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Capillary Rheometry: Analysis of Low-Viscosity Fluids, and Viscous Liquids and Melts at High Shear Rates

Rheology is defined as the study of the flow and deformation of fluids. Based on the need to quickly and accurately set and control processing conditions, optimize product performance, and/or ensure product acceptance, accurate rheological measurements have become essential in the characterization of any flowable materials. By utilizing rheological measurements on new materials, process conditions can easily be determined, and the final product properties and performance can be predicted. Historically, many processes impart high-shear deformation and/or high-shear-rate conditions on a material. Obtaining reliable and accurate data under these conditions has sometimes proven to be problematic and difficult.

Traditionally, capillary rheometers have been used to measure the shear viscosity and elasticity of viscous materials at high shear rates. More recently, extensional viscosity has been obtained through the work of Cogswell et al.[1] The interest in high shear rates stems from the mode of deformation a material will undergo in processes like extrusion, film blowing, and injection molding. The design and operational principle of a capillary rheometer are conducive to providing rheological data under these unique processing conditions. The moving piston/die arrangement produces high shear rates on the order of 10^7 s^{-1}. A measure of elasticity can be determined by measuring expansion of the sample at the die exit, called die swell. Melt fracture can be studied by observing the extrudate.[2] Extensional viscosity can be obtained as noted above. As a result, capillary rheometers are widely used in both research environments and quality control laboratories.

Capillary rheometers are versatile and widely used in the rheological measurement of viscous materials where the die sizes normally range from 0.5 to 2.0 mm. However, capillary rheometers suffer from several limitations when attempting to measure fluids with viscosity lower than 1 Pa s: 1) sample flow by gravity through the traditional vertical capillary die when no instrument driving force is applied, and 2) low-pressure readings from the transducer during the measurement. Many times the measured pressure signal can reach the low-end limit of the pressure transducer used.

Another concern is the required length-to-diameter ratio (L/D) of the die for the measurement to be rigorous. According to Macosko,[3] an L/D of 60 or higher is required to eliminate the die entrance/exit effects of low-viscosity fluids at high-shear-rate range. This constraint requires that a die with a very small diameter and long length be produced, which is difficult, if not impossible, to fabricate based on normal machining techniques. In addition, other concerns may arise in the measurement of low-viscosity fluids at high shear rates, including viscous heating of the sample during testing, and high-kinetic-energy effects.

A force balance of the translation mechanical system shows that the measured pressure drop ΔP in the capillary die includes the following components: 1) pressure drop due to viscous dissipation (the sample's viscosity) within the capillary P_{visc}, 2) pressure needed to obtain the kinetic energy of the testing fluid P_{kin}, 3) pressure loss due to end effects including the entrance and exit pressure loss P_{ent} and P_{exit}, and 4) pressure drop for viscoelastic fluids associated with elastic energy $P_{elastic}$. The overall measured pressure drop can be written as follows[3]:

$$\Delta P = P_{visc} + P_{kin} + P_{ent} + P_{exit} + P_{elastic}$$

The kinetic energy pressure contribution for a capillary die is given by:

$$P_{kin} = \rho v^2$$

where ρ is the density of the fluid, and v is the average velocity of the flow. The well-known Bagley correction includes both viscous and elastic components and is used to account for the entrance and exit pressure effects of non-Newtonian viscoelastic fluids.

