EVALUATION OF MULTI-SAMPLE MICRO-CAPILLARY RHEOMETER

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Abstract

We present a Multi-sample Micro-capillary Rheometer (MMR) which is capable of measurements over a broad range of temperatures, viscosities and shear rates. The instrument is simple as the flow is generated by external gas pressure and the shear rate is measured optically. We test the MMR against two National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs), three low viscosity standards and one (Polydimethlysiloxane, commercial polymer Polyisobutylene solution, Oils and Polystyrene) and report a high level of accuracy and precision. This instrument will be particularly useful as a combinatorial method and in cases of limited material quantity (typical sample size $\approx 20 \ \mu$ L). The dynamic range of the instrument is eight orders of magnitude in viscosity and four orders of magnitude in shear rate.

Introduction

*Melt rheometry is essential to the polymers industry because it provides critical information regarding the processability of new materials and provides insights into a wide-range of fundamental material properties [1-2]. However, bulk rheological techniques are problematic in cases where material supply is limited, where large numbers of sample measurements are required and when rapid sample loading and cleaning procedures are needed. For example, in modern combinatorial methods, the synthesis of large numbers of new polymers and the fabrication of libraries of polymer blends create severe challenges for rheological characterization [3].

Two principle classes of rheometers have wide-scale use in polymers research: capillary rheometers and rotational rheometers [4]. But these two classes of rheometers are not amenable to the high throughput approach being developed in many laboratories. Several methods have emerged recently which enable rheological measurements on significantly smaller samples than had hitherto been possible [5-6] but which is also not suitable for high throughput measurement as well. Recently, Srivastava and Burns developed a micro fabricated nanoliter capillary viscometer based on capillary pressuredriven flow inside microfluidic channels [7-8]. Their micro-rheometer has been demonstrated on room temperature polymer solutions. Despite these advances, these instruments cannot be applied to high temperature, high viscosity fluids such as polymers. Indeed, to our knowledge, the fields of micro-fluidics and microrheology have not yet developed methods that are applicable to polymer melts.

Here we present an instrument designed to meet these requirements- termed a Multi-sample Micro-fluidic Rheometer (MMR), it is essentially a pressure driven slit rheometer. In our current design, we require approximately 20 μ L per sample and measure four samples simultaneously. The MMR offers the simplicity of capillary rheometry and a design that enables parallel measurements on limited quantity samples.

Apparatus

†The primary design considerations were mechanical simplicity (no moving parts), high temperature capability (materials of construction are stainless steel, aluminum and sapphire), cleanability (no inaccessible cavities), multi-sample capability and optical access to the fluid. A pressure-driven capillary rheometer with miniaturized dimensions can meet these requirements. Figure 1 shows the cross-section of the main fixture of the MMR and the main auxiliary components. The heart of the device is the steel shim which contains four slits through which four independent fluids can flow. The thickness of shim used here is 132 µm and the slits are 1.3 mm in width and 13 mm in effective viewing length. Polyimide film (25 µm thickness, Kapton, Dupont) is used as a thin channel spacer to measure low viscosity fluids (less than 0.1 Pa-s). The shim is sandwiched between a stainless steel sample chamber on the upper side and a disc-shaped sapphire window (47 mm diameter x 5 mm thickness) on the lower side. The samples are loaded into four holes.

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[†] Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

The temperature can be elevated to at least 300 °C using a band heater with a control thermocouple and controller. For pressure control, nitrogen gas from a standard laboratory cylinder is input into a programmable electronic pressure controller (ER3000 series, TESCOM Corporation). For pressures beyond the ER3000 limit of 2100 kPa, we flow the gas directly from the cylinder's Most experiments reported here utilized regulator. constant inlet pressure, but we can also apply pressure ramps or more complex profiles. Upon application of pressure, the four fluids flow down from the sample chamber and radially outward into the four slits, displacing the air. The flow front is imaged by a high-end consumer video camera through a mirror (placed for geometrical convenience.) Proper illumination is critical in order to observe the flow-front – we placed a fiber optic ring light. The motion of the flow front is analyzed by commercial motion tracking software (SIMI MatchiX, SIMI Reality Motion Systems) which uses a pattern matching algorithm to track an object as shown in Fig. 2.

Six materials are used to demonstrate the capabilities of the device. Two of them are NIST SRMs Materials, PIB solution (polyisobutylene dissolved in 2, 6, 10, 14tetranmethlypentadecane, SRM2490, NIST) [10] and PDMS (polydimethlysiloxane, SRM2491, NIST) [11]. The third is a polystyrene (PS612, DOW Chemical), which is chosen to demonstrate the high temperature capabilities. The other three are viscosity standard Newtonian oils (S6, N44, N250, CANNON Instrument Company) for low viscosity evaluation. The measured viscosity from the MMR was compared to the reference data for the five standard reference materials and the measured results of a capillary rheometer (Rheo-Tester 2000, Goettfurt) for the polystyrene. The experiment was possible with only one pellet but in the current design of the sample chamber holes, it is unstable with half pellet, consequently, the minimum sample quantity of the MMR rheometer is approximately 20 µL.

