

The Application of Statistical Process Control to Rheological Measurements

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SYNOPSIS

This article presents data on and discusses the application of statistical process control (SPC) to rheological measurements. With the help of case studies on capillary rheometry and dynamic oscillation, it is shown how SPC, coupled with careful calibration and maintenance of rheometers, can demonstrate significant improvement in the accuracy and precision of rheological measurements. This improvement is evident on examination of the various control charts discussed and the narrowing of their control limits. Specifically, individual and moving range control charts for the apparent viscosity measured at an apparent shear rate of 100 s^{-1} using capillary rheometers are discussed. For the dynamic oscillatory rheometer, the charts presented are for the magnitude of the complex viscosity measured at a frequency of 1 Hz. This article shows how SPC provides quality assurance by assuring that erroneous data will not be inadvertently reported. The issues discussed are of universal interest and relevance, not only to rheologists, but to all scientists and engineers who make and/or use measurements. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Statistical process control (SPC) is the application of statistical techniques for measuring and analyzing the variation in processes affecting product quality.¹ The "product" the rheologist produces is the rheological measurements he provides and, to improve quality, the values he supplies must be accurate and reproducible. Although the application of SPC to production and manufacturing processes is widely appreciated and understood, the aim of this article is to demonstrate that the application of SPC to rheological measurements in the laboratory is just as relevant and important.

The general advantages and importance of SPC are well known and documented.¹⁻⁵ However, an SPC tool like the control chart cannot, by itself, improve a measurement system; it can only monitor. With the help of case studies, this article demon-

strates how the proper use of control charts, coupled with careful calibration and maintenance of rheometers, can demonstrate significant improvement in the accuracy and precision of rheological measurements. This is also of interest with the overwhelming acceptance of ISO-9000 quality standards in the chemical and plastics industry. Though ISO does not specifically require SPC, it does require a determination that the "measuring and test equipment . . . is capable of the necessary accuracy and precision."⁶ SPC is an excellent way of making and continually assuring this determination.

The ideal measurement system would produce "correct" measurements (i.e., measurements that agree exactly with a master standard) every time it is used. Such a measurement system would have the statistical properties of zero bias and zero variance. In addition, the measurement system would always be stable with time. Unfortunately, rheological measurement systems with such desirable properties do not exist, and so the rheologist is left to wrestle with the problem of dealing with measurements that have less desirable statistical properties.

One obvious requirement is that the measurement variability should be less (preferably a tenth or less) than the variability of the process being measured.

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However, this is not always the case. More often than not, though, this issue is entirely ignored, and frequently analysis and conclusions are based on the entirely incorrect assumption that the measurements are exact. The rheologist (or any other scientist) must realize that there is inherent variation in any measurement system that affects the individual measurements, and consequently, the conclusions based upon that data. It is important to know if an apparent production problem is truly due to the producing system or merely an artifact of the measurements.

It is customary to purposely manufacture a product to tighter than required specifications in order to allow for testing errors. The larger these testing errors, the greater the excess quality that must be built into the product to ensure the acceptance of nearly all lots that are in fact equal to or better than the specification. Considerable savings in manufacturing costs can be effected by reducing the margin between the quality level set for production and that called for in the specification. The savings attainable with improved test procedures are a strong inducement for the improvement of measurement procedures.⁷

BACKGROUND

Shewhart first made the distinction between controlled and uncontrolled variation, due to what is now called common and special causes.⁸ Common causes refer to the many sources of variation within a process that have a stable and repeatable distribution over time. This controlled variation can be attributed to change causes inherent (or “common”) to the system. An example of common cause can be random noise in a force or torque transducer. Special causes refer to any factors causing variation that are not always acting on the process. That is, when they occur, they make the (overall) process distribution change. This uncontrolled variation can be attributed to assignable causes that are not inherent. Unless all the special causes of variation are identified and acted upon, they will continue to affect the process output in unpredictable ways. An example of a special cause is a burnt-out heater band. Simple SPC techniques can detect special causes of variation and are also sensitive to changes in common causes. Statistical tools are useful for identification and elimination of special causes and then for monitoring reduction of common causes of the process variability.

Shewhart⁸ developed a simple but powerful tool (“the control chart”) to separate the above two types of causes. A run chart is simply a plot of any variable of interest (e.g., viscosity) with time (or equivalently, with the number of measurement). A run chart that has statistically determined control limits placed on it is a control chart. Accurate control limits can be calculated only from data obtained when the process is in “statistical control.” Statistical control means that the distribution of data can be attributed to a constant, stable system of chance causes.⁹ Feigenbaum defines control charts as “a graphical method for evaluating whether a process is or is not in a state of statistical control.”⁵

Control charts effectively direct attention toward special causes of variation when they appear and reflect the extent of common cause variation that must be reduced by system improvement. Variable charts explain process data in terms of both its location (process average) and its spread (measurement-to-measurement variability). Because of this, control charts for variables should always be prepared and analyzed in pairs: one chart for location and another for spread. These give information on the accuracy and precision of the measurements, respectively. The advantage of control charting a rheometer by running a monitor on a regular basis is that any “special causes” or system changes (like a burnt-out heater band, dirty die, etc.) are easily and routinely detected, thereby assuring that erroneous data will never be inadvertently reported.

