Practical Applications of Capillary Extrusion Rheometry to Problems in the Processing of Energetic Materials

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ABSTRACT

Energetic materials are manufactured by processes involving flow, often under conditions of elevated temperature and pressure. Such processes include extrusion, casting and pressing. If the manner in which the material flows under these conditions is not well understood, production and quality problems may result.

A capillary extrusion rheometer is essentially a laboratory-scale extrusion press that is highly instrumented and accurately controlled. As such, it provides an ideal tool for studying and quantifying the properties of the materials as they flow under conditions likely to be encountered in practice. Additionally, the extruded output from the instrument may be subjected to further testing such as for mechanical and ballistic properties to relate changes in processing conditions to product properties.

Keywords: processing, extrusion, filling, analysis, rheology, rheometry, flow, viscosity

Introduction

Working at the United Kingdom's Propellants, Explosives and Rocket Motor Establishment in the 1970's and 1980's, Carter and Baker[1,2] designed and built a laboratory to study the flow properties, or rheology, of filled nitrocellulose/nitroglycerine (Cordite) gun propellants. Attempts to modify the solvent-wet production process by changing solvent types resulted in instabilities ("Twiglets") during extrusion of the solvent-wet doughs. Detailed and systematic studies of the effects of changes in process parameters and formulation on the rheology and the mechanical and ballistic properties allowed short-term manufacturing difficulties to be resolved. In the longer term, this permitted new processing technology to be designed with a high degree of confidence around the materials' processing requirements.

In the fullness of time, the facility was used to study many types of energetic material, including solventless double-base propellants, plastic explosives and propellants, and pyrotechnic binders.

In this paper, some of the many parameters that may be deduced with the aid of a capillary extrusion rheometer will be defined, and the relevance of these parameters to practical processing issues discussed.

Equipment

A capillary extrusion rheometer is, in essence, a laboratory-scale, ram-operated, vertically oriented extruder; see Figure 1. It has a barrel with an accurately honed bore in which the temperature can be accurately controlled, typically to better than ±0.5 °C. An orifice or extrusion die of precisely known geometry is fastened at the lower end of the barrel, and the barrel is filled with the test specimen. A closely fitting piston is driven down the barrel at a series of constant speeds. The equilibrium pressure required to extrude the material through the die at that speed is recorded via a pressure transducer. Various dies with different diameters, bore lengths, and entrance angles are used to investigate the flow properties of the sample to eliminate geometrical effects. Several ranges of pressure transducers are usually used to optimise the precision of

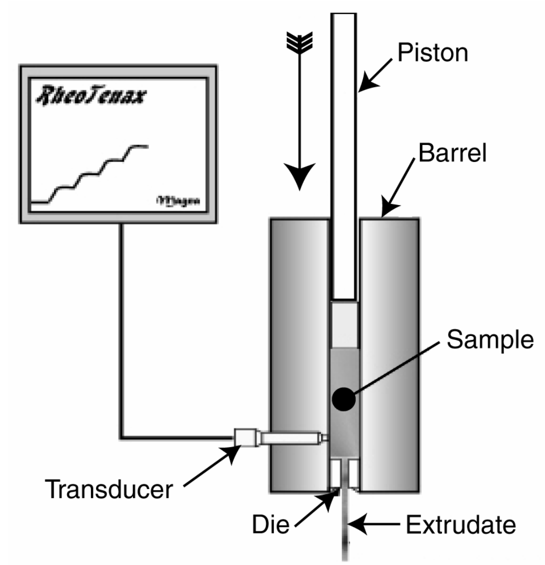

Figure 1. Diagram of a capillary extrusion rheometer.

measurement under a particular set of operating conditions.

Other Devices That Enable Additional Analyses

A slit die is a die of rectangular profile fitted along its length with three or four flush-mounted pressure transducers. It may be used directly to obtain corrected flow data and allow the investigation of some viscoelastic parameters. The pressure coefficient of viscosity,[3] is an important, yet much-overlooked, parameter describing how the viscosity of a material changes with hydrostatic pressure. This parameter may be measured using a tandem-die technique as shown in Figure 2. With this instrument, the pressure drop across the upper die is measured with the two-melt pressure transducers. Several runs are carried out with different geometries of the lower die to develop a range of hydrostatic pressures in the intervening chamber.

Several devices exist for examining the condition of the extruded material immediately after it leaves the die. Optical equipment can measure the diameter and detect any expansion due to elastic effects ("die swell"). Other optical devices can measure the surface temperature of the extrudate to detect an increase in temperature caused by frictional heating during passage through the die.