Slit Rheometry

Several assumptions are commonly made: the flow is laminar and side-wall effects are ignored. In our study, the ratio of height to width is approximately 10, justifying the latter assumption. The slit flow in our study is a pressure driven – except where noted, the inlet pressure is constant with time. The apparent viscosity can be described by Eq. (1) [9].

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_a} = \frac{\frac{h}{2} \left(\frac{\Delta P}{l}\right)}{\frac{6}{h} V_f} = \frac{h^2 \Delta P}{12} \frac{1}{l V_f}$$
(1)

where τ_w is the wall shear stress, $\dot{\gamma}_a$ is the apparent wall shear rate, V_f is flow velocity of the flow front, ΔP is the

pressure drop, h is the slit height, and l is the length of sample in the channel. By measuring the flow velocity V_f at flow length l, the apparent viscosity can be easily obtained from Eq. (1).

The measured data are the flow length l and flow time t, but the flow velocity is needed to calculate viscosity. Therefore, a curve fitting is used to calculate the viscosity. Here, we use 4^{th} order polynomial equation.

For a shear thinning fluid, slit rheometry also requires a correction in order to obtain the correct wall shear rate, known as the Rabinowitsch procedure [4]. With the flow length-time equation, the viscosity corrected with the Rabinowitsch procedure can be obtained according to shear rate as a function of flow length l, flow velocity dl/dt and its 1st derivative. Moreover, in standard pressure driven rheometry, there is an additional pressure drop due to flow in the entrance and flow front regions, known as Bagley correction [4]. In the present case of flow through a slit with visualization of the flow front, we do not need multiple die lengths. Instead, the procedure is to run experiments at multiple inlet pressures and to then plot the iso-shear rate curves in the parameter space of pressure flow length. Each iso-shear rate curve is extrapolated to l= 0 and the resulting pressure is then the entrance and flow front pressure drop. The corrected viscosity can be obtained by subtracting this Bagley pressure from the total pressure at each shear rate.

Results and Discussion

Figure 3 compares the certified viscosity data of PDMS with the results from the MMR rheometer and finds good agreement at two temperatures over a wide range of shear rates. The coverage of shear rates in one experimental run of the MMR is approximately one order of magnitude. The results shown in Fig. 3 are a master curve of 4 different pressure experiments ranging (34 to 2070) kPa.

The high temperature capability of the rheometer is important for measuring polymer melts. The MMR rheometer can elevate to at least 300 °C. Figure 4 shows a comparison of the viscosities of polystyrene measured by the MMR and a conventional capillary rheometer (Rheotester 2000, Goettfelt) at 190 °C. Good agreement between the two was observed.

The repeatability uncertainty is described in Fig. 5. It is less than 5% in the range of (1 to 100) 1/s when PDMS is used. The compounded uncertainty range is (5 to 10) % according to shear rate range for this MMR design.

Conclusions

Each type of rheometer has an operational window of shear rate, temperature and viscosity. In this study, we show that the MMR has a range of eight orders of magnitude in viscosity, four orders of magnitude in shear rate (Fig. 6), and operates from room temperature to 300 °C. MMR has a low viscosity limit (≈ 0.01 Pa-s) due to capillary force of the free surface but high limit can be expanded easily by introducing higher pressure source. It is applicable to any polymer type which can flow. The MMR has several unique capabilities compared with other macro scale rheometers such as multi-sample capability. sample requirement and micro-fluidic small characteristics. The measured results of the MMR rheometer show that good agreement with the certified reference data and the results of conventional capillary rheometer as well as standard corrections could be applied successfully.

We believe that this rheometer is a good choice for applications with limited sample quantity, for highthroughput experimentation, for quality control and for cases where ease of use is desirable. The operating window can be expanded by changing the shim thickness, by utilizing longer channels, a high speed camera, and pressure controllers that exceed the range (both higher and lower) of the one used here. In order to consider lower viscosity fluids, one needs to explicitly address the contribution of capillary forces to the flow [7, 8]. By changing the shim thickness, the effect of slippage and size dependent measurements can be made.

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Figure 1. Schematic cross-section of micro rheometer fixture.





Figure 2. Procedure to obtain a time-flow length relation of slit flow. Pattern of flow front is tracked by motion tracking software.



Figure 3. Comparison between certified and measured viscosity data using MMR. Measured data is a master curve from 5 pressure experiments (34, 172, 517, 1400, 2070) kPa



Figure 4. Comparison between capillary rheometer and Micro-rheometer viscosity data of polystyrene at 190 °C. Results of 3 pressure experiments.



Figure 5. Repeatability uncertainty versus shear rate with PDMS at 50 °C, 160 kPa for low pressure and 1600 kPa for high pressure experiments.



Figure 6. Operating window of the micro rheometer's shear rate, temperature and viscosity.

Key Words: Micro-rheometer, Multi-sample, Rheometry, Viscosity, Motion tracking, Microfluidics