

# *Syringe-Based Capillary Rheometry of Dense Pastes*

*A method for viscosity measurements and processability characterizations*

## **Introduction**

Extrudability is a central tenant of many manufacturing processes, this is especially true for direct ink write (DIW) additive manufacturing (AM) [1]. When dealing with dense pastes, defined as having > 50vol% solids [2], extruding a material is no longer a simple process. As solids loading increases the conditions under which a material is extrudable are increasingly constrained and, when successful, the process through which extrusion is achieved can change the behavior of the material being extruded [3].

In polymer processing capillary rheometry is recognized as the critical instrument for characterizing shear viscosity and predicting flow behavior under different conditions, including extrusion. Commercially available capillary rheometers required large quantities of material, up to 100g, and require the experimenter to have the material loaded into a narrow cylindrical chamber within the rheometer, only accessible from the top. Originally developed for high temperature polymer processing, these capillary rheometers are not fit for use with research materials in dense paste form that are limited to small batch sizes, exhibit memory effects and time-dependent behavior. Additionally, loading paste-like material into a narrow cylindrical chamber without capturing large pockets of air [4] is difficult and time consuming. Properly cleaning these instruments between tests introduces yet another challenge to attaining quality data in a timely manner.

To achieve quality data existing capillary rheometry experimental procedures call for a large set of experiments to correct for assumptions inherent in the testing procedure, like there being no slip at the wall of the capillary or the exit pressure of a capillary being zero. These requirements further consuming large quantities of material while highlighting difficulties in loading and cleaning the instrument.

Existing capillary rheometer configurations are not fit for research and development dense paste rheometry needs. This report details an affordable, small-scale syringe-based capillary rheometer that operates with low material requirements, is easily filled to mitigate handling effects, and is configured to replicate processing equipment to eliminate data-correction requirements. It will be shown that this rheometer can accurately gather data on dense paste formulations and that this data matches data gathered from processing equipment. By replicating processing conditions within the test equipment, the need to perform corrections for slip and exit effects are eliminated, as the 'apparent' viscosity becomes the 'process' viscosity observed in manufacturing. The syringe-based capillary rheometer is shown to be a critical tool for screening materials for extrudability and eliminates waste accrued due to in-process failures. Additionally, the sensor configuration used paves the way for process monitoring and in-situ control via viscosity data feedback.

**Materials, methods, and assumptions**

**Materials:**

*Reference Oil:*

The N30000 viscosity standard [5] from the Cannon Instrument Company was used to verify the capillary rheometer proposed in this report. At 20C its viscosity is 105.2 Pa.s and at 25C its viscosity is 66.31 Pa.s. Testing with this reference oil was done at 23.2C and the viscosity calculated at 80.31 Pa.s.

*Paste:*

Monomodal Melafine from OCI Nitrogen [6] was mixed into a SYLGARD 182 [7] binder system with a neat Newtonian viscosity of 5.5 Pa-s. Filler particle size distribution is shown below in figure 1. Paste density was calculated at 1.33 g/mL. SEM images of the Melafine particles are shown in figure 2.

