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# A mathematical and rheological study of the pastes that make up obturator endodontic cement from MTA base

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**Abstract.** The MTA-Fillapex endodontic cement is constituted from base and catalyst pastes. In the present work we investigated, from several rheological models, the model that described the best relationship between the shear stress and shear rate for the pastes. To the investigation, five paste lots were selected, and the Brookfield RST-CPS rheometer was used to the measurements. The rheological laws were deduced according to the models: Bingham, Ostwald-de Waele, Herschel-Bulkley, and Casson. The models parameters were calculated by means of our code. We used the Levenberg-Marquardt Method, from the computational platform OCTAVE on the version 5.2.0. Additionally, we analyzed the parameters' existence domain, the fitted determination coefficient, the maximum deviation, and the correlation matrix. From this, the preliminary results showed that the Ostwald-de-Waele was most representative rheological model to characterize the base paste, and to the catalyst paste we had the Herschel-Bulkley model as the better representation.

**Keywords:** Mathematical Modeling, Rheology, Levenberg-Marquardt Method, MTA, Rheological Model.

## 1 Introduction

An endodontic cement from MTA base is indicated for filling root canals at the permanent dentition in combination with endodontic sealing materials (gutta-percha cones). The endodontic treatment success depends mainly on the elimination of microorganisms present in the root canal infection, which is performed through chemical-mechanical preparation, of the irrigating substances and the total filling of the root canal system [1]. The filling of the root canal system (RCS) – the last step of endodontic treatment – is performed with materials at the shape of cones, and cements.

There are several endodontic cements kinds available on the market. They are classified according to their basic constituent. A new mineral trioxide aggregate (MTA) formulation has been extensively studied, it is a white or gray powder of thin hydrophilic particles that hardens in the presence of humidity [2].

An endodontic filling cement at the MTA base is a paste-paste cement, constituted by base and catalyst pastes. The base paste contains a composition from disalicylate and for the catalyst paste we have the active ingredient MTA. By mixing the pastes we obtain an ionic polymer.

An ideal endodontic cement should flow along of the canal wall surface, to fill the voids and gaps between the core filling material and the dentin, and finally, adhere to both dentin and gutta-percha [3]. In this context the Rheology helps to model the best cement composition that brings it closer to the ideal.

The main function of a rheological model is to represent mathematically the relationship between the experimental values of stress and shear rates, and thus allows the analytical treatment of the flow. Furthermore, they are useful to relate other rheological properties of a fluid such as: concentration or temperature as well. This knowledge is necessary at design and dimensioning of equipment and processes, and in quality control [4].

In this work, which is part of an ongoing master's work, we aim to identify the most better models that describe the rheological behavior of base and catalyst pastes.

## 2 Materials and methods

Data collection was performed from five different lots for each pastes, base and catalyst. The lots referring to the base paste were identified like 56821, 57151, 57286, 57287, 57715. And the lots of the catalyst paste like 57119, 57121, 57291, 57293, 57714. Therefore, for each lot we checked the rheological measurements for three distinct samples, which are named as triplicates.

The rheological measurements of the triplicates were performed at a constant temperature of 25ºC, using a rotary rheometer of the *BROOKFIELD* model RST-CPS. We emphasize that the reading and recording of experimental data were established by the *software REO3000*, according to the standard measurement protocols described below.

To the base paste we used the (*spindle*) plate-plate rheometer configuration in a protocol with 45 total points following the structure: 15 points in a constant rotation of the 1.9 $s^{-1}$ shear rate, with 60 seconds of the analyze; 15 points on the ascending slope at the 1.9 – 8.0 $s^{-1}$ shear rate range, with 60 seconds analysis time; 15 points on the descending slope in the 8.0 – 0.0 $s^{-1}$ shear rate range, with 60 seconds analysis time as well. However, for our investigation, the constant rotation points were discarded. Since our interest is purely the state where the fluidity happens.

Regarding the catalyst paste the rheometer *splindle* cone-plate configuration was used, in a protocol with 90 total points following the structure: 45 points on the ascending ramp in the 0.0 – 500.0 $s^{-1}$ shear rate range, with 180 seconds of analyze time; 45 points on the descending slope in the 500.0 – 0.0 $s^{-1}$ shear rate range, with an analysis time 180 seconds as well.