Control charts are effective tools that lend themselves to being maintained at the job station by the technician. They give the people closest to the operation reliable information on when action should be taken and, more importantly, when action should *not* be taken (to avoid overcontrol). Overcontrol is the practice of treating each deviation from the target as if it were the result of the action of a special cause of variation in the process.¹⁰ If a stable process is adjusted on the basis of each measurement made, then the adjustment itself becomes an additional source of variation. One of the most common and least appreciated mistakes is “tweaking” the calibration parameters (like torque in oscillatory rheometers) too often. This is done because of a failure to understand that some level of common variation is inherent to any process, and the process has not necessarily shifted just because the latest measurement is not exactly identical to the nominal value. Instead, attempts are made to adjust the process “back” to the nominal based on the output value of the measurement just completed. Each such adjustment changes the process level, which results in sig-

nificantly greater variation for the process as a whole.

Various decisions need to be made while setting up control charts. To a large degree, these are subjective and dependent upon the specific needs attempted to be addressed, availability of resources, and a balancing of the costs and benefits of increasing rigor. Some guidelines on various issues as applied to rheological measurements are suggested below.

Monitor Material

Any homogeneous sample will generally suffice as the monitor material. The sample should be blended as thoroughly as possible for uniformity and should have been produced when the production process was operating smoothly (no reactor upsets, etc.). Use of a sample similar to the one most frequently tested would be advisable.

Variables to Monitor

In view of the effort and expense required to establish and maintain a control chart, only the most important system variables can be chosen. If the viscosity (or other rheological variable) at a specific shear rate/frequency is of particular interest, then the choice is simple. However, this choice is not always so obvious. In such a case, a reasonable choice can be viscosity values at the highest and lowest shear rates/frequencies and preferably, also one at the midpoint of the logarithm of the shear rate/frequency range. Depending on the particular situation and lab, it may be more appropriate to choose the apparent or corrected viscosity as the variable to monitor. The apparent viscosity will generally suffice if the objective is to assure relative consistency in rheometer performance. If the corrected viscosity is chosen then the computational procedure will be important and corrections for shear heating, pressure effects, pressure loss in barrel, etc., may also be necessary.¹¹ For capillary rheometry, measurements from higher to lower rates (or stress) are recommended¹² to reduce the time necessary to achieve steady state and at least one measurement should be repeated in the same run. For oscillatory measurements, duplicate measurements are recommended.¹³

Frequency of Monitor Measurement

This depends upon the process and resources available. For an R&D lab, a reasonable frequency could

range between once per day to once per week. For a QC lab, a higher frequency may be desirable. More detailed guidance is given by Taylor.¹⁴

Type of Control Chart

Simple Shewhart-type control charts⁸ will generally suffice for rheological measurements. Traditional Shewhart SPC application generally involves grouping individual measurements into subgroups (usually of 3–7 individual measurements) and plotting the average (“ x -bar”) of the subgroup instead of each individual measurement. However, x -bar charts require multiple measurements (the subgroup size) before any point can be plotted and action (if any required) can be taken. Rheological measurements (except perhaps for the melt index) are too time and labor consuming to be amenable to the repeat measurements required for subgrouping. In the experience of this author, individual charts are more suited for rheological measurements. The relative merits/demerits of the x -bar versus the individual charts are discussed in the literature.^{1,2,9} The individual chart (monitoring accuracy) is accompanied by a moving range chart (monitoring precision). Moving range is the magnitude or absolute value of the difference between consecutive measurements.