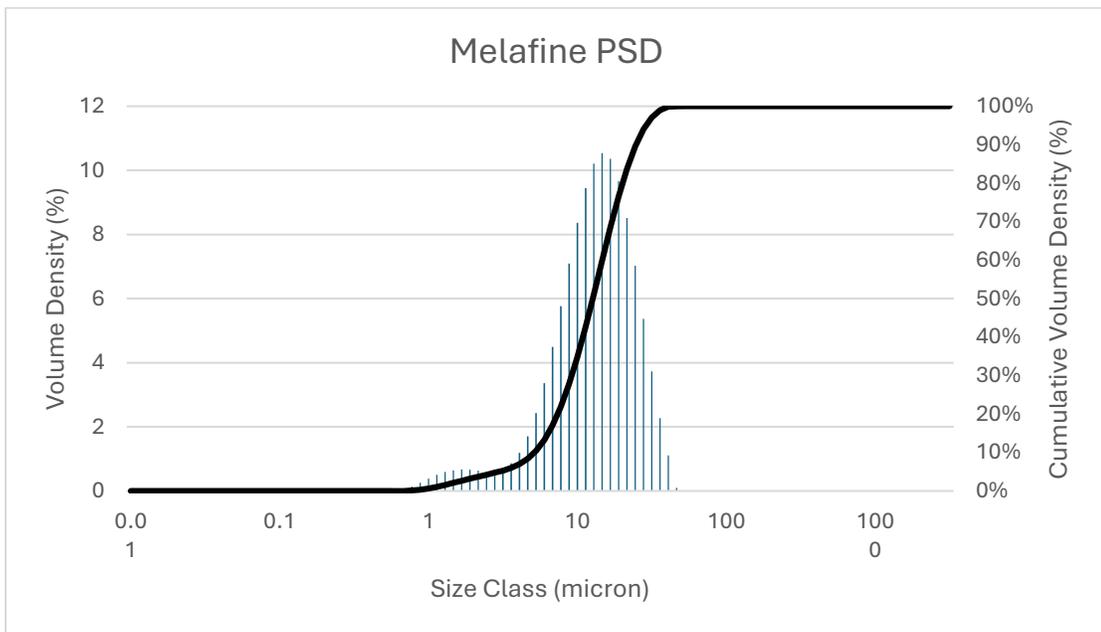


Figure 1: Melafine PSD

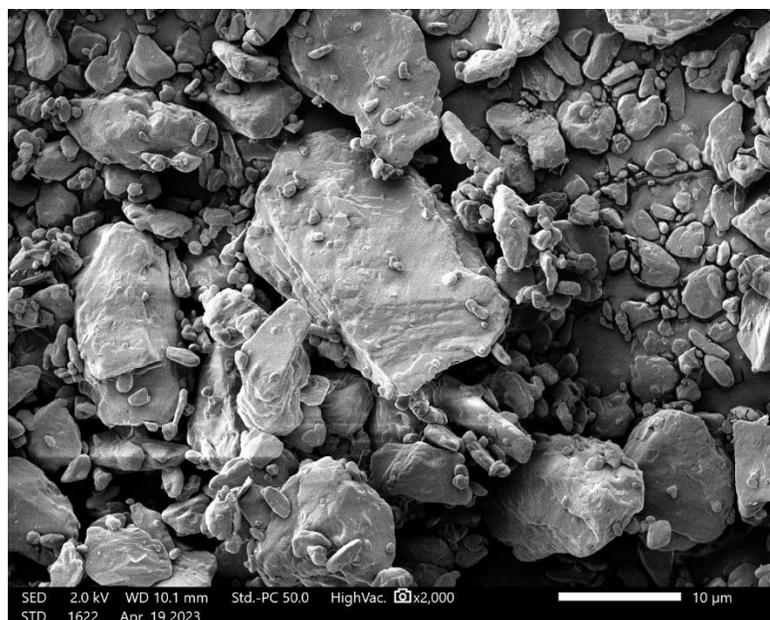


Figure 2: Melafine SEM at 2000x

#### *Mixer:*

FlackTek SpeedMixer [8] was used to produce the ink reported on in this paper. Mixing was done in accordance with the following procedure. All material for this report was mixed in one 75g batch, done in a 185mL container with a rounded bottom.

#### *Syringe and Tips:*

After having mixed the material, it was allowed to cool for one hour. After it had cooled, 10g each was loaded into 10mL Nordson EFD syringes [9] which were centrifuged using a Cole-Parmer 17250-10 Fixed-Speed Centrifuge [10] to remove entrained air. These syringes were then allowed to rest overnight.

All materials were extruded using a 16-gauge Luer-Lock tip from Nordson EFD that was 38.1mm long and had an ID of 1.54mm [11]. The tolerance values from the tip drawings are as follows: length of 38.1 +/- 0.38mm, diameter between 1.51 and 1.56mm.

#### *Process Equipment, Progressive Cavity Pump (PCP) and controller:*

A Viscotec ecoPEN-330 [12] progressive cavity pump (PCP) was used as the target processing equipment in this report. The PCP was controlled via an eco-CONTROL EC200 2.0 controller [13], also from Viscotec, that was commanded via a bespoke Python script communicating over RS-232 interfaces.

#### *High-Pressure Adapter (HPA):*

For the syringe-based capillary rheometer a 10mL high-pressure adapter (HPA) from Nordson EFD was used [14]. This adapter can take a maximum inlet pressure of 100psi and produces up to 400psi dispensing pressure.

*Transducer:*

A flowplus-SPT M6 [15] pressure transducer from ViscoTec was used for all pressure readings done in this report. This pressure transducer can measure up to 40bar. The 3D model of the transducer is shown in figure 3.