With the measurements, we created data files referring to all lots of the pastes, with values of rates and shear stresses. The computer program Octave was used to build a code that fits the rheological models of the created files. The Levenberg-Marquardt method – whose algorithm is already implemented in a Octave library – was incorporated into our code to fit the rheological models to the data. The library use's benefit is that to each data fit, it also calculates several statistical values as well. For the present work we used in our analyses: the correlation matrix, and the determination coefficient.

The algorithm proposed by Levenberg [5] and Marquardt [6] was developed to solve minimization problems of the nonlinear functions by means of least square method. It is one of the most used optimization algorithms today. In general, the Levenberg-Marquardt algorithm combines the gradient descent algorithm and the iterative Gauss-Newton method.

For the present work, the Table 1 displays the rheological models – Bingham, Ostwald-de Waele or Power Law, Herschel Bulkley and Casson – which are the most common to describe the pastes rheology mentioned. They have been adjusted to the files data aforementioned.

Table 1. Rheological models used to adjust the flow curves of the pastes.

| Bingham | Ostwald- de Waele | Herschel-Bulkley | Casson |
|---|---|---|---|
| $\tau = \tau_o + K\,\dot{\gamma}$ | $\tau = K\,\dot{\gamma}^n$ | $\tau = \tau_o + K\,\dot{\gamma}^n$ | $\tau^{1/2} = {\tau_o}^{1/2} + (K\,\dot{\gamma})^{1/2}$ |

The $\tau$ variable is the shear stress ($Pa$); $\dot{\gamma}$ the shear rate ($s^{-1}$); $\tau_o$ the initial stress ($Pa$);
$K$ the consistency index ($Pa.s^n$); and the dimensionless $n$ is called of behavior index.

We used as criteria to determine the models best fit of the experimental data: the parameters domain, the correlation matrix, the adjusted determination coefficient ($R^2_{aj}$), and the maximum deviation ($d_{max}$). In particular, the equations of $R^2_{aj}$ and $d_{max}$ are given by:

$$R^2_{aj} = 1 - (1 - R^2)\left[\frac{m-1}{m-(p+1)}\right] \quad \text{e} \quad d_{max} = \underset{1\le k\le m}{\text{máx}} \left\{\left|\chi_k^{exp} - \chi_k^{aju}\right|\right\},$$

where $m$ is the experimental data total number, $p$ the model parameters' number, $\chi_k^{exp}$ the experimental value and $\chi_k^{aju}$ the predicted value from the adjusted model.

For a results accurate analysis, we considered the arithmetic means of the adjusted determination coefficients ($\overline{R^2_{aj}}$) and the maximum deviation ($\overline{d_{max}}$), to the different lots, in order to make the model as representative as possible.

We calculated the correlation matrix coefficients magnitude to investigate the relationship between model parameters. In other words, in terms of magnitude, how much change experienced by one parameter implies change in another parameter as well. For example, $C^{BI}_{\tau_o,K}$ is the correlation matrix coefficient of the Bingham model, whose magnitude quantifies the relationship between $\tau_o$ and $K$. We remember that the positive coefficient defines variations in the same direction, negative means in the opposite direction. Finally, null coefficient means that the parameters are not related.

## 3 Results and Discussions

According with the Table 2, the Herschel-Bulkley model was not adequate to describe the base paste behavior, because $\tau_o$ assumes negative values, which is contrary to its physical meaning.

Table 2. Parameters, adjusted determination coefficients and maximum deviation, referring to the rheological models adjusted to the base paste data.

