(t) \cong \frac{\sigma}{R_{mid}(t)} \qquad (3)$$

where we have used the fact that the magnitude of the deformation rate tensor in any time-varying uniaxial flow is $\dot{\gamma} = |\dot{\gamma}| = \sqrt{3}\,\dot{\varepsilon}_{mid}(t)$.

The kinematic definition of the deformation rate near the midplane in terms of the measured radius of the thread at the midpoint gives $\dot{\varepsilon}_{mid} = -2\dot{R}_{mid}/R_{mid}$, and hence

$$\sqrt{3}\,\tau_y + (3\mu)\left(-\frac{2}{R_{mid}(t)}\frac{dR_{mid}(t)}{dt}\right) \cong \frac{\sigma}{R_{mid}(t)} \qquad (4)$$

This differential equation can be solved to give the predicted evolution in the midpoint radius as a function of time. Integration in time gives

$$R_{mid}(t) = \frac{1}{\sqrt{3}}\frac{\sigma}{\tau_y}\left[1 - \delta_0 \exp\left(\frac{\tau_y\, t}{2\sqrt{3}\mu}\right)\right] \qquad (5)$$

where δ_0 is the "intial defect" size that measures how far below the critical radius (R_y) the fluid sample is stretched by the initial axial deformation imposed by the endplates. It is found from the boundary conditions on the integration to be

$$\delta_0 = 1 - \sqrt{3}\frac{\tau_y R_1}{\sigma} \qquad (6)$$

As δ_0 increases, the filament necks down and breaks increasingly rapidly.; if δ_0 = 0 then there is no capillary thinning. The critical radius is thus found to be $R_y = \sigma/\sqrt{3}\,\tau_y$. (The extra factor of $\sqrt{3}$ arises from the kinematics of uniaxial extensional flow).

Finally, the critical time to break-up can be found by setting $R_{mid}(t = t_c) \to 0$ and is

$$t_c = \frac{2\sqrt{3}\,\mu}{\tau_y}\ln\left(\frac{1}{\delta_0}\right) = \frac{2\sqrt{3}\,\mu}{\tau_y}\ln\left(\frac{1}{1-\sqrt{3}\,\tau_y R_1/\sigma}\right) \tag{7}$$

This equation can also be used to eliminate the initial defect size from the evolution equation for the midpoint radius (eq. (5)) in favor of the time to break-up (which is directly measured by CABER®). We thus obtain

$$R_{mid}(t) = \frac{1}{\sqrt{3}}\frac{\sigma}{\tau_y}\left[1-\exp\left(\frac{\tau_y(t-t_c)}{2\sqrt{3}\,\mu}\right)\right] \tag{8}$$

This equation is the key result that is to be used in the CaBER® software. If the surface tension is known, then the parameters to be fitted are the time to break-up (t_c), the plastic viscosity, μ (which dominates slope close to break-up) and the yield stress (τ_y), which dominates the initial part of the curve.

Mathematical Notes:

(i) Very close to break-up (*i.e.* when $t_c - t = \delta t$ is small), then the exponential term in eq.(8) can be simplified using a Taylor expansion ($\exp(x) \approx 1 + x\ldots$) to show that $R_{mid}(t) \approx (\sigma/6\mu)\delta t$ which agrees with the Newtonian result: *i.e.* when the deformation rate is large (near break up) and the Newtonian-like viscous stress part of the Bingham plastic constitutive model dominates, then the midpoint radius decreases to zero linearly in time.

(ii) At very short times (t small), the expression in eq. (5) can be expanded to show that the defect grows linearly in time (i.e. the radius initially decreases linearly..)

$$R_{mid}(t) \approx \frac{\sigma}{\sqrt{3}\tau_y}\left[(1-\delta_0) - \frac{\tau_y}{2\sqrt{3}\,\mu}t\right]$$

(iii) Note that this final expansion can also be used to show formally that if $\tau_y \to 0$ then the expression reduces to the Newtonian fluid limit (with a front factor of 1/6 corresponding to the axially-uniform cylindrical approximation that was used in deriving the initial force balance).

Examples

References

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