The specimen, extruded under a range of controlled conditions, may then be examined by other techniques to establish the relationships between raw material, formulation, process parameters and the properties of the final product. Such techniques include dynamic mechanical analysis and dynamic thermomechanical analysis (DMA/DMTA), thermomechanical analysis

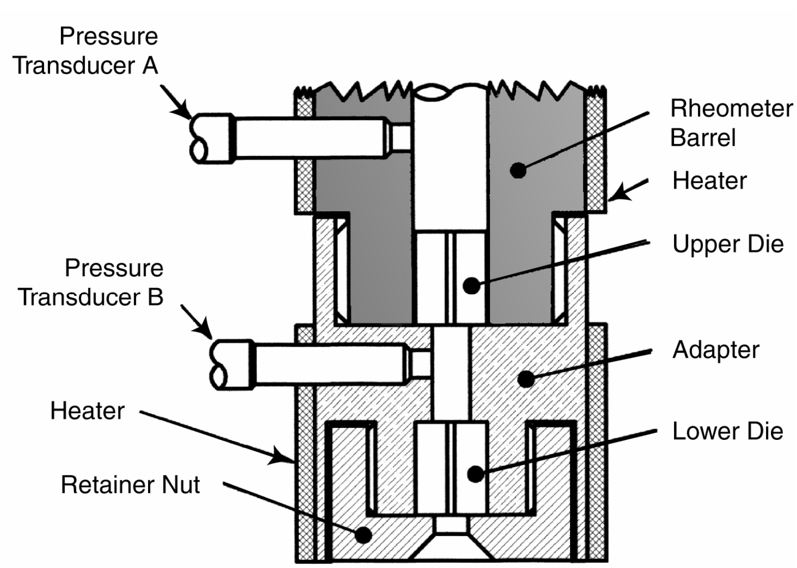

Figure 2. Diagram of a rheometer with tandem dies showing an adaptor for measuring the pressure coefficient of viscosity.

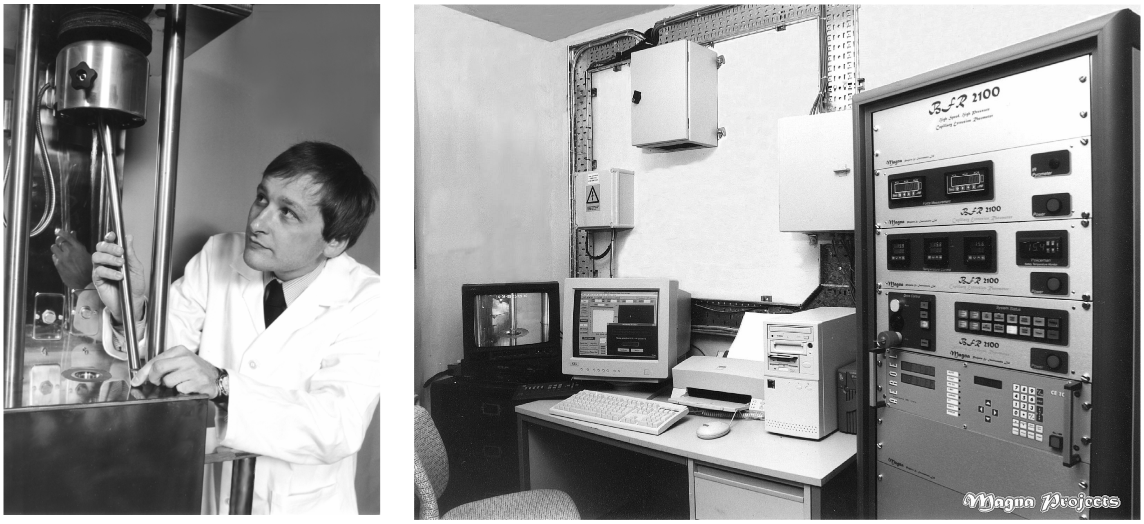

Figure 3. BFR 2100 capillary extrusion rheometer for energetic materials: (left) extrusion head; (right) remote control console.

(TMA), differential scanning calorimetry (DSC), optical and electron microscopy, tensile testing, and many others.

To use the technique safely with energetic materials, the design of the capillary extrusion rheometer must be modified to minimise the risk of danger to the operator and to the equipment: Blind holes and cracks should be removed. Materials that are likely to react with the energetic materials must be replaced. Electrics and electronics should be sealed or the signals routed through intrinsic-safety barriers. Preferably, the instrument should be fully remote controlled, with observation of the extrusion head on closed-circuit television (CCTV). Such an instrument, the BFR 2100, shown in Figure 3, has recently been installed by Magna Projects at a major UK defence R & D laboratory.