| Models | Lots | Parameters | | | Adjustment measures | |
|---|---|---|---|---|---|---|
| | | $\tau_o$ | $K$ | $n$ | $R^2_{aj}$ | $d_{max}$ |
| Bingham | 56821 | 247.7243 | 147.1970 | | 0.8111 | 276.61 |
| | 57151 | 250.1271 | 148.6362 | | 0.7856 | 249.06 |
| | 57286 | 233.1220 | 134.6475 | | 0.8267 | 242.33 |
| | 57287 | 271.9965 | 114.2920 | | 0.7442 | 277.61 |
| | 57715 | 93.7136 | 130.2814 | | 0.8352 | 265.04 |
| Ostwald-de Waele | 56821 | | 342.3481 | 0.6710 | 0.8370 | 245.37 |
| | 57151 | | 353.0332 | 0.6586 | 0.8168 | 225.59 |
| | 57286 | | 313.0807 | 0.6748 | 0.8506 | 198.07 |
| | 57287 | | 327.1867 | 0.6043 | 0.7817 | 229.76 |
| | 57715 | | 206.1344 | 0.8095 | 0.8451 | 254.84 |
| Herschel-Bulkley | 56821 | -466.9425 | 737.7491 | 0.4347 | 0.8466 | 234.37 |
| | 57151 | -200.6492 | 510.8370 | 0.5430 | 0.8236 | 230.49 |
| | 57286 | -437.0876 | 678.9964 | 0.4376 | 0.8596 | 172.18 |
| | 57287 | -767.0929 | 1011.4711 | 0.3007 | 0.7995 | 189.91 |
| | 57715 | -150.9529 | 318.5555 | 0.6557 | 0.8479 | 250.37 |
| Casson | 56821 | 85.7560 | 99.4263 | | 0.8259 | 260.45 |
| | 57151 | 89.8203 | 98.9606 | | 0.8032 | 231.01 |
| | 57286 | 79.2547 | 91.4059 | | 0.8402 | 221.10 |
| | 57287 | 110.9683 | 69.8970 | | 0.7650 | 207.70 |
| | 57715 | 19.7844 | 105.5199 | | 0.8405 | 260.26 |

Furthermore, it is indicated that the Ostwald-de Waele model presented the best adjustments for the lots, since it admits the highest values of $R^2_{aj}$, all greater than 0.78. And the lowest $d_{max}$ values, except to the lot 57287 when compared to the Casson model. Additionally, we calculate $\overline{R^2_{aj}} = 0.8262$ and $\overline{d_{max}} = 230.72$, which signals that the model is in agreement with the data.

Table 3. Correlation matrix coefficient values, referring to the base paste lots.

| Lots | Bingham $C^{BI}_{\tau_o,K}$ | Ostwald-de Waele $C^{OW}_{K,n}$ | Casson $C^{CS}_{\tau_o,K}$ |
|---|---|---|---|
| 56821 | -0.91304 | -0.97655 | -0.97998 |
| 57151 | -0.90897 | -0.97550 | -0.97913 |
| 57286 | -0.91713 | -0.97724 | -0.98073 |
| 57287 | -0.91718 | -0.97488 | -0.97993 |
| 57715 | -0.90901 | -0.98043 | -0.98124 |

Besides, at the Table 3 we present the correlation matrix coefficients values for the base paste. Evidently, from the table, the parameters are strongly correlated. But, we discarded the Herschel-Bulkley model values because the parameter $\tau_o$ was inconsistent.

The Figure 1 shows, in the same graphic window, the base paste experimental data, and the respective curves fitted. We emphasize, it seems that any model would be adequate. But reasoned on the statistical data described above, the Ostwald-de Waele model was consolidated as the best model for the base paste.

