

# Rheological Measurements: Some Basic Yet Vital Considerations

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## SYNOPSIS

This article addresses a seemingly trivial question—"Based on rheological measurements, when are two samples different beyond experimental error?"—and proceeds to give a non-trivial answer. The preferred answer requires the application of *t* statistics to multiple measurements on each sample. The larger the number of multiple measurements made, the lower is the uncertainty in conclusively discriminating between two samples. However, such multiple measurements on every sample are seldom feasible in real life and then it becomes necessary to resort to the use of *Z* statistics. A stepwise procedure for the application of both, *t* and *Z* statistics is given. Knowledge of the measurement precision is a prerequisite for scientifically answering this seemingly trivial question. Hence, the precision of capillary rheometry measurements (apparent viscosity, extrudate swell ratio, and entrance pressure loss) is discussed in detail. The precision of these capillary rheometry measurements improves as the magnitude of the variable measured (force/pressure or swell) increases. This implies that the precision of capillary rheometry measurements can be improved by lowering the experimental temperature. Extensive numerical data on various high-density polyethylenes generated using two different capillary rheometers are given and are compared with the ASTM round-robin data. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

This article is the part of a series<sup>1-4</sup> exploring various issues related to the accuracy and precision of rheological measurements and how they affect data interpretation. The first two articles<sup>1,2</sup> discussed the application of statistical process control (SPC) to rheological measurements. The other two articles<sup>3,4</sup> examined in detail the precision of the magnitude of the complex viscosity measurement made using a dynamic oscillatory rheometer, both in the constant stress and constant strain modes. The within-sample variation (or variation due to causes inherent in the rheometer, such as random noise in torque or angular position transducer) and between-sample variation (or systematic variation between samples due to operator variability during sample preparation, loading, etc.) were determined separately for poly(dimethyl siloxane) (PDMS) and high density

polyethylene (HDPE). To do this for HDPE, rather than the traditional standard deviation (SD), a different statistical parameter called moving range average had to be used.

## EXPERIMENTAL

### Materials

All measurements were made at 190°C on HDPE monitor resins specially prepared and blended to make them as uniform and homogeneous as possible. The details of the resins are given in Table I.

### Equipment

The Instron Capillary Rheometer Model 3211 used has a 2000-kg load cell and was set at 50% of full span. The load cell at 50% full span was calibrated according to ASTM E 4-94 in compression to within a tolerance of  $\pm 0.5\%$  using verification equipment traceable to NIST standards (per ASTM E 74-91).

**Table I** Details of HDPE Resins and Number of Measurements

	90A	K46	88B	A60	91C
MI (2.16 kg), g/10 min	7.3		2.0	0.65	
MI (5 kg), g/10 min	21.4	0.15	6.4	3.3	0.5
MI (10 kg), g/10 min	52	0.95	17	10.7	1.9
MI (21.6 kg), g/10 min	186	4.2	69	93	11.4
Density (kg/m <sup>3</sup> )	961.8	946.0	953.7	961.0	943.6
$M_n$ (g/mol)	20200	18600	24700	22200	20300
$M_w$ (g/mol)	74500	176600	105800	113500	191600
$M_z$ (g/mol)	200300	763800	324700	482700	775500
$M_w/M_n$	3.68	9.49	4.29	5.11	9.45
No. repeat meas. on					
Instron	31		32	52	
Vimeg	47	31	27	56	62

MI, melt index. The load value is given in parentheses. Units of melt index are g/10 min.

Further details of calibration are given in the SPC papers.<sup>1,2</sup> Details of operation of the rheometer are given in the rheometer manual.<sup>5</sup> The die used had a diameter of 0.767 mm, length of 25.5 mm, and an entrance angle of 90°.