Interpretation of Data

In shear flow, materials tend to flow in one of several different ways. See Figure 4. An ideal or Newtonian material shows a linear relationship between shear rate (proportional to piston speed) and shear stress (proportional to pressure). The slope of the line is by definition the viscosity. However, apart from water, very few materials exhibit such ideal behaviour. Many common industrial materials, such as polymer melts, show *pseudoplastic* or *shear-thinning* behaviour. Here, as the shear rate is increased, proportionately less pressure is required to maintain extrusion at that rate. This can be beneficial in industrial processes. On the other hand, some materials—especially those such as pastes containing high filler levels—can exhibit *dilatant* or *shear thickening* behaviour. With such materials, die and tool design is crucial and process monitoring and control is vital as sudden increases in pressure can occur. Some normally pseudoplastic materials can switch to dilatant behaviour at high pressures. Polypropylene and polycarbonate, for example, can stress-crystallize, and some filled materials "bridge". With energetic materials, such a sud-

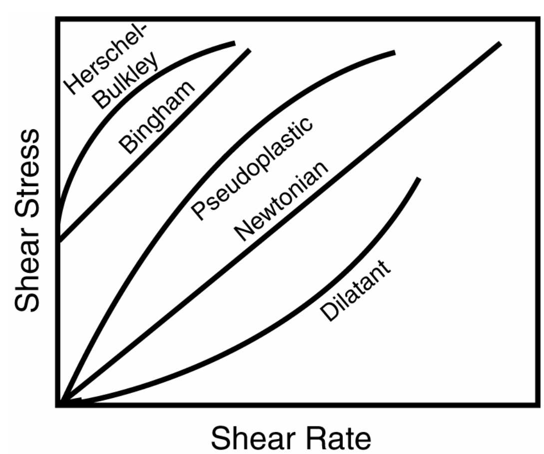

Figure 4. Types of shear flow behaviour.

den increase in pressure can be extremely dangerous.

Some materials will not start to flow (within the experimental timescale) until a *yield stress* has been exceeded. Those that flow in a linear manner after yielding are termed *Bingham Fluids*, an example of which is wet cement paste. Some fluids, such as doughs, flow in a pseudoplastic manner after yielding, and these are termed Herschel-Bulkley Fluids. Carter, Baker and Warren[1,2,4] found that, for solvent-processed Cordite doughs, yield stresses of significant magnitude were present and were necessary for the extruded profile to maintain its shape until the process solvent was removed. In one case, the yield stress was found to be high enough to exceed the tensile strength of the central pin of a small tubular profile die causing it to snap, with subsequent product being produced without the hole; the problem was resolved by redesigning the die with a shorter pin. Indeed, in those studies, it was found that the logarithmic flow curve, Figure 5, was S-shaped. After much work, it was discovered that the non-linearity at lower shear rates was due to the presence of a yield stress, and that the non-linearity at higher shear rates was due to frictional heating as the material passed through the die. In some cases, the magnitude of the temperature increase was sufficient to boil the processing solvent. This discovery solved a manufacturing problem that had been thought to be due to air inclusion but was shown by rheological studies to be due to the solvent boiling at high pressure. The problem was overcome by redesigning the extrusion die.

The temperature dependence of the various flow parameters may be measured easily with the capillary extrusion rheometer system. In one study, it was found that a change of filler from a needle-shaped crystal to a spherical crystal resulted in a profound increase in the temperature sensitivity of viscosity, necessitating a major increase in process control at the factory. In another study, it was found that the yield stress of a formulation went through a minimum as the temperature increased and then it increased again as the temperature continued to rise. This explained why processing problems with this material were experienced at the higher temperatures.