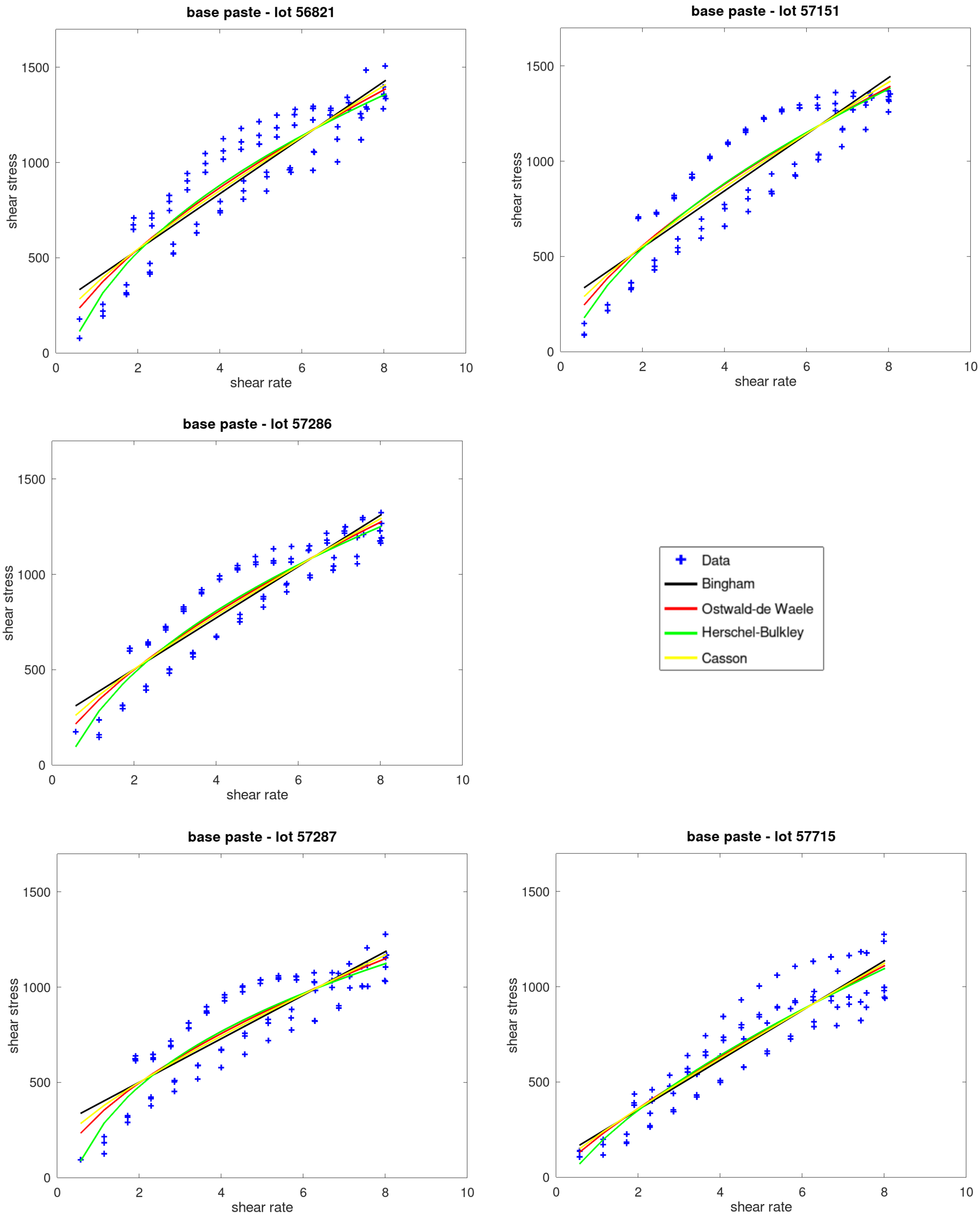


Figure 1. Flow curves for the base paste lots.

Now, in Table 4 we present the parameters of the catalyst paste rheological models. All models are candidates to model the flowability of the catalyst paste. But, the Bingham and Herschel-Bulkley models showed the best fits, with the highest $R^2_{aj}$, greater than 0.33, and the lowest $d_{max}$, less than 4250. However, we accept that the Herschel-Bulkley model was the one that best agreed with the data. This will be demonstrated below.

Table 4. Parameters, adjusted determination coefficients and maximum deviation, referring to the rheological models adjusted to the catalyst paste data.