The other capillary rheometer used was the Scientific Vimeg. The die used for all Scientific Vimeg measurements (except on resin K46) had a diameter of 1 mm, length of 15 mm, and entrance angle of 180°. For resin K46 only, an orifice die was used to determine the entrance pressure loss. The use of an orifice die was explained by Laun and Schuch.<sup>6</sup> Both the capillary rheometers are kept under statistical control.<sup>1,2</sup>

## RESULTS AND DISCUSSION

The magnitude of the SD usually increases as the magnitude of the variable measured (viscosity) increases. For shear-thinning fluids, this happens as the shear rate (or shear stress) decreases. The relative standard deviation or RSD is defined as

$$\text{RSD} = 100 * (\text{standard deviation}) / (\text{average}). \quad (1)$$

Rather than the SD itself, the RSD is a more appropriate parameter to use when comparing data measured at different shear rates (or shear stresses). This is because, in the RSD calculation, the SD is normalized by the average of the magnitude of the variable measured.

The precision of melt index measurements can be obtained from the ASTM melt index round-robin data.<sup>7</sup> RSD generally decreases as the melt index value increases. Hence, fractional melt-index mea-

surements are inherently prone to greater experimental error. For polyolefins, RSD of melt index typically ranges between 1 and 4% for within-lab RSD and between 3 and 12% for between-lab RSD.<sup>7</sup>

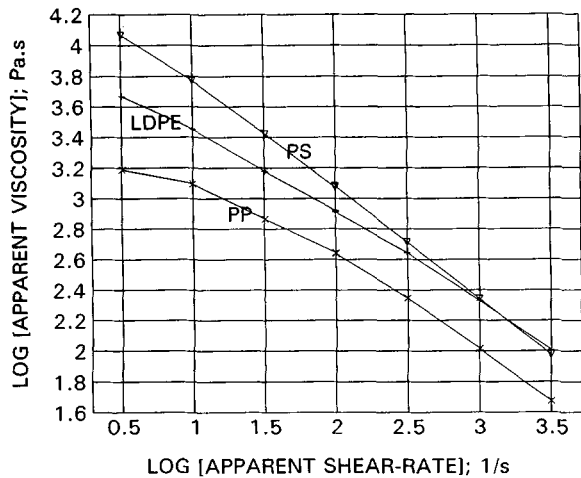
As mentioned earlier, the precision of the complex viscosity measurement has already been discussed by Bafna and Ford,<sup>3,4</sup> and hence that discussion is not repeated here. The precision of the complex viscosity measurement in the constant strain mode can be found in the literature.<sup>8-11</sup>

### Capillary Rheometry

The precision of capillary rheometry measurements is discussed in detail below.

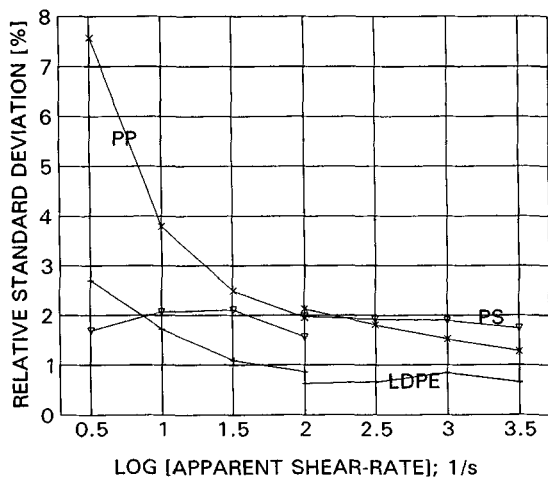
### Apparent Viscosity

The ASTM round-robin<sup>12</sup> involving 13 laboratories using polystyrene (PS), low density polyethylene (LDPE), and polypropylene (PP), provides preliminary indications of the behavior of the precision of the apparent viscosity measurement using capillary rheometry. The test was run starting with the highest apparent shear rate and going down progressively to the lowest one. At the end of this test, the measurement at the apparent shear rate of 100 s<sup>-1</sup> was repeated. Both the measurements at 100 s<sup>-1</sup> are shown in Figures 1 and 2. These two measurements, although made in the same run at the same shear rate and on the same material, did not give exactly the same numerical value for either the apparent viscosity or for the RSD. This could be due to a number of reasons like time effects on viscosity (due to resin degradation, crosslinking, etc.) and barrel pressure drop effect (if a plunger force sensor



