**Cambridge
Polymer Group, Inc.**

Testing, Consultation, and Instrumentation for Polymeric Materials

*Not for Duplication or Distribution*

## *The Capillary Breakup Extensional Rheometer (CABER™)*

### *Introduction*

The recent advances in the development of filament stretching extensional rheometers has generated new enthusiasm for measurements of the extensional properties of polymer solutions and melts (Tirtaatmadja & Sridhar, 1993; Spiegelberg *et al.* 1996a,b). The prevalence of extensional flows in most processing methods, coupled with the inability to discern the extensional properties from shear rheometry experiments, emphasizes the need to perform extensional rheometry in order to accurately monitor variations in product uniformity (QC/QA), and predict processing characteristics such as conditions for onset of rate-dependent flow instabilities, and optimal processing conditions.

While devices such as CPG's Filament Stretching Extensional Rheometer (FISER) have wide applicability in the study of viscous polymer solutions and melts, the resolution of the force transducer can limit their use with low viscosity solutions. Additionally, the cost associated with these sophisticated devices is sometimes an unnecessary expense for those only interested in assessing a relative measure of the extensional viscosity in a series of materials.

Filament breakup studies using a Capillary Breakup Extensional Rheometer (CABER™) provide a low-cost approach to the measurement of effective extensional properties, and such tests can be performed with low viscosity polymer solutions. By monitoring the dynamics of breakup of a fluid filament following a short, rapid extensional deformation, one can obtain information about the relaxation time spectrum, the extent of non-Newtonian behavior, and the time to breakup for the fluid. 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.

### *Theory and Experimental Approach*

The theory of capillary thinning of fluid filaments has been discussed extensively by Entov and co-workers (1990, 1997), who pioneered this technique, and more recently by Szabo & Kolte (1999) and Tripathi & McKinley (2000). As opposed to conventional extensional rheometers, which impose a carefully prescribed velocity history on the fluid, a filament breakup rheometer imposes a rapid axial step strain of prescribed magnitude to induce a statically-unstable shape and then allows the 'necked' fluid sample to relax and breakup under the action of capillary forces. Sample images showing the time evolution of the liquid filament formed for a Newtonian oil (of constant viscosity) and a dilute polymer solution are shown in Figure 1 below.

# BREAKUP OF NEWTONIAN AND VISCOELASTIC FLUIDS
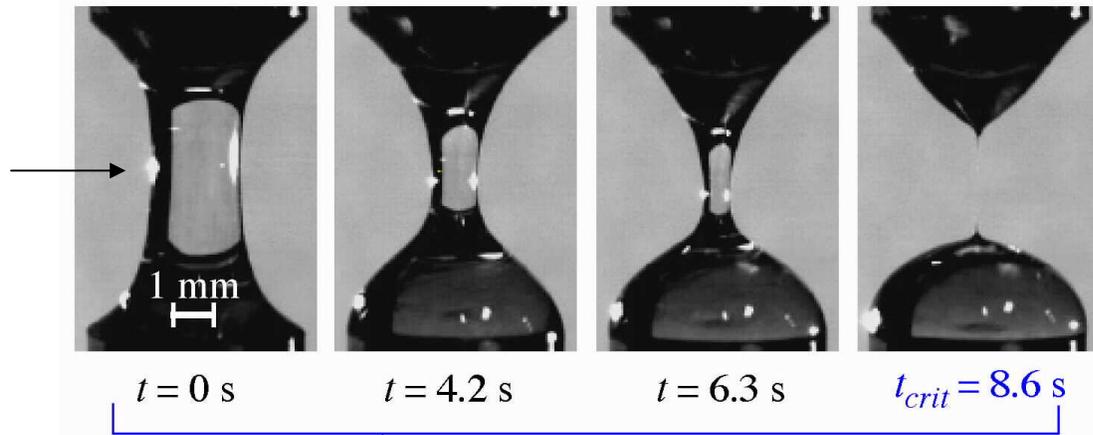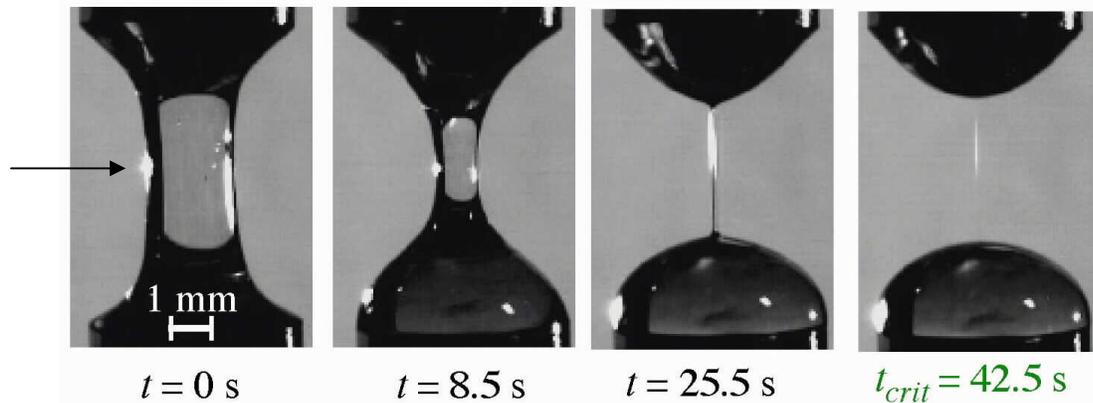