The basic components of a capillary rheometer consist of a barrel, ram (piston), capillary die fitted inside the barrel, pressure gauge, and force transducer (*Figure 1*). The material is located within the barrel, and then the ram (or piston) attached with a force transducer pushes the material through the capillary die at a specified rate. Above the die inside the barrel is a pressure transducer, which allows for the measurement of the gauge pressure ΔP within the barrel of the capillary rheometer. The force transducer attached to the ram can be substituted for the pressure transducer and is used as the measured signal ΔP inside the barrel. However, any friction in the system not associated with the sample resistance to flow is also included in the measured output. Using the measured pressure ΔP
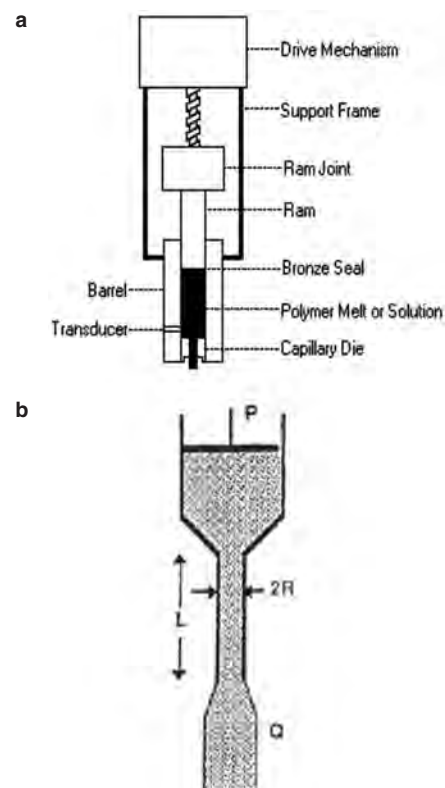

Figure 1   a) Schematic of complete capillary rheometer, and b) closeup of the die structure with variables.

Figure 2   *SmartRHEO capillary rheometer.*

Figure 3   *Viscosity of HDPE at 190 °C using a NOVA rotational rheometer and SmartRHEO capillary rheometer.*

and known controlled flow rate, one can calculate the viscosity of the test sample. By controlling the velocity of the ram, one can control the shear rate of the sample through the die and calculate the viscosity of the sample at fixed, control shear rates. By varying the components of the capillary rheometer, the range of shear rates and testing condition can be extended to fit the requirement of the experimenter.

Operation of a capillary rheometer is simple but can be more time consuming than a rotational rheometer. This is because the larger sample charge requires more time to reach thermal equilibrium. In addition, it can take significant time for the sample to attain steady-state flow at each shear rate. Further, the operator must assess when the measured stress/force or shear rate reaches steady state for a particular point in the measurement before changing to the next measurement point.

This paper describes the SmartRHEO capillary rheometer (**REOLOGICA Instruments**, Bordentown, NJ) (*Figure 2*). The data presented demonstrate the instrument's ability to measure not only high-viscosity materials at high shear rates, but also low-viscosity fluids. The ability to test low-viscosity fluids extends the usefulness of the capillary rheometer to a wider range of materials. In addition, the Equilibrium Stress Prediction (ESP) instrument control
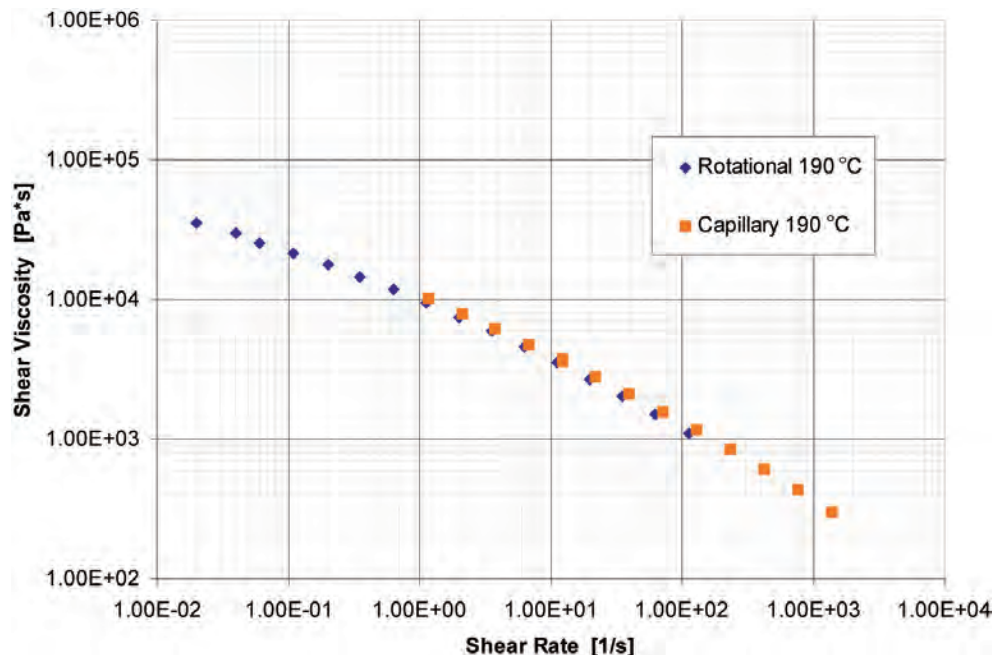
algorithm permits automatic, operator-free use of the capillary rheometer.