**Figure 1** The shear-thinning behavior of ASTM round-robin<sup>12</sup> resins: PS, LDPE, and PP.

is used). The results of the ASTM round-robin<sup>12</sup> show that the variation in the apparent viscosity measurement increased significantly as the apparent shear rate (or equivalently, the shear stress) was reduced. Over the apparent shear rate ranges of 30–3000 s<sup>-1</sup>, the interlab RSD was less than 9% while the within-lab RSD was less than 2.5%. RSD rose significantly at lower apparent shear rates. Figure 1 shows the shear-thinning behavior of the three resins used in the round-robin and Figure 2 shows the respective within-lab RSD values. However, these data do not provide a systematic understanding of the effect of different grades of a resin (e.g., the effect of varying the molecular weight or the

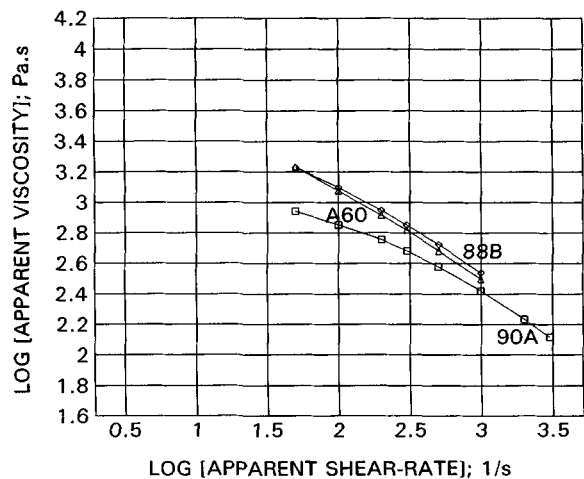


**Figure 2** The within lab relative standard deviation of the apparent viscosity of the ASTM round-robin<sup>12</sup> resins as a function of the apparent shear rate.

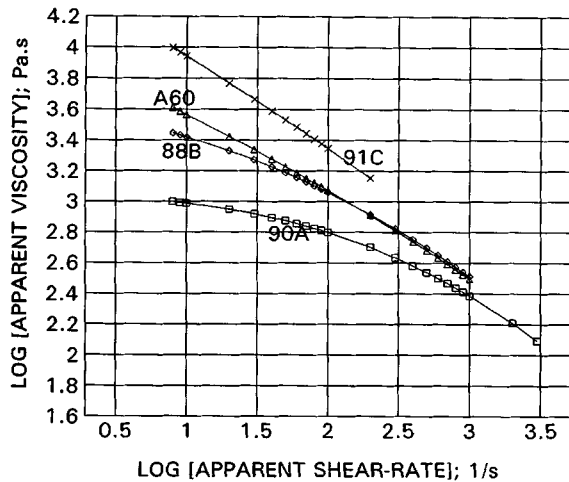
molecular weight distribution) on the precision behavior and also do not separate out the effect of different rheometers. It should also be noted that, to calculate the within-lab RSD of the apparent viscosity, the ASTM round-robin pools together data from different laboratories measured on different rheometers and most importantly, using different dies. It is therefore emphasized that the ASTM round-robin RSD cannot be directly compared with the HDPE RSD reported here (because the manner in which the measurements were made and how the calculations were done are not exactly identical). However, for the sake of completeness and comparison, ASTM data are also discussed here and are shown in Figures 1 and 2. Typically each of the 13 labs participating in the round-robin ran only three repeats per material. The number of measurements used in the calculation can affect the value of the average and SD obtained. This issue is discussed in detail in the SPC article.<sup>2</sup>

Figures 3 and 4 show the shear-thinning behavior of the various HDPE resins tested using, respectively, the Instron and Vimeg Capillary Rheometers. The number of repeat measurements made on each of the HDPE resins discussed here is listed in Table I for both the capillary rheometers. Because different dies were used in the Instron and Vimeg, the apparent viscosity values from the Instron (Fig. 3) are slightly higher than those from the Vimeg (Fig. 4). Figures 5 and 6 show the corresponding RSD values. RSD for measurements at comparable apparent shear rates made with the Instron are, in general, higher than those made with the Vimeg.