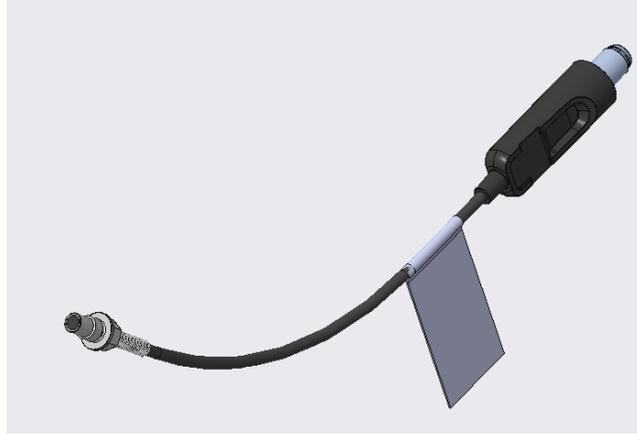


Figure 3: flowplus-SPT M6 Pressure Transducer

From both the PCP and HPA capillary rheometer adapters had to be designed and manufactured to enable data gathering. The PCP adapter and internal section are shown below in figure 4 a-b. The HPA adapter and internal section are shown below in figure 5 a-b.

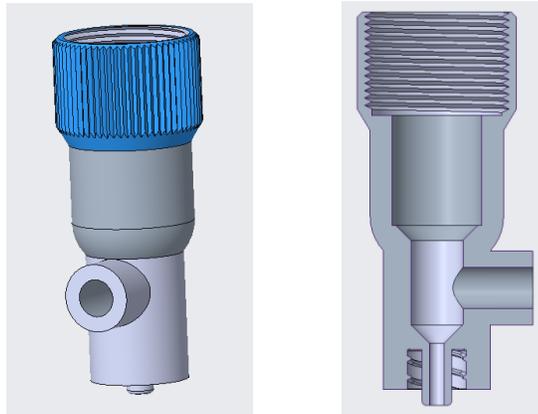


Figure 4 a-b: PCP Transducer Interface Adapter

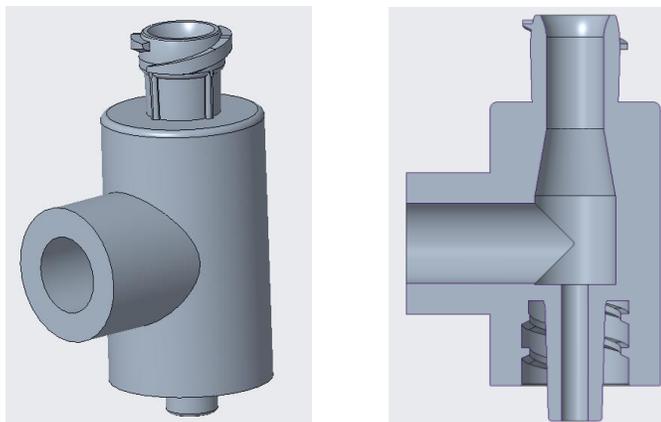


Figure 5 a-b: HPA Transducer Interface Adapter

Each printed adapter shown above has a smooth bore transducer interface perpendicular to the vertical axis of flow. This transducer interface was hand-tapped using an M6 tap and cleaned with water, then dried thoroughly, before being fitted with the transducer. The transducer interfaced directly with the eco-CONTROL EC200 2.0, hereafter referred to as ‘controller’, and was able to transmit pressure data periodically via that connection.

#### *3D Printers:*

All transducer interface adapters were printed on a Phrozen Mega8k MSLA 3D Printer [16]. The resin used 80% Siraya Tech Fast Grey and 20% Siraya Tech Tenacious by volume [17].

#### *Scale:*

A Mettler Toledo ME-T [18] scale with +/- 0.001g sensitivity and 210g max was used for all weighing in this report.

#### *Pressure Controller:*

An Alicat PC Series 500PSIG pressure controller with an RS232 interface was used to modulate the pressure applied to the syringe in all cases [19].

#### *Software:*

Python 3.11.5 [20] was used via the Spyder IDE Version 5 [21] to process data, produce summary statistics and visualizations in this report. Python packages used were: PySerial [22], pandas [23], matplotlib [24], SciPy [25], and NumPy [26]. Creo 7.0.3.0 [27] was used to design each of the additively manufactured transducer adapters and UltiMaker Cura 5.9 [28] used to slice files for printing.

#### Methods:

##### Rheometer Construction

After mixing the material, loading it into syringes, and allowing it to rest overnight each rheometer can be constructed: the instrumented process PCP (PCP) and the high-pressure adapter syringe-based capillary rheometer (SCR).