Samples

A commercial, fractional melt index extrusion-grade high-density polyethylene (HDPE) was evaluated at 190 °C to demonstrate the capability of the instrument for testing high-viscosity materials. To demonstrate the instrument's ability to measure medium-viscosity samples, a polydimethylsiloxane (PDMS) gum was evaluated at 105 °C. Both the HDPE and PDMS were then compared to small amplitude oscillatory shear (SAOS) results obtained with a NOVA rheometer (**REOLOGICA Instruments**) (*Figure 3*) at comparable shear rates/frequencies using the Cox-Merz rule.

A low-viscosity Newtonian oil, along with a modified oil, were evaluated to demonstrate the system's ability to measure low-viscosity fluids at high shear rates. The role of the modifier is to raise the zero shear viscosity while also imparting pseudoplastic, shear-thinning behavior to enhance flowability and providing elasticity, leading to an increase in lubricity at high shear rates.

To demonstrate the utility and accuracy of the ESP algorithm in the SmartRHEO's VisualRheo operational software, both the

HDPE and PDMS samples were evaluated using the ESP mode. These automated ESP results were then compared with the traditional manual-testing mode.

Instruments

A SmartRHEO capillary rheometer was used to measure the rheological properties of samples over a wide range of shear rates and test conditions. SmartRHEO is the most technically advanced laboratory capillary rheometer for the determination of the flow behavior of a wide range of materials. The rheometer can measure shear rates from 0.01 to over 10,000,000 s⁻¹, with force capability from 0.1 to 50 kN. A wide variety of die sizes and L/Ds are available. Corrosion-resistant sample chambers, pistons, and dies are also offered. Temperature control is better than ±0.1 °C. Other options include: 1) automatic cleaning, 2) nitrogen blanket, 3) pressure-volume-temperature system, 4) thermal conductivity system, 5) slit die geometry, 6) die swell, 7) stretching unit, and 8) extension viscosity by the Cogswell method. The VisualRheo software can be run in manual, plateau, and automatic ESP mode. The ESP mode is a significant time saver, allowing experiments to be run without user intervention. Other available features in the software are the Weissenberg-Rabinowitsch and

Figure 4   *NOVA rotational rheometer.*

Figure 5   *Viscosity of PDMS at 105 °C using a NOVA rotational rheometer and SmartRHEO capillary rheometer.*

Bagley corrections, advanced curve-fitting module, elongational viscosity module, wall slip module, and thermal degradation analysis module. Data exportation to other Windows programs is included as standard.