**Figure 1.** Video images of the breakup of fluid columns composed of (a) Newtonian styrene oil (upper images); (b) same oil with 500ppm of a high molecular weight polystyrene additive (lower images). The approximate location of the laser micrometer is shown by the arrow.

During the relaxation and breakup process, it is assumed that the filament profile remains spatially self-similar, so that the dynamics can be characterized by measuring the time evolution of a single point. Using a laser micrometer, the CABER™ monitors the diameter of the filament at the midpoint, $D_{mid}(t)$ as a function of time (see Figure 2). Three representative examples of the resulting dynamics observed are shown in Figure 2 for a viscous Newtonian oil, a viscoelastic polymer solution and a pressure-sensitive adhesive consisting of a thermoplastic elastomer dissolved in a volatile organic solvent. It is clear that the Newtonian fluid undergoes a more rapid filament breakup than the non-Newtonian fluid, whilst the PSA sample does not break at all, but eventually approaches a constant finite value corresponding to a thin residual strand. This propensity to form threads is perceived heuristically as 'stringiness' or 'stickiness'.

The characteristic shapes of the evolution in $D_{mid}(t)$ for each fluid are clearly different and contain encoded information about the material properties of the test fluid which can be extracted using the proprietary software developed by CPG.
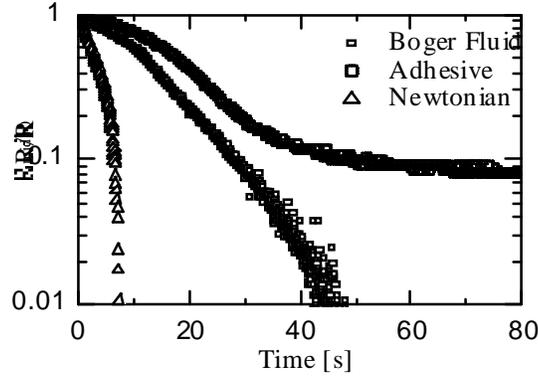


Figure 2: Typical results for the evolution in the midpoint diameter of three test fluids in the CABER™; including a Newtonian fluid, a viscoelastic polymer solution and a pressure sensitive adhesive.

The evolution in the midpoint profile is governed by a force balance on the fluid filament. This can be written compactly in the following form (Yarin, 1993; Renardy, 1995):

$$3\eta_s\left\{-\frac{2}{D_{mid}}\frac{d\,D_{mid}}{d\,t}\right\}=\frac{F_z}{\pi\left(D_{mid}(t)/2\right)^2}-\left[\tau_{zz}-\tau_{rr}\right]-\frac{\sigma}{\left(D_{mid}(t)/2\right)} \qquad (1)$$

where $\sigma$ is the surface tension of the fluid, $F_z$ is the tensile force acting on the column ends, $\eta_s$ is the Newtonian viscosity of the solvent, and $\left[\tau_{zz}-\tau_{rr}\right]$ represents the non-Newtonian contribution to the total normal stress difference in the fluid. This last term is model-dependent and the resulting solution to the differential equation depends on how the polymeric contribution to the stress varies with the rate of deformation. Solutions to this evolution equation have been found for a number of models (cf. Entov & Hinch, 1997; Basilevskii *et al.* 1997; McKinley & Tripathi, 2000) and are summarized in table 1

| Constitutive Model | Form of Solution | Parameters found from regression to data |
|---|---|---|
| Newtonian, $\tau=\eta_s\dot{\gamma}$ | $D_{mid}(t)=0.142\left(\sigma/\eta_s\right)\left(t_c-t\right)$ | $t_c,\,\sigma/\eta_s$ |
| Power-Law Fluid $\tau=K\dot{\gamma}^n$ | $D_{mid}(t)=2^{1-n}\left(0.142\right)\left(\sigma/\mathrm{K}\right)\left(t_c-t\right)^n$ | $t_c,\,\sigma/K,\,n$ |
| Upper Convected Maxwell | $D_{mid}(t)=D_0\left(GD_0/\sigma\right)^{1/3}\exp\left(-t/3\lambda_c\right)$ | $\lambda_c,\,G/\sigma$ |