In agreement with the general trend seen from

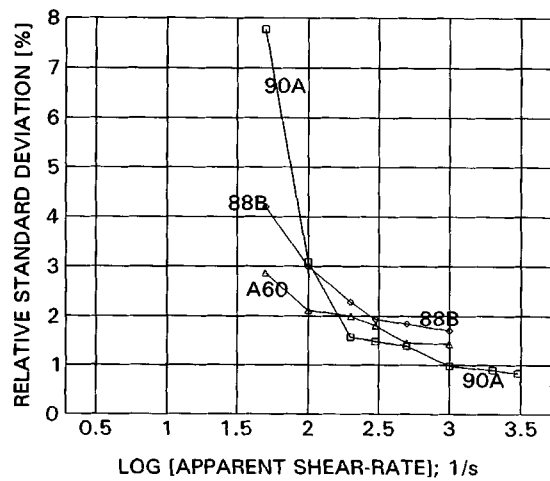


**Figure 3** The shear-thinning behavior of HDPE resins measured using the Instron.

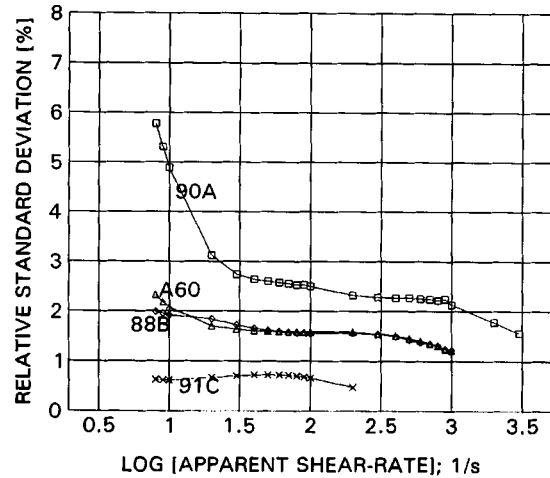


**Figure 4** The shear-thinning behavior of HDPE resins measured using the Vimeg.

the ASTM round-robin data, RSD for the HDPE resins rises at lower apparent shear rates. It is important to understand the implications of this trend. Low shear-rate data are sometimes extrapolated to determine the zero-shear viscosity (which is known to correlate with the molecular weight). Such an extrapolation will amplify the noise already present in the low shear-rate data and consequently the zero-shear viscosity calculated will have a wide confidence interval. It is more desirable to use dynamic oscillatory data measured in the constant stress mode for such extrapolation because in that case, the precision improves as the frequency is decreased. However, this trend is reversed if dynamic oscillatory



**Figure 5** The relative standard deviation of the apparent viscosity of HDPE resins measured using the Instron as a function of the apparent shear rate.



**Figure 6** The relative standard deviation of the apparent viscosity of HDPE resins measured using the Vimeg as a function of the apparent shear rate.

data measured in the constant strain mode are used for such extrapolation. This issue is discussed in detail in the articles<sup>3,4</sup> dealing with the precision of dynamic oscillatory measurements.

The exact onset of the rise in RSD with drop in apparent shear rate depends upon the resin and the experimental conditions (die, rheometer, etc.). The reason for the rise in RSD with a decrease in apparent shear rate for rheometers that use a plunger force sensor (e.g., load cell) and/or a pressure transducer is that, as the apparent shear rate decreases, the magnitude of the force/pressure measured generally decreases as well and gets further away from the full-span value. This worsens the precision because the signal to noise ratio is less favorable now.

A similar decrease in the magnitude of the force and/or pressure measured is also obtained when a less viscous resin is used. For the ASTM round-robin, PP has the lowest apparent viscosity (Fig. 1), and hence the highest RSD at lower apparent shear rates (Fig. 2). The apparent viscosity value for LDPE is lower than that for PS at the lower apparent shear rates, but because LDPE is more shear thinning this trend is reversed at apparent shear rates greater than 1000 s<sup>-1</sup>. However, ASTM data show that PS has higher RSD than LDPE. This is contrary to what would be expected and may be due to differences in resin stability with time and/or due to the manner in which the within-lab SD is calculated (by pooling data from 13 different labs).