Capillary testing and results

For the testing of high- and medium-viscosity materials at high shear rates, the SmartRHEO capillary rheometer was utilized with a 1.0-mm die and a die length of 20.0 mm. An L/D of 20 or greater is normally preferred in capillary testing of viscous materials. A standardized procedure was used for all of the capillary testing. First, the instrument was set to the desired test temperature. After the instrument reached the test temperature, the sample was loaded into the barrel of the capillary rheometer and the test was started. The test was set up so that the sample would be at thermal equilibrium for 10 min in the first step of the test. The piston was then lowered until it touched the sample and a maximum load of 0.200 kN was applied. The measuring steps proceeded after the loading and movement of the piston with a controlled velocity and shear rate. Once the steady-state stress at a particular shear rate was reached, a data point was collected, and the next selected shear rate was applied. This step was repeated until all shear rates were completed or the sample began to exhibit flow instability (melt fracture).

HDPE was selected as a high-viscosity sample for its ease of use and well-known rheological behavior in both capillary and rotational measurements. The HDPE was
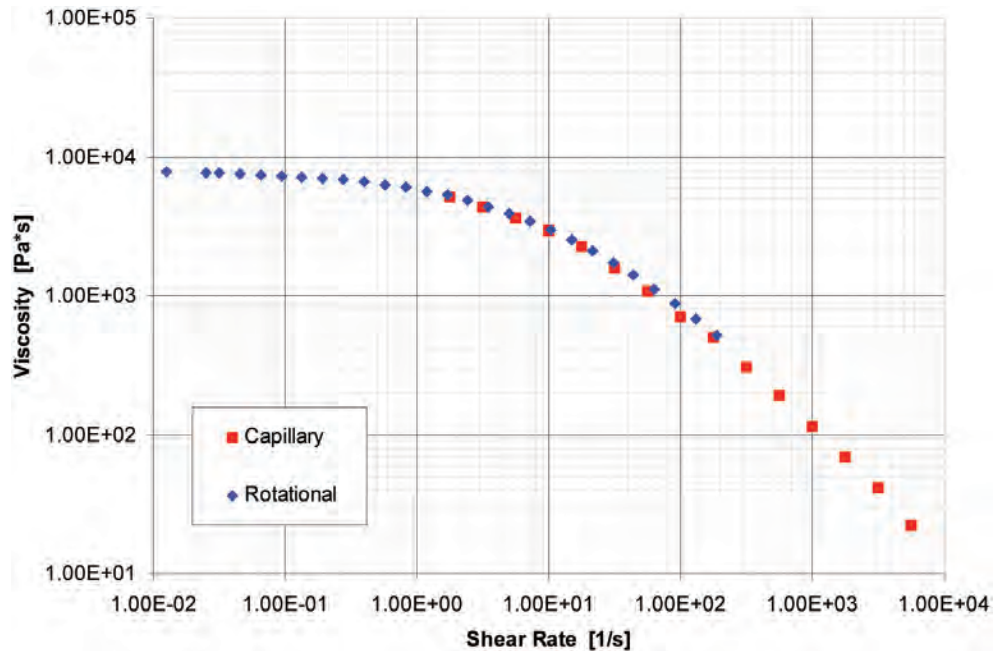
tested at 190 °C, and the viscosity was measured over a shear rate range from 1 to 1000 s^{-1}. At rates greater than 1000 s^{-1}, melt fracture of HDPE occurred, and the experiment was stopped. Results of this measurement are presented in Figure 3. To confirm the capillary data, the HDPE sample was also evaluated on a NOVA rotational rheometer (*Figure 4*) under SAOS at 190 °C. By applying the Cox-Merz rule, the steady shear viscosity from the capillary rheometer can be directly compared with dynamic shear viscosity from the rotational rheometer. This comparison is also presented in Figure 3. As seen in the figure, the steady shear viscosity of HDPE at 190 °C using the capillary rheometer matched the viscosity measurement from the rotational rheometer. By utilizing both measurement techniques (rotational and capillary), one can accurately measure the viscosity of HDPE from low (0.05 s^{-1}) to high shear rates (1000 s^{-1}).