**Table 1**: Evolution of the midpoint diameter in a fluid thread undergoing capillary-driven breakup.

For a Newtonian fluid the decrease in midpoint diameter is linear in time and the slope of this visco-capillary pinching is characterized by the ratio of surface tension to viscosity ($\sigma/\eta_s$) which has SI units of [m/s] and may be termed a *capillary velocity*. If the surface tension is known then the shear viscosity may be determined (or vice versa). For a power-law fluid the response is very similar, although the rate of decrease in diameter is no longer linear but polynomial with exponent given by the power-law index *n*. For

an elastic fluid a balance of elastic stress and capillary pressure shows that the diameter decreases exponentially in time with a rate of decay given by $(3\lambda_c)^{-1}$ where $\lambda_c$ is the characteristic relaxation time of the fluid. More complicated multi-mode models predict a spectrum of relaxation times, which is more realistic for real polymeric fluids. These models will usually capture the initial more rapid decay in radius during relaxation. This initial rapid drop is usually attributed to the relaxation of shorter time scales, after which point the longer time scales yield a more gradual radial decay consist with a single exponential (Kolte & Szabo, 1999; Anna & McKinley, 2000).

Time to Breakup

In each case, one of the parameters determined is the critical time to breakup, . This is not strictly a material property, of course, but depends on the properties of the fluid, the flow geometry and the surrounding medium (e.g. the relative humidity or partial pressure of solvent). However, this parameter is of utility as a possible way of quantifying concepts such as 'stringiness', stranding' and processability of complex materials such as foodstuffs, shampoos and other consumer products. It is also of great importance in commercial applications involving drop deposition, atomization and spraying.

The Apparent Extensional Viscosity

The principal experimental results obtained from the CABER™ device are the evolution of the midpoint diameters of fluid samples with time. This evolution is driven by the capillary pressure and resisted by the extensional stress in the fluid. The measurements can thus also be represented in terms of an *apparent extensional viscosity*, which we define by $\overline{\eta}_{app}(\varepsilon) \equiv [\tau_{zz} - \tau_{rr}]_{total} / \dot{\varepsilon}(t)$ (Schümmer & Tebel, 1983). By rearranging eq. (1) and a suitable treatment of the far-field boundary conditions on the thread, it can be shown that the apparent extensional viscosity is given by

$$\overline{\eta}_{app}(\varepsilon) = \frac{2\sigma / D_{mid}(t)}{\left\{ -\dfrac{2}{D_{mid}} \dfrac{d D_{mid}}{d t} \right\}} = \frac{\sigma}{\dfrac{d D_{mid}}{d t}} \tag{2}$$

where the instantaneous rate of stretching $\dot{\varepsilon}(t)$ is given by the term in the braces. If the surface tension, $\sigma$, of the test fluid is known from independent measurements, then CABER™ data can be replotted as an extensional viscosity as we show in Figure 3. For the Newtonian fluid – which evolved linearly in time – the extensional viscosity approaches a constant, independent of strain as expected from eq. (2). For the viscoelastic polymer solution, the extensional viscosity increases with strain. Detailed comparison of the steady-state asymptote shows excellent agreement with independent filament stretching tests using a FISER (Anna & McKinley, 2000). For the pressure-sensitive adhesive the extensional viscosity diverges as the volatile solvent evaporates and the fluid solidifies forming a permanent elastic thread.
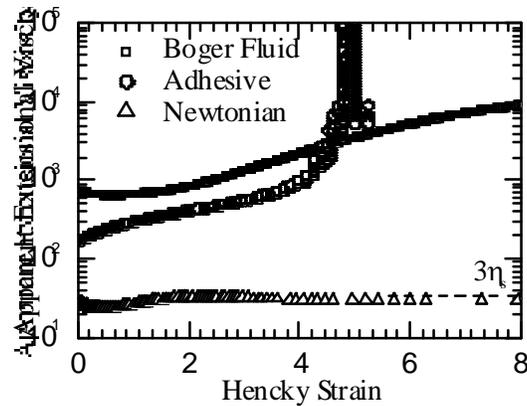
Figure 3: Evolution in the apparent extensional viscosity of the three fluids undergoing
visco-elasto-capillary breakup as shown in Figure 2

### Applications

The range of test fluids that can be studied in visco-elasto-capillary breakup is extremely wide. The CABER™ device has successfully been used by Cambridge Polymer Group, to examine the breakup dynamics of several complex fluid formulations including foodstuffs (chocolate, caramels), consumer products (shampoos, gels), polymeric barrier coatings, adhesives and printing inks. A compact environmental chamber and convection oven (capable of achieving temperatures in the range $25\degree C \le T \le 200\degree C$) is available to expand the range of materials that can be tested in the device.