*Instrumented PCP:*

An image of the instrumented PCP is shown below in figure 6.

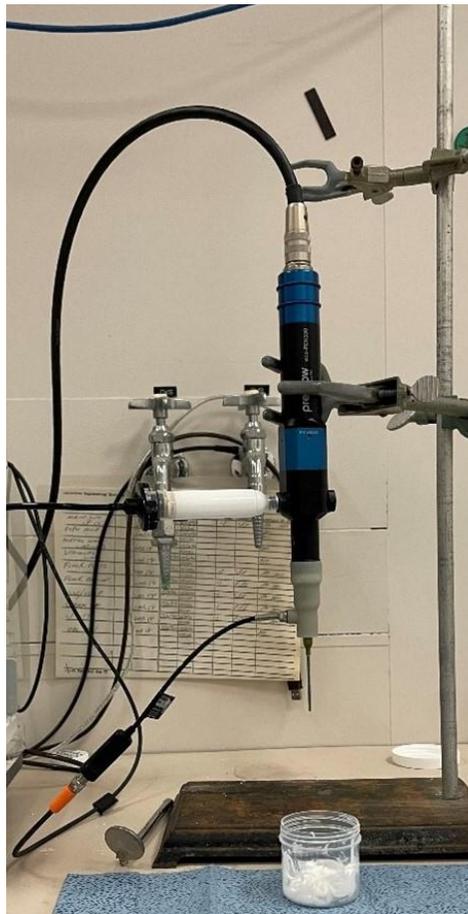


Figure 6: instrumented pcp

To configure the instrumented PCP first the stator must be lubricated, then the rotor loaded onto the stator and fully seated in position in accordance with the eco-PEN330 manual [12] as shown in figure 7 below.

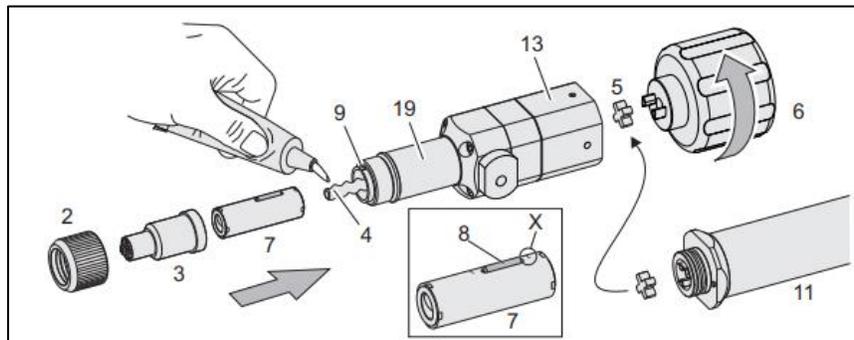


Figure 7: seating stator

However, rather than configuring the PCP with items 2 and 3 as shown in figure 7, the PCP transducer adapter from figure 4 was used. With the transducer adapter in place, the transducer was fitted to the PCP via the adapter and then the Luer-Lock tip attached to the bottom of the adapter. After fully fitting the PCP together the motor (item 11 in figure 7) was fitted, a loaded syringe attached, and the PCP bled IAW the eco-PEN330 manual.

Bleeding the PCP consisted of increasing the pressure on the syringe to induce flow into the reservoir above the rotor-stator assembly (item 19 in figure 7), waiting 60 seconds, then setting the PCP to a low flow rate (0.2 mL/min) to slowly fill the PCP with material, remove any air, and set the equipment up for extrusion.

#### *Syringe-based Capillary Rheometer (SCR):*

An image of the syringe-based capillary rheometer is shown below in figure 8 a-b.



Figure 8 a-b: Syringe-based Capillary Rheometer and High Pressure Adapter Section

The construction of the syringe-based capillary rheometer is much simpler than the PCP. A syringe filled with material is loaded into bottom portion of the HPA, the transducer adapter is fitted to the syringe via a Luer-Lock, and the top of the HPA attached. Then, with the syringe fixed in place, the transducer can be fitted into the transducer interface of the adapter and a Luer-Lock tip attached. Lastly, only air need be supplied to the HPA to induce flow and begin testing. Figure 8b shows the model cross-section of the loaded HPA, without the transducer adapter. The total cost of

this SCR -- including the pressure controller, transducer, and controller – was less than \$10,000. Though a high price tag, it is at least an order of magnitude cheaper than commercially available capillary rheometers and offers marked benefits as detailed below.