Figures 3 and 4 show 90A has the lowest viscosity and Figures 5 and 6 show it has the highest RSD (except at the highest shear rates for the Instron

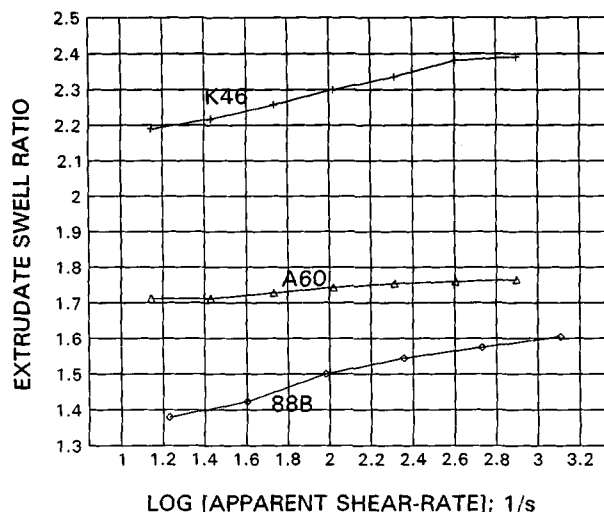
only). A60 has higher apparent viscosity values than 88B at lower apparent shear rates. Because A60 is more shear thinning (Table I), this trend is reversed above apparent shear rates of about  $100 \text{ s}^{-1}$ . However, the magnitude of the apparent viscosity at the higher apparent shear rates is quite similar for A60 and 88B. There is little difference in their RSD as measured on the Vimeg, but 88B has higher RSD than A60 on the Instron.

91C is the most viscous HDPE studied and, on the 15/1 die, goes into oscillating flow above  $200 \text{ s}^{-1}$  (hence data above  $200 \text{ s}^{-1}$  are not available). 91C exhibits the lowest RSD. The RSD of 91C is almost constant in the shear-rate range studied. A similar behavior is also seen for PS in Figure 2. Again, this is consistent with the fact that PS has the highest viscosity of the three ASTM round-robin resins (Fig. 1). This is a significant finding because it implies that precision can be improved by increasing the viscosity without making any other changes in the measurement system (rheometer, operator, etc.). An increase in viscosity can be accomplished by simply lowering the experimental temperature. Hence, for distinguishing between similar but not identical resins, it is desirable to make measurements at the lowest possible temperature. Of course, sometimes data at a specific temperature are required, in which case such a strategy cannot be used. In that case, use of a narrower and longer die may be desirable for apparent viscosity measurements, because that will increase the magnitude of the force/pressure generated. Both the 91C (Fig. 6) and the ASTM PS (Fig. 2) data seem to imply that for measurements on a certain resin using a given measurement system (rheometer, die, operator, experimental conditions, etc.), there is a limiting value below which the RSD cannot be improved.

### Extrudate Swell Ratio (ESR)

The ESR values shown in Figure 7 were measured using the Scientific Vimeg. Figures 7 and 8 give the ESR and the corresponding RSD values, respectively. RSD for A60 and 88B on the 15/1 die falls as the apparent shear rate increases; this is because the magnitude of the ESR increases with apparent shear rate. Because A60 has a broader molecular weight distribution or MWD (Table I) and is more shear thinning than 88B (Fig. 4), it has greater ESR. Because the magnitude of ESR for A60 is greater than that for 88B, A60 has better precision (or lower RSD).