| Models | Lots | Parameters $\tau_o$ | $K$ | $n$ | Adjustment measures $R^2_{aj}$ | $d_{max}$ |
|---|---|---|---|---|---|---|
| Bingham | 57119 | 2312.5376 | 3.1574 | | 0.3378 | 4163.23 |
| | 57121 | 1951.7038 | 3.2565 | | 0.5302 | 2566.92 |
| | 57291 | 1824.8219 | 2.7806 | | 0.3564 | 2202.44 |
| | 57293 | 1778.6357 | 2.9531 | | 0.6304 | 2028.94 |
| | 57714 | 1977.3496 | 3.0308 | | 0.4206 | 2910.64 |
| Ostwald-de Waele | 57119 | | 1362.2069 | 0.1551 | 0.2001 | 4335.10 |
| | 57121 | | 928.5004 | 0.2049 | 0.4028 | 2566.92 |
| | 57291 | | 938.1916 | 0.1857 | 0.2569 | 2582.41 |
| | 57293 | | 873.6935 | 0.1987 | 0.4462 | 2417.24 |
| | 57714 | | 1050.9406 | 0.1798 | 0.2734 | 3289.07 |
| Herschel-Bulkley | 57119 | 2240.0056 | 1.8641 | 1.0993 | 0.3369 | 4249.77 |
| | 57121 | 1990.7602 | 1.8321 | 1.0890 | 0.5325 | 2538.69 |
| | 57291 | 1861.2295 | 1.4527 | 1.0987 | 0.3573 | 2176.75 |
| | 57293 | 1863.1189 | 0.7300 | 1.2175 | 0.6457 | 1964.46 |
| | 57714 | 2007.8472 | 1.3453 | 1.1205 | 0.4196 | 2894.37 |
| Casson | 57119 | 1944.2371 | 0.5879 | | 0.2877 | 4267.28 |
| | 57121 | 1552.6960 | 0.7550 | | 0.4886 | 2766.86 |
| | 57291 | 1484.1171 | 0.5932 | | 0.3223 | 2367.06 |
| | 57293 | 1425.8586 | 0.6684 | | 0.5650 | 2197.07 |
| | 57714 | 1619.7831 | 0.6319 | | 0.3668 | 3077.85 |

The arithmetic means found for the Bingham model were $\overline{R^2_{aj}} = 0.4550$ and $\overline{d_{max}} = 2774.43$, and for the Herschel-Bulkley model we calculated $\overline{R^2_{aj}} = 0.4584$ and $\overline{d_{max}} = 2764.20$. This confirms that the Herschel-Bulkley model would be the best modeling of the catalyst paste. Unfortunately, the Herschel-Bulkley model's $\overline{R^2_{aj}}$ is low because there is a lot of dispersion in the data.

Furthermore, the correlation matrix coefficients values to the different lots of the catalyst paste are presented in Table 5, note that the parameters are also strongly correlated. In particular, the Herschel-Bulkley model showed correlations above 85%.

Table 5. Correlation matrix coefficient values, referring to the catalyst paste lots.

| Lots | Bingham $C^{BI}_{\tau_o,K}$ | Ostwald-de Waele $C^{OW}_{K,n}$ | Herchel-Bulkley $C^{HB}_{\tau_o,K}$ | $C^{HB}_{\tau_o,n}$ | $C^{HB}_{K,n}$ | Casson $C^{CS}_{\tau_o,K}$ |
|---|---|---|---|---|---|---|
| 57119 | -0.87081 | -0.99129 | -0.88621 | 0.86695 | -0.99887 | -0.95516 |
| 57121 | -0.87089 | -0.99245 | -0.88904 | 0.86996 | -0.99887 | -0.95690 |
| 57291 | -0.87092 | -0.99206 | -0.88769 | 0.86863 | -0.99888 | -0.95624 |
| 57293 | -0.87093 | -0.99233 | -0.86996 | 0.85113 | -0.99900 | -0.95679 |
| 57714 | -0.87090 | -0.99193 | -0.88439 | 0.86536 | -0.99891 | -0.95615 |

The catalyst paste experimental data – from lots 57119, 57121, 57291, 57293, 57714 – and the adjustments curves of the rheological models, are shown in the same graphic window at the Figure 2. It see that apparently any propose model in this work models the rheology of the paste. But, based on statistical calculations, the Herschel-Bulkley model would be the most adequate to describe the catalyst paste rheological behavior.