#### Data Collection

Upon construction of both rheometers basic extrusion tests were undertaken to measure the relationship between extrusion pressure and volumetric flow rate. This data, combined with test geometry, enables the calculation of shear stress, shear rate, and thus shear viscosity [29]. Due to their slightly differing configurations, different test procedures were undertaken.

For the PCP the volumetric flow rate was set via the controller, then the actual volumetric flow rate and extrusion pressure measured. The actual volumetric flow rate is used in the subsequent calculations. The set volumetric flow rate was increased between test runs to gather data over the full range of the PCP operating window, from 0.2 -3.3 mL/min.

For the HPA the inlet pressure is set via the pressure controller, then the extrusion pressure and volumetric flow rate measured. The inlet pressure is increased over a series of test runs to gather data over the full range of HPA operating conditions, from 0-100 PSI.

Though each configuration is different procedurally, the way the extrusion pressure and volumetric flow data was collected was the same. Volumetric flow rate data was collected by collecting the extruded mass of sample in a tared cup over a set period. The cup was then weighed after the test concluded. The density of the material was calculated from its constituent elements' density and mass fractions, and the volumetric flow rate was calculated from mass flow rate and density. Extrusion pressure was sampled once per second on a local laptop from the controller via the RS232 interface. All the data was stored in .csv files for later analysis.

#### Assumptions:

Critically, it is assumed that by loading the syringes and letting them rest overnight any handling effects by the experimenter is mitigated by this extended relaxation period. Additionally, it is assumed that the material's behavior is not changing throughout the test. It is assumed that the reference oil viscosity varies linearly between 20 and 25C. Additionally, all calculations assume that the tip geometry is as-advertised, namely with a diameter of 1.54mm and a length of 38.1mm. Tip dimensions were not measured each time the tip was changed due to frequent tip exchanges throughout testing. All the tips used were from the same batch.

## Results and Discussion

### Results

#### *Reference Oil Data:*

All reference oil testing was performed at 23.2C with the N30000 Cannon Reference oil. The results at five different set pressures are shown below in table 1. Set pressure is defined as the air pressures supplies to the syringe rheometer. Extrusion pressure is defined as the measured pressure from the transducer above the tip.

Set Pressure (PSI)	Extrusion Pressure (Pa)	Apparent Shear Rate (sec <sup>-1</sup> )	Apparent Shear Viscosity (Pa.s)	Reference Oil Viscosity (Pa.s)	Error (%)
30.00	108.28	94.53	82.99	80.31	3.34%
40.00	146.63	122.53	86.70	80.31	7.96%
50.00	181.81	145.12	90.77	80.31	13.02%
75.00	255.54	218.43	84.76	80.31	5.54%
100.00	323.18	289.16	80.97	80.31	0.82%
Average			85.24	80.31	6.14%

Table 1: Reference Oil Data

It has previously been accepted that averaging the error in this configuration is acceptable because the reference oil is Newtonian and has a constant viscosity across all shear rates [29]. 6.14% average error is taken as an acceptable amount of error when viewing the assumption that the tip dimensions are as advertised. If the tip dimensions are varied in this calculation between their upper and lower bounds, the average error can range from -0.91 – 10.65%. That this contains a tip dimension set that results in no error lends credence to the acceptability of this test configuration.

*Extrusion Data:*

The data gathered in both test configurations is shown below in table 2.

Test	Run #	Inlet Pressure [PSI]	Measured Extrusion Pressure [PSI]	Extrudate Mass Collected [g]	Set Volumetric Flow Rate [mL/min]	Actual Volumetric Flow Rate [mL/min]	Test Duration [sec]	Shear Stress [Pa]	Apparent Shear Rate [sec <sup>-1</sup> ]	Apparent Shear Viscosity [Pa-s]
PCP	1	50.00	128.26	0.85	0.20	0.13	300.00	8.94E+03	5.92	1,510.44
	2	50.00	130.03	0.84	0.20	0.12	311.38	9.06E+03	5.65	1,604.35
	3	50.00	189.24	1.60	0.50	0.23	311.39	1.32E+04	10.76	1,225.03
	4	50.00	231.34	2.34	1.00	0.34	311.47	1.61E+04	15.77	1,022.18
	5	50.00	259.81	2.94	1.50	0.43	311.42	1.81E+04	19.76	915.90
	6	75.00	320.76	4.30	2.00	0.62	311.40	2.23E+04	28.98	771.16
	7	75.00	330.33	3.53	2.50	0.77	207.90	2.30E+04	35.64	645.71
	8	75.00	330.36	1.17	3.00	0.86	61.43	2.30E+04	39.92	576.55
	9	100.00	358.12	4.61	3.30	1.00	207.32	2.50E+04	46.60	535.45
SCR	1	40.00	87.89	0.42	-	0.06	309.20	6.12E+03	2.82	2,167.86
	2	50.00	116.57	0.69	-	0.10	309.26	8.12E+03	4.64	1,748.59
	3	60.00	146.21	1.06	-	0.15	309.43	1.02E+04	7.15	1,423.85
	4	70.00	178.49	1.45	-	0.21	309.33	1.24E+04	9.81	1,268.01
	5	80.00	209.60	1.86	-	0.27	309.37	1.46E+04	12.60	1,158.80
	6	90.00	256.00	1.15	-	0.42	122.98	1.78E+04	19.68	906.43
	7	100.00	319.75	1.84	-	0.67	123.18	2.23E+04	31.28	712.17