The magnitude of ESR for K46 is much greater because the die used is an orifice die. This large swell

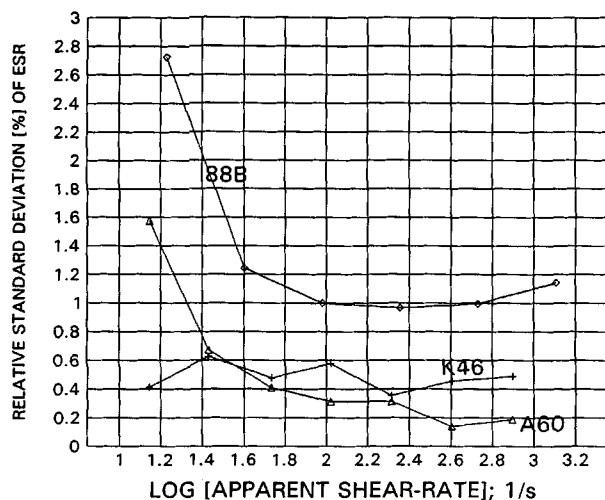


**Figure 7** The extrudate swell ratio of HDPE resins measured using the Vimeg as a function of the apparent shear rate.

ratio is a manifestation of the molecular orientation that is generated by the flow into the die. At the inlet from a large reservoir, streamlines converge rapidly, and this generates a high degree of stretching along streamlines. In an orifice die, this leads to a large swell at the exit, where the melt is free to deform in response to the anisotropic stresses associated with the molecular orientation.<sup>13</sup> However, if the entrance leads to a capillary, relaxation will lead to a loss of the orientation generated at the entrance, and as the capillary is lengthened the degree of swell is reduced.<sup>14</sup> RSD for the ESR of K46 is almost independent of apparent shear rate even though the ESR itself does increase with apparent shear rate; this may be due to the fact that the magnitude of ESR for K46 is high even at the lowest apparent shear rate measured. As with the behavior of RSD of the apparent viscosity of PS (Fig. 2) and 91C (Fig. 6), the RSD behavior of ESR of K46 seems to indicate that there may be a limiting plateau beyond which precision cannot be improved (for a specific resin with a certain measurement system).

### Entrance Pressure Loss

The pressure drop using the orifice die is reported in the literature as coinciding nicely with the end correction from Bagley plots.<sup>6</sup> The magnitude of the pressure drop using an orifice die for K46 resin is shown in Figure 9 and the corresponding RSD is shown in Figure 10.  $3\text{-}\sigma$  error bars are also shown in Figure 9. The use of  $3\text{-}\sigma$  error bars is explained in the SPC paper.<sup>2</sup> Figure 10 shows that RSD improves substantially when the shear rate increases

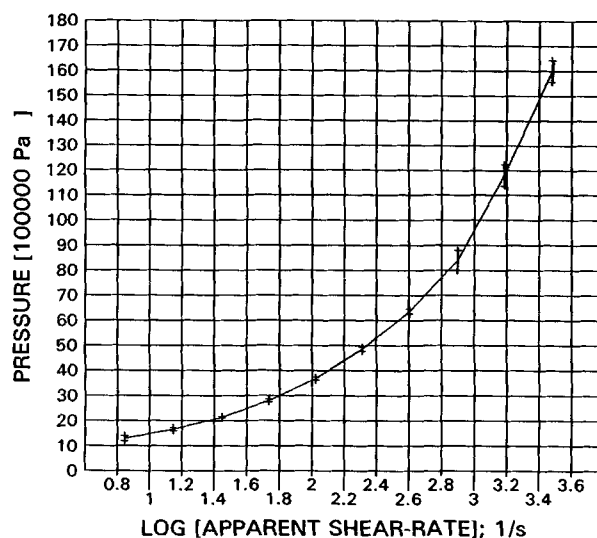


**Figure 8** The relative standard deviation of the extrudate swell ratio of HDPE resins measured using the Vimeg as a function of the apparent shear rate.

from 7 to 28  $s^{-1}$  and then levels out. However, it rises sharply at 791  $s^{-1}$ . This may be due to some form of the "slip-stick" phenomenon. Because the consequent variation in pressure is small (the length of the orifice die is minimal), oscillating flow would not have been detected without the help of Figure 10. The fact that the extrudate becomes somewhat rough at 791  $s^{-1}$  tends to support this interpretation. Gross melt fracture was observed at the highest apparent shear rate of 3023  $s^{-1}$ .