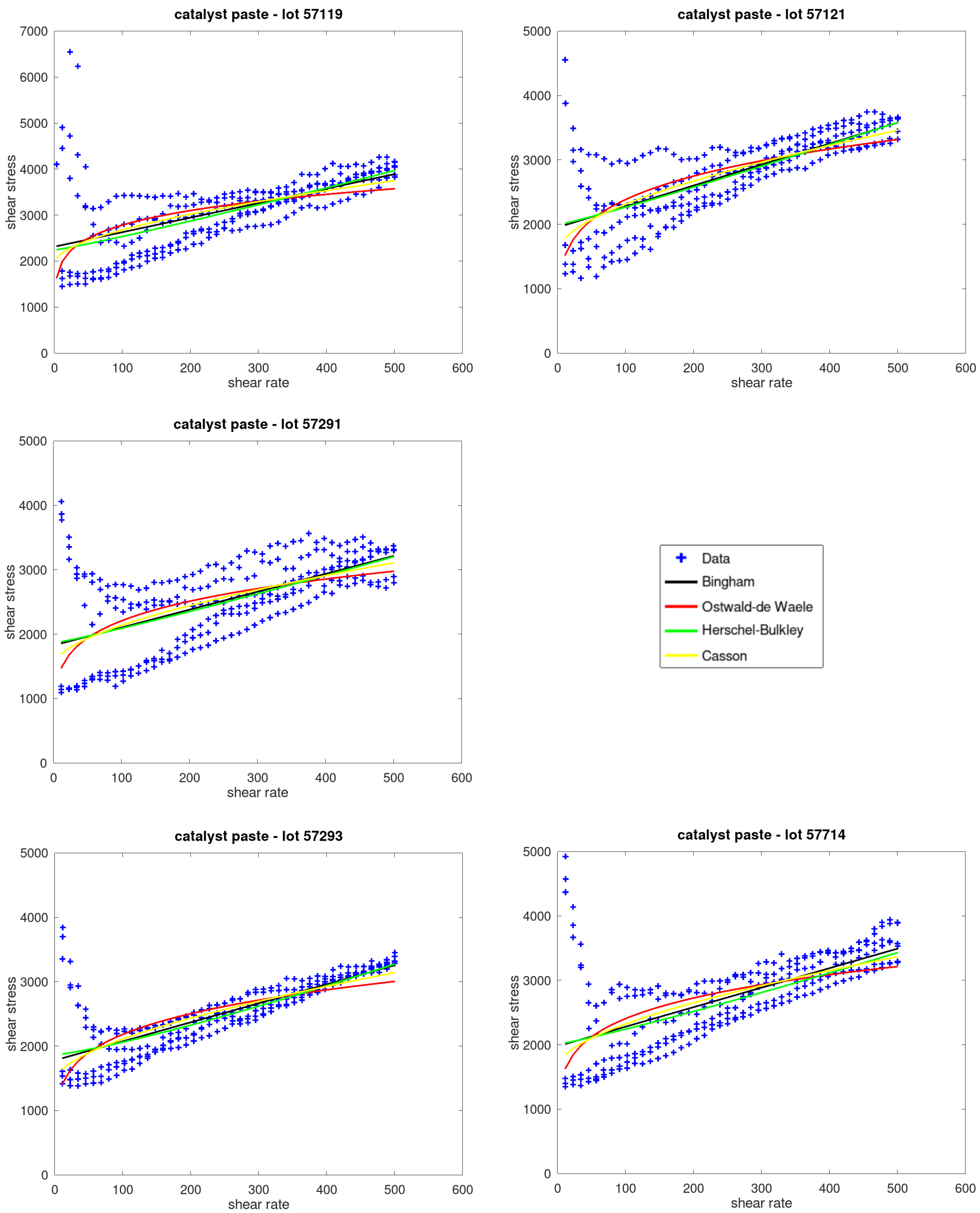


Figure 2. Flow curves for the catalyst paste lots.

## 4 Conclusions

We conclude that the Levenberg-Marquardt algorithm was capable of fitting rheological curves to experimental data measured by the Brookfield RST-CPS rheometer. Moreover, supported by statistical calculations, the fluidity of the base paste can be better characterized by the model $\tau = K\,\dot{\gamma}^n$ (Ostwald-de Waele), and the fluidity of the catalyst paste can be best represented by the model $\tau = \tau_o + K\,\dot{\gamma}^n$ (Herschel-Bulkley). Now, our next step in a future work will be to develop a general rheological law that models flow for all lots.

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