Table 2: Extrusion Test Data, PCP and SCR

When viewed graphically, as shown in figure 9, it is clear that both processes are reporting the same profile for the material in question even though there is a slight diversion in flow rate data as extrusion pressures reach the upper limit attained here.

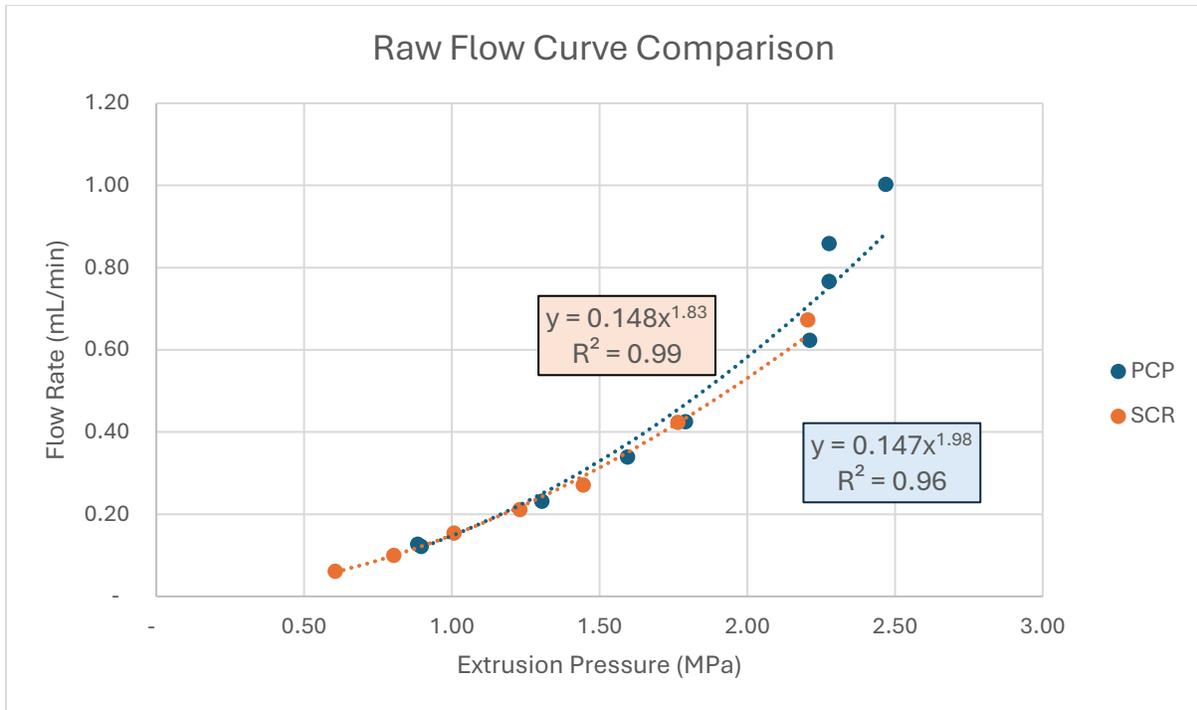


Figure 9 – Raw Flow Curve Comparison

Both the PCP and SCR show similar profiles for the material in question. This is also attested to by the curves fitting this data.

Assuming the PCP as the target value, the SCR constant value represents a 0.9% error and the exponent a -7.3% error. Within the operating range as shown here, the SCR can credibly predict the PCP extrusion behavior.