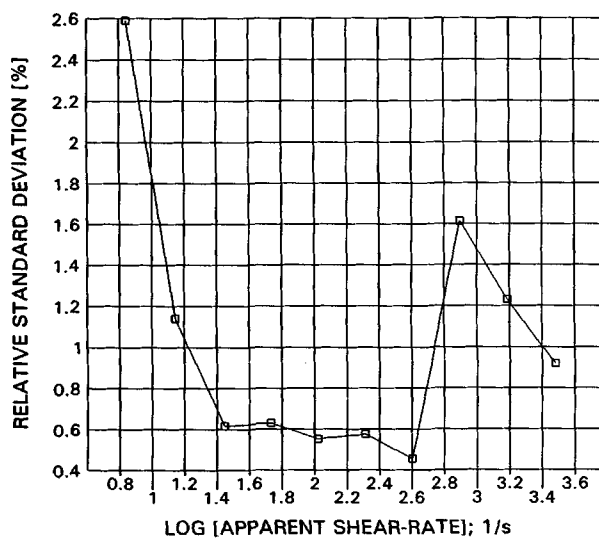
### DISCRIMINATING BETWEEN MEASUREMENTS BEYOND EXPERIMENTAL ERROR

We now turn to the original question of deciding how, based on a certain measurement  $m$ , to discriminate between two samples (A and B) beyond experimental error. The assumption in the analysis given below is that the data distribution is normal. Data that do not follow a normal distribution require more sophisticated statistical treatment than can be discussed here. First the case where multiple measurements on both samples A and B are available is addressed. Let the number of measurements made on samples A and B be  $n_A$  and  $n_B$ , respectively. Hence, the corresponding degrees of freedom are  $f_A = n_A - 1$  and  $f_B = n_B - 1$ . Let the averages of these multiple measurements on A and B be  $m_A$  and  $m_B$ , respectively, and the corresponding standard deviations be  $s_A$  and  $s_B$ . In the case of multiple measurements, there are two possibilities:



**Figure 9** The pressure drop of K46 resin across an orifice die measured using the Vimeg as a function of the apparent shear rate.

1. *Case 1:* There is no reason to believe that the SDs differ, e.g., same method, operator, experimental conditions, equipment, etc. are used to make measurements on both A and B.
2. *Case 2:* There is reason to believe that the SDs differ, e.g., different method and/or different operator and/or different experimental conditions and/or different equipment, etc. are used to make measurements on A and B.



**Figure 10** The relative standard deviation of the pressure drop of K46 resin across an orifice die measured using the Vimeg as a function of the apparent shear rate.

Listed below is the procedure to be used in each case for determining whether A and B can be discriminated between beyond experimental error.<sup>15,16</sup>

### Case 1

*Step 1:* Choose the confidence level (typically 95% confidence level).

*Step 2:* Calculate a pooled SD,  $sp$ .

$$sp = [(f_A * s_A * s_A + f_B * s_B * s_B) / (f_A + f_B)]^{0.5}. \quad (2)$$

*Step 3:* Calculate the uncertainty,  $U$

$$U = t * sp * [(n_A + n_B) / (n_A * n_B)]^{0.5} \quad (3)$$

where  $t$  is the numerical value of the  $t$  statistic based on  $(f_A + f_B)$  degrees of freedom. Selected values of the  $t$  statistic as a function of the degree of freedom and confidence level are listed in Table II and complete listings are available in any standard statistics reference.<sup>15-17</sup> As the number of measurements (or equivalently, the degrees of freedom) increase, the value of the  $t$  statistic decreases and hence, the uncertainty,  $U$ , decreases as well.

*Step 4:* Compare  $\Delta$  = absolute value of  $(m_A - m_B)$  with  $U$ . If  $\Delta$  is greater than  $U$ , then one can distinguish between A and B beyond experimental error based on the measurement  $m$ .

To illustrate the above procedure, let us consider an example of two A60-type samples, A and B. The apparent viscosities of samples A and B (at an apparent shear rate of  $100 \text{ s}^{-1}$ ) were measured five and three times, respectively, on the Scientific Vimeg to obtain an average value of  $m_A = 1160 \text{ Pa s}$  for A and  $m_B = 1205 \text{ Pa s}$  for B. Hence, the corresponding degrees of freedom  $f_A$  and  $f_B$  are 4 and 2, respectively, and  $\Delta = 45 \text{ Pa s}$ . From the multiple measurements, the SDs for A and B were calculated to be  $s_A = 18 \text{ Pa s}$  and  $s_B = 21 \text{ Pa s}$ .