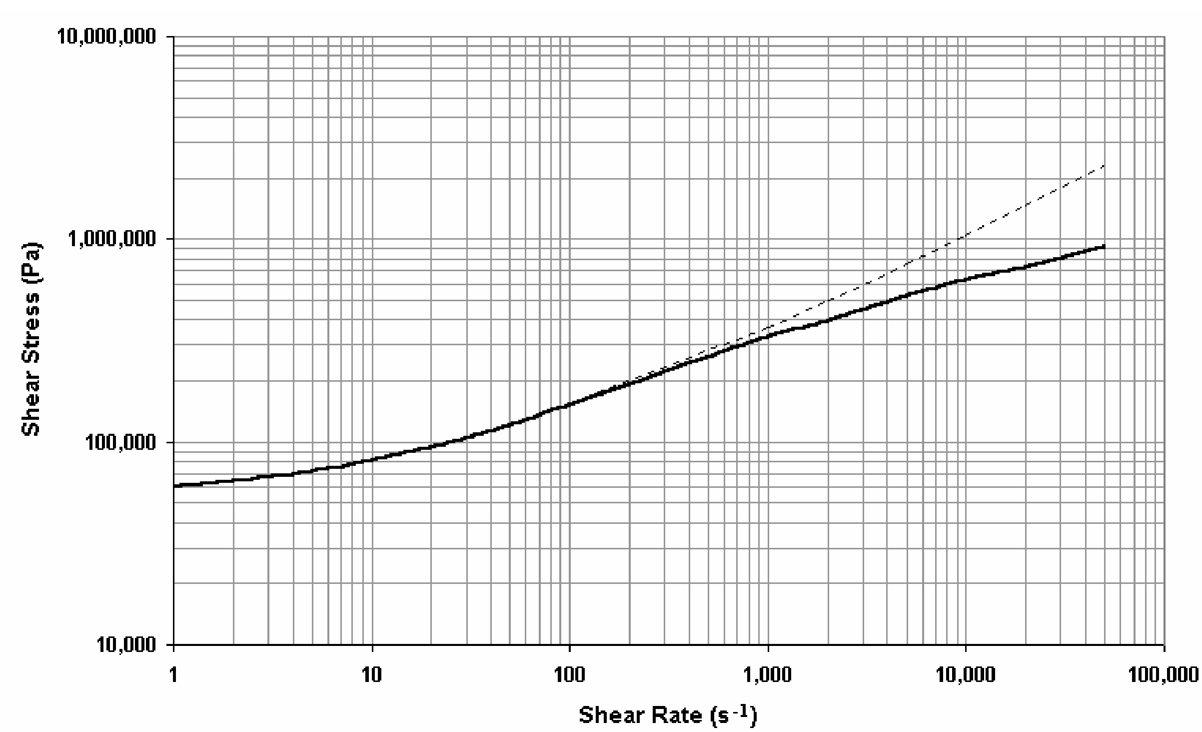

Figure 5. Typical flow curve for nitrocellulose/nitroglycerine (Cordite) gun propellant dough.

Another rheological phenomenon that may be detected and quantified with capillary extrusion rheometry is *wall slip*. This is caused by the extruding material ceasing to adhere to the die wall, giving a discontinuity in the flow curve at a critical shear stress. This can be caused by a low-molecular weight component such as a solvent or plasticizer layer acting as a lubricant, or by a pressure-induced filler-enriched layer appearing close to the die wall. The mere presence of this effect is sufficient to rule out the use of processing techniques such as single-screw extrusion that relies upon the adhesion of the material to the screw and to the extruder barrel, and to explain the inefficiency of the batch-mixing machines, which had hitherto been used. Based on their rheological research in the 1980's, the team at Waltham Abbey selected the co-rotating twin-screw extruder for processing energetic materials. The twin-screw extruder acts as a positive pump to move material through the barrel rather than relying on surface adhesion. Much work has been carried out since on such machines for processing propellants, plastic explosives and other energetic compositions.

Over the past decade or two, the mathematical understanding of capillary extrusion rheometry has developed such that the extensional properties may be separated from the shear flow properties.[5,6] These properties are important in processes where stretching flows dominate, such as extrusion. Often, materials with similar shear flow behaviour but markedly different extensional properties process in different ways.

Conclusions

Capillary extrusion rheometry provides a powerful and versatile technique for studying the flow behaviour of energetic materials under conditions that are similar to those encountered during processing. Potential hazards may be identified in the safety of the laboratory. Additionally, the method is invaluable for trouble-shooting processing problems and for routine quality assurance work.

References

1) Frank S. Baker and Roy E. Carter, "The Development of Modern Gun Propellants as a Function of Basic Research", ADPA Meeting, Picatinny Arsenal, NJ (1984).

2) Frank S. Baker and Roy E. Carter. "Processing Characteristics of Gun Propellants", *Propellants, Explosives & Pyrotechnics*, No. 7 (1982) pp 139–147.

3) R. E. Carter, G. J. Privett, C. R. G. Allen, C. S. Brown, S. Chakravorty and M. Rides, "PRECO: A Novel Means of Determining The Pressure Coefficient of Viscosity Using a Modified Capillary Extrusion Rheometer", ASME Conference *IMECE: International Mechanical Engineering Congress & Exposition*, Nashville, TN (Nov 14–19 1999); Fluids Engineering Division Seminar: *Rheology and Fluid Mechanics of Nonlinear Materials 1999*, FED, Vol. 249, pp 31–34.

4) F. S. Baker, R. E. Carter and R. C. Warren, "The Rheological Assessment of Propellants", in *Rheology*, Ed. G. Astarita, G. Marrucci and L. Nicolais, Plenum Publishing, NY, Vol. 3 (1980) pp 591–596.

5) A. G. Gibson, "Converging Dies" in *Rheological Measurement*, 2nd ed., Ed. A. A. Collyer and D. W. Clegg, Chapman & Hall, London (1998) pp 455–491.

6) M. Rides and C. Allen, "Extensional Flow Properties Of Polymer Melts Using Converging Flow Methods", *Measurement Good Practice Guide* No. 16, National Physical Laboratory, Teddington, UK (1999).