When geometric considerations are introduced then shear stress, rate, and viscosity can be calculated [30, 31]. The viscosity versus shear rate is the curve of most interest, as it shows how the material's resistance to flow changes between different processing conditions. This is shown below in figure 10.

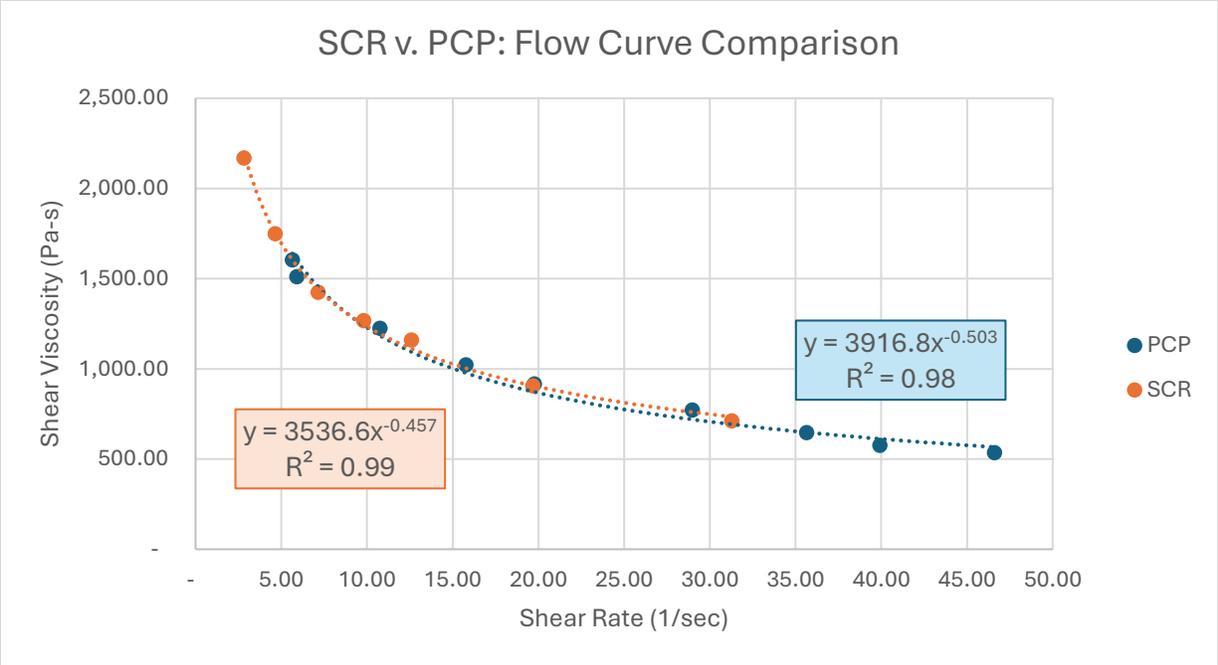


Figure 10: Viscosity Flow Curve Comparison

This very clear overlap between the two flow curves inspires confidence that both processes are measuring the same material behavior, and the procedural assumptions set forth in this study are acceptable. The power law fits attained here serve as a tool to predict the material behavior in other flow configurations. If the PCP fit is taken as the correct value, as the process flow behavior is that which we wish to replicate in the SCR, then the SCR power law fit constant, or consistency, contains a 9.7% error, and the exponent, or non-Newtonian flow index, represents a 9.1% error. Both errors being below 10% for the range of analysis suggests solid agreement and gives confidence to the use of the HPA as a tool for mimicking process flow behaviors.

Discussion

With a tool for mimicking process flow behaviors, pastes can be screened for the PCP using the SCR. By knowing the PCP process limitations as used in this configuration, syringe and tip included, we can build an adaptable process window within which extrudability will be contained. First, the PCP has both lower and upper flow rate limits, 0.2 and 3 mL/min, respectively. Additionally, the maximum attainable pressure with the 10mL syringes used is 100 PSI. With this information, figure 11 below can be constructed and the data gathered in this report plotted onto it.