*Step 1:* Choose 95% confidence level.

*Step 2:*  $sp = 19 \text{ Pa s}$ .

*Step 3:*  $t = 2.447$  (corresponding to  $f_A + f_B = 6$  from Table II) and hence,  $U = 34 \text{ Pa s}$ .

*Step 4:*  $\Delta = 45 \text{ Pa s}$ . Because  $\Delta$  is greater than the uncertainty,  $U$ , it is possible, at the 95% confidence level, to discriminate conclusively between A and B beyond experimental error.

### Case 2

*Step 1:* Choose the confidence level (typically 95% confidence level).

**Table II Numerical Values of the  $t$  Statistic**

Degrees of Freedom ( $f$ )	Confidence Level	
	95%	99%
1	12.706	63.657
2	4.303	9.925
3	3.182	5.841
4	2.776	4.604
6	2.447	3.707
8	2.306	3.355
10	2.228	3.169
20	2.086	2.845
30	2.042	2.750
Infinity	1.960	2.576

*Step 2:* Compute the estimated variances,  $v_A$  and  $v_B$ .

$$v_A = s_A * s_A / n_A, \quad (4)$$

$$v_B = s_B * s_B / n_B. \quad (5)$$

*Step 3:* Compute the effective number of degrees of freedom,  $f^*$ .

$$f^* = \{(v_A + v_B)^2 / [ [(v_A)^2 / (n_A - 1)] + [(v_B)^2 / (n_B - 1)] ]\}. \quad (6)$$

*Step 4:* Compute the uncertainty,  $U$ .

$$U = (t') * [v_A + v_B]^{0.5} \quad (7)$$

where  $t'$  is the numerical value of the  $t$  statistic based on  $f^*$  degrees of freedom.

*Step 5:* Compare  $\Delta$  with  $U$ . If  $\Delta > U$ , then one can distinguish between A and B beyond experimental error based on measurement  $m$ .

The previous example of A and B will now be considered for case 2.

*Step 1:* Choose 95% confidence level.

*Step 2:*  $v_A = 65$ ,  $v_B = 147$ .

*Step 3:*  $f^* = 4$ .

*Step 4:*  $t' = 2.776$  from Table II and hence,  $U = 40 \text{ Pa s}$ .

*Step 5:* Because  $\Delta = 45 \text{ Pa s}$  is greater than the uncertainty  $U$ , it is again possible at the 95% confidence level to discriminate between A and B beyond experimental error.

As expected, using the same data, the uncertainty,  $U$ , for case 2 is greater than that for case 1.

### Single Measurement

The multiple measurements on each sample required to use the strategy given above for cases 1 and 2 are seldom feasible in real life. In a typical lab, usually only one measurement is made on each sample. In this case, the uncertainty,  $U$ , can be estimated from the following formula

$$U = 1.414 * Z * s \quad (8)$$

where  $s$  is the known SD of a sample most similar to the one tested and  $Z$  is the value of the  $Z$  statistic.<sup>15-17</sup> The values of  $Z$  are 1.96, 2.58, and 3.29 for, respectively, 95, 99, and 99.9% confidence levels.

As an illustration, let 1160 and 1205 Pa s now be the apparent viscosity values obtained from a single measurement each on A and B, respectively. Thus  $\Delta$  is still 45 Pa s (same as previously). Because A and B are known to be A60-type resins,  $s$  can be estimated to be 19 Pa s (based on Figs. 4 and 6). Using Eq. (8), the uncertainty,  $U$ , is calculated to be 53 Pa s. Note that now the uncertainty is greater than the magnitude of the difference between the measurements, and A and B can no longer be distinguished beyond experimental error (at a 95% confidence level). This is the penalty to be paid due to the fact that the SD cannot be calculated (as multiple measurements are not made), and hence the best estimate available for the SD had to be used.

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