PDMS was selected as a medium-viscosity material. A similar procedure and testing method was used for the PDMS as described for the HPDE above. The main difference between the two sets of experiments is that the PDMS was run at 105 °C instead of 190 °C. The temperature of 105 °C was chosen to demonstrate the midrange viscosity capability

of the SmartRHEO capillary rheometer. PDMS exhibits less flow instability at high shear rates, permitting accurate data collection at shear rates in excess of 5000 s^{-1}. Results of this experiment are presented in *Figure 5*. Similar to the HPDE sample, the PDMS was also tested in SAOS using a NOVA rheometer at 105 °C. As seen in the figure, the capillary and rotational data match well, as observed for the HDPE sample. The results from Figure 5 show a wider range of shear rate, from 0.05 to 5000 s^{-1}, compared to the HDPE sample.

To extend the capability of the capillary rheometer to measure low-viscosity material, a small-diameter die (0.13-mm) with large L/D (160 and 240) was designed and fabricated.[4,5] One concern when testing at high shear rates is viscous heating of the sample. To investigate whether die viscous heating could have an effect during sample testing at higher shear rates, the Nahme (*Na*) number was calculated. The *Na* number needs to be less than 1 for die viscous heating to be neglected. The *Na* number can be calculated by the following equation[3]:

$$Na = \frac{\beta \eta \, \gamma \, R^2}{4k}$$

Where β is the temperature sensitivity of viscosity, η is the viscosity of the fluid, γ is
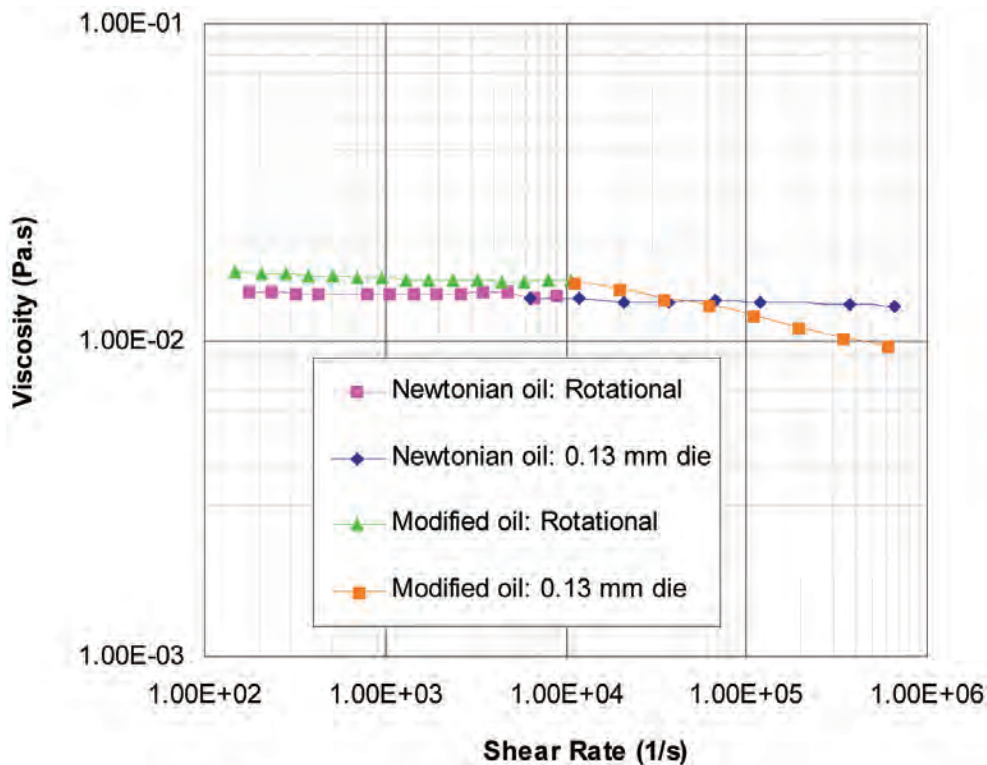
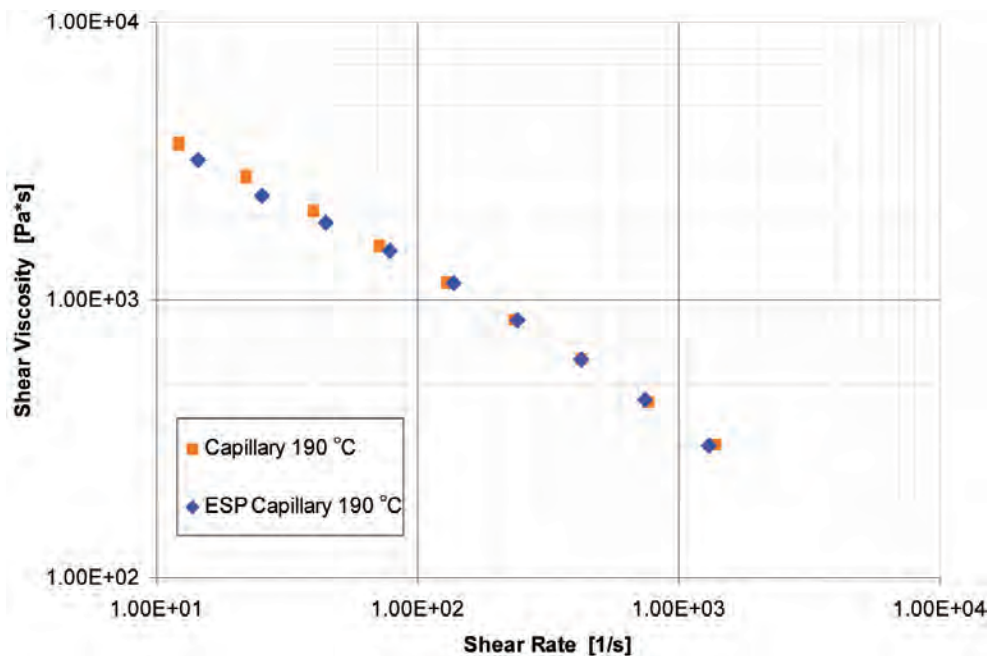*Figure 6*   *Comparison of flow curves using a 0.13-mm die for Newtonian oil and modified oil at 70 °C.*