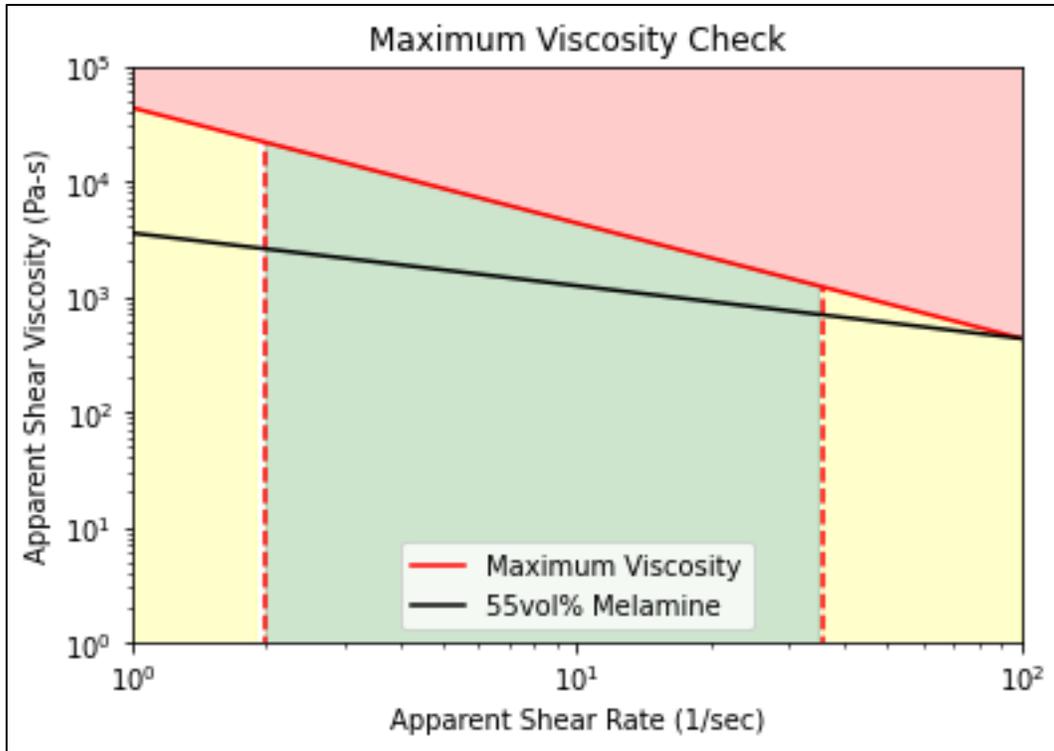


Figure 11: maximum viscosity check

The left-most yellow portion represents flow rates below the operating window of the PCP, and the right-most yellow portion represents flow rates above the operating window of the PCP. The vertical lines correspond with the shear rates calculated for these flow rates and the geometries in this configuration. These shear rates are  $2.17$  and  $35.85 \text{ sec}^{-1}$ . The red portion at the top of the graph shows the viscosity region in which the material is not extrudable into the PCP. Above this line, the material viscosity is so high that the PCP cannot be filled with material. This line is calculated from the maximum applied shear stress on the material, limited by the 100psi inlet pressure and 10mL syringe geometry, of 43,092 Pa. With the maximum applied shear stress known the maximum shear viscosity at each point can be calculated and a curve fit – generating the maximum viscosity line shown on figure 11.

Using the SCR detailed in this study the viscosity curve of a material can be found, as shown in black on the above graph, and checked against this maximum viscosity curve. As long as the viscosity at the selected processing conditions is within the extrudable (green) range, the material is predicted to be successfully extrudable. Based off this information it can be concluded that the 55vol% melamine formulation used here is extrudable across the entire operating range of the PCP as configured in this study.

This maximum viscosity curve is detailed for a specific process configuration but can readily be adapted to include different maximum inlet pressure, inlet syringe configurations, and tip geometry.

## Conclusions:

In this report an affordable, small-scale syringe-based capillary rheometer purpose built for the research and development of dense paste formulations was detailed that can directly mimic extrusion-based processing equipment, namely a PCP, perform viscosity measurements and enable the predictive screening of candidate materials for processing. This instrument, the SCR, was verified using a viscosity standard, obtaining accurate viscosity values within 6% of the reference value. The SCR enables rapid formulation and testing of candidate materials in a streamlined fashion through ease of loading, minimal cleaning, and quick sample swapping that mitigates user error and resultant sample variability. Data gathered on the SCR can provide a power-law curve fit of raw instrument data, extrusion pressure and volumetric flow rate, within 7% and of the material flow curve, viscosity and shear rate, within 10% of the same values measured on the instrumented process equipment. These abilities can accelerate the characterization of developmental material formulations and pave the way for in-situ process control in the future.

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<https://www.python.org/downloads/release/python-3115/>
- [21] Install Guide — Spyder 5 documentation: <https://docs.spyder-ide.org/5/index.html>
- [22] pyserial · PyPI: <https://pypi.org/project/pyserial/>
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