The compact and robust design of the device, the simplicity of test operation, coupled with robust software analysis make the CABER™ suitable for quality control applications and process monitoring on the factory floor. Small samples extracted from the process line can be rapidly and repeatedly tested to ensure that their extensional rheological properties remain within acceptable bounds. For example; by prior calibration tests and fitting to a suitable rheological model using the CABER™ software, the research scientist may be able to quantify heuristic concepts such as 'stringiness' or 'stickiness' of a particular fluid. Such user-perceived concepts are directly manifested in the time to breakup, $t_c$ measured by the instrument. In some applications it may be desired for this value to be small (e.g. in roll-coating or batch filling operation to prevent formation of long-lived residual threads) whereas in others it may be required to be large (e.g. in food and consumer products in which structure development and high viscosity is required to fulfill user anticipations of concepts such as 'creaminess' and 'stringiness').  By pre-setting acceptable upper and lower bounds on this parameter, the laboratory scientist is able to provide plant operators in different factories or different process lines  with a single test parameter that can be continuously monitored to ensure product uniformity.

### Conclusions

Filament breakup rheometry using the CABER™ presents a simple and cost-efficient technique to obtain information about the extensional properties of polymer materials. In its simplest form, it can be used as an extensional viscosity indexer, providing ranking of fluids according to their breakup times. In a more quantitative form, the data obtained from these experiments can be used to extract material properties such as viscosity, viscoelastic relaxation time, and apparent extensional viscosity. Such parameters are useful, for example, in complex flow modeling and in QA/QC applications. The effects of solvent loss, phase

change (i.e. vitrefication, solidification), and environmental conditions such as temperature and humidity, can all be probed with this technique.

### *Acknowledgements*

### References

Anna, S.L. and McKinley, G.H., Filament Breakup of Model Elastic Liquids, *J. Rheol.*, (2000), submitted.

Bazilevskii, A.V., Entov, V.M., Lerner, M.M. and Rozhkov, A.N., Failure of Polymer Solution Filaments, *Polymer Science Ser. A (translated from Vysokomolekulyarnye Soedineniya Ser. A pp. 474-482)*, **39**(3), (1997), 316-324.

Bazilevsky, A.V., Entov, V.M. and Rozhkov, A.N., "Liquid Filament Microrheometer and Some of its Applications", Third European Rheology Conference, D. R. Oliver (ed.), Elsevier Applied Science, 1990.

Eggers, J., Nonlinear Dynamics and Breakup of Free-Surface Flows, *Rev. Mod. Phys.*, **69**(3), (1997), 865-929.

Entov, V.M. and Hinch, E.J., Effect of a Spectrum of Relaxation Times on the Capillary Thinning of a Filament of Elastic Liquid, *J. Non-Newt. Fluid Mech.*, **72**(1), (1997), 31-54.

Kolte, M.I. and Szabo, P., Capillary Thinning of Polymeric Filaments, *J. Rheology*, **43**(3), (1999), 609-626.

McKinley, G.H. and Tripathi, A., How to Extract the Newtonian Viscosity from Capillary Breakup Measurements in a Filament Rheometer, *J. Rheol.*, **44**(3), (2000), 653-671.

Renardy, M., A Numerical Study of the Asymptotic Evolution and Breakup of Newtonian and Viscoelastic Jets, *J. Non-Newt. Fluid Mech.*, **59**, (1995), 267-282.

Schümmer, P. and Tebel.K.H., A New Elongational Rheometer for Polymer Solutions, *J. Non-Newt. Fluid Mech.*, **12**, (1983), 331-347.

Tirtaatmadja, V. and Sridhar, T., A Filament Stretching Device for Measurement of Extensional Viscosity, *J. Rheol.*, **37**(6), (1993), 1081-1102.

Tripathi, A., Whittingstall, P. and McKinley, G.H., Using Filament Stretching Rheometry to Predict Strand Formation and "Processability" in Adhesives and Other Non-Newtonian Fluids, *Rheol. Acta*, (2000), in Press.

Spiegelberg, S.H., Ables, D.C. and McKinley, G.H., The Role of End-Effects on Measurements of Extensional Viscosity in Viscoelastic Polymer Solutions With a Filament Stretching Rheometer, *J. Non-Newtonian Fluid Mech.*, **64**(2-3), (1996), 229-267.

Spiegelberg, S.H. and McKinley, G.H., Stress Relaxation and Elastic Decohesion of Viscoelastic Polymer Solutions in Extensional Flow, *J. Non-Newtonian Fluid Mech.*, **67**, (1996), 49-76.

Yarin, A.L., Free Liquid Jets and Films: Hydrodynamics & Rheology, Interaction of Mechanics and Mathematics Series, Longman, Wiley, New York, 1993.