Figure 7   *Viscosity of HDPE at 190 °C using ESP capillary measurement and manual capillary measurement.*

According to Macosko,[3] the L/D of the die should be larger than 60 to eliminate the entrance and exit effects at the high shear for low-viscosity fluids. Data here indicate that the L/D value for a 0.13-mm die should be greater than 150 to eliminate the need to correct for Bagley, kinetic energy, and entrance and exit pressure contributions. The small-diameter and, more importantly, high L/D requirement of the die make it difficult to manufacture by traditional means. These machining limitations were overcome by the use of some unique engineering concepts and techniques for producing the 0.13-mm die.

Two low-viscosity materials were used for this test—a Newtonian oil and an oil with modifier. A procedure was used that is similar to that used for the HPDE and PDMS materials. However, the temperature was 70 °C and the samples were tested at much higher shear rates (10,000–1,000,000 s^{-1}). Steady shear rotational viscosity was measured on a NOVA rheometer. Results are presented in *Figure 6*, where both the capillary and rotational viscosity data of the two oil samples are plotted versus shear rate from 100 to 1,000,000 s^{-1}. The modified oil shows shear thinning at high shear rate compared to the Newtonian oil sample. The samples possess very low viscosity, in the range of 13 cP for Newtonian oil and 15 cP for modified oil, respectively. The excellent agreement between the rotational and capillary data underscores the reliability of the technique. Clearly, utilizing the appropriate test condition, pressure transducer, and customized die, low-viscosity materials can be measured routinely at very high shear rate with the SmartRHEO capillary rheometer.

Equilibrium stress prediction

One of the limitations of capillary testing is the time of the testing procedure and the requirement of the presence of an operator to collect data during the experiment. As a result, the ESP software function was developed to eliminate the need for operator intervention during a run; in addition, it speeds up the experimental measurement process. For well-behaved materials, i.e., where

the shear rate, *R* is the radius of the die, and *k* is the thermal conductivity of the fluid.

Using a shear rate at 10^6 s^{-1} and properties of the tested fluid, the *Na* number was estimated to be 10^{-7}, which is well below 1. This value of the *Na* number confirms that

even if the shear rate were increased by 100 times, the die viscous heating would not have an effect on the measurement. Similarly, calculations for the kinetic energy and Bagley corrections showed both terms to be negligible for the 0.13-mm die in the shear rate range 10,000–1,000,000 s^{-1}.
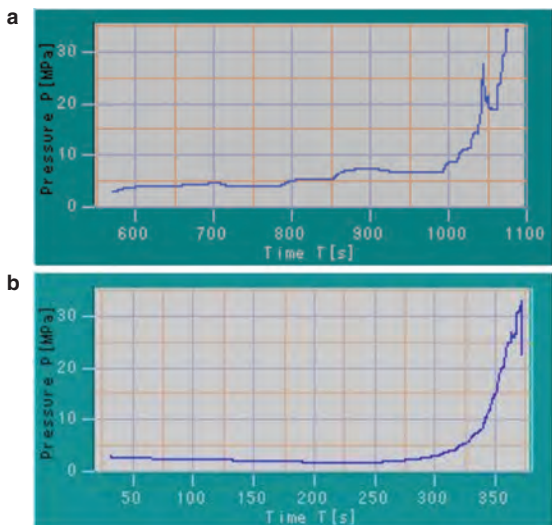
a

b

Figure 8   Raw data showing pressure versus time for a) manual experiment with a total time of approximately 1100 sec, and b) ESP experiment with a total time of approximately 400 sec.

stress growth is exponential, the stress growth curve can be fitted with a specific equation. The steady-state stress value at the applied shear rate can be predicted using the fitted equation constants. By applying a special algorithm and the fitting equation, ESP uses the data for the first several seconds to estimate the constant for the equation from which the steady-state value can be determined without the experimental waiting time to attain steady-state flow. HDPE was used to test the ability of the ESP function. Similar testing conditions as used in the manual control mode testing of the HDPE were used. The major difference is that the ESP mode was set up to measure the data over the first 10 sec of each shear rate, and then uses the data to predict the steady-state viscosity. After 10 sec of measurement, the

software automatically changes to the next shear rate until the end of the experiment.

The comparison between manual and ESP mode testing is presented in *Figure 7*. It can be seen that the ESP function successfully predicted the steady shear viscosity of the sample without the presence of an operator. In addition, the ESP mode significantly reduced the time of the experiment. *Figure 8* shows the duration of the experiment using manual and ESP mode. The ESP mode reduced the amount of time to perform the experiment by 70%, yet still provided data comparable to the manual mode. This feature will significantly reduce testing time and can be applied for quality control process where time and, more importantly, operation intervention, are minimized.

Conclusion

The SmartRHEO capillary rheometer can be used to investigate rheological properties of a wide range of materials from low-viscosity fluids in the range of 1–10 cP to highly viscous materials such as HDPE. Also, capillary rheometry can provide the high-shear-rate region beyond the limit of rotational rheometers. By applying the Cox-Merz rule, the range of shear rate measurements can be extended from very low shear rate using a rotational rheometer to very high shear rate using a capillary rheometer. The combination of data from both rheometers gives the engineer and scientist a much better understanding of the full spectrum of material flow behavior.

The SmartRHEO capillary rheometer is versatile and easy to customize to inves-

tigate a wide range of materials over a broad range of shear rates. With customized dies, the rheometer can be used routinely to test low-viscosity materials at very high shear rate. The ease of use and the ESP function will shorten the testing time and reduce the operating cost of obtaining rheological results.

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