Calculation of Limits

It should be recognized that the values calculated for the average and standard deviation (and hence the control limits) depend upon the number of data points used in that calculation. The experimentally determined dependence of the average and standard deviation of the apparent viscosity on the number of measurements used in their calculation is shown in Figures 1 and 2, respectively. Statistically, it is desirable that the number of historical values used in calculating the limits be as large as possible so that the normal variation is known as accurately as possible. However, obvious practical considerations require that this number be kept to a reasonable minimum. The standard deviation, s , computed from a finite amount of historical data is an estimate of the true standard deviation, σ (which we would obtain if we had an infinite amount of data). Based on Student’s t -distribution,¹⁵ a minimum of 31 historical data points are suggested for calculating s . However, at times it may not be possible to gather 31 data points, in which case a fewer number of data points may need to be used. An estimate of the standard deviation based on just 10 observations may

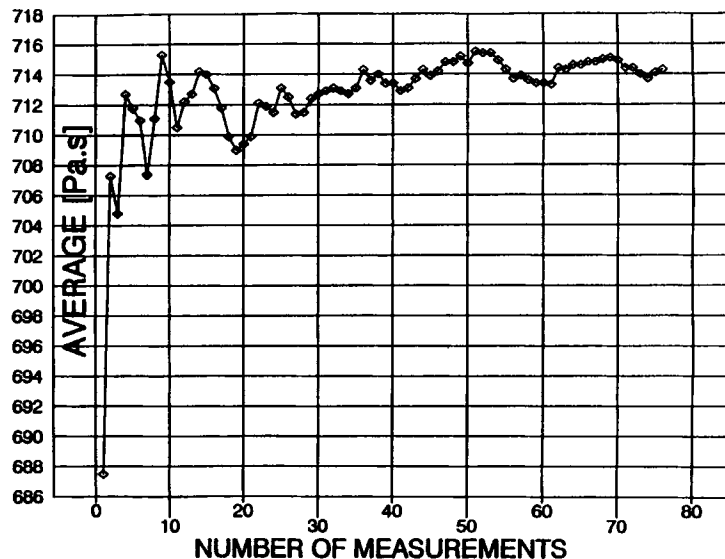


Figure 1 The dependence of the average of the apparent viscosity for HDPE monitor 90A at 190°C measured at an apparent shear rate of 100 s⁻¹ using the Instron Capillary Rheometer on the number of measurements.

deviate from σ by a factor of 0.7–1.7. Estimates of σ based on fewer than 10 observations can be misleading and must be used with caution. An estimate based on just five observations may deviate from true standard deviation by a factor of 0.5–2.¹⁴

It is advisable to recalculate the limits after a large number of data points have been gathered. The control limits define the bounds of the normal variation in the process and the more accurately these

limits are determined, the better the discrimination between normal variation and “special cause” will be. The presumption in the above discussion is that the data follow a normal distribution and should be tested by appropriate statistical tests (constructing a histogram, normal probability plot, etc.). Data that do not follow a normal distribution require more sophisticated statistical treatment than can be discussed here.

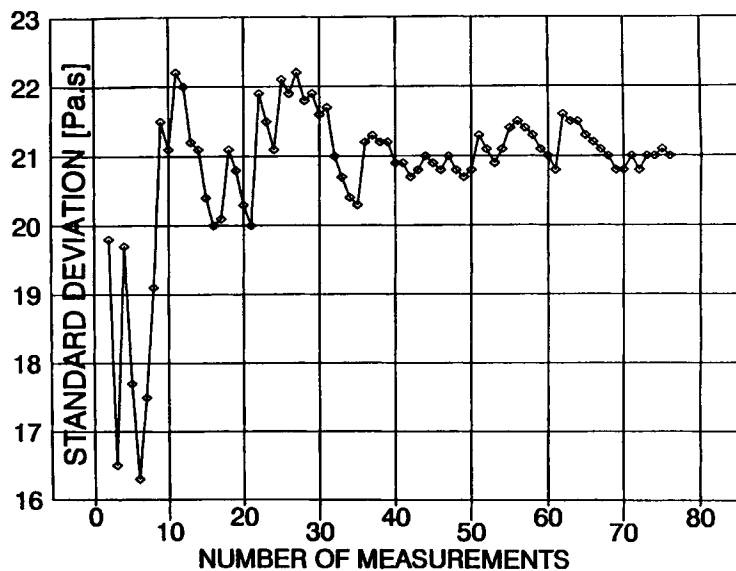


Figure 2 The dependence of the standard deviation of the apparent viscosity for HDPE monitor 90A at 190°C measured at an apparent shear rate of 100 s⁻¹ using the Instron Capillary Rheometer on the number of measurements.

Placement of Limits

For the individual measurement (viscosity) control chart, the center line will be the average of a predetermined number of historical values and the control limits will be at a distance of 3σ from the center line. Certain statisticians^{2,5} consider it desirable to use " 2σ " limits for individual control charts. This is recommended when, with points occurring rather far apart in time, a greater risk of looking for an assignable cause when none is present can be afforded. This will give less risk of failing to look for an assignable cause when one is present; but, on the other hand, it will also increase the risk of incorrectly considering a normal variation as an assignable or special cause. Experience indicates though that, in most cases, 3σ limits strike a satisfactory economic balance between these two types of errors.⁴ This ensures that, for measurements that follow a normal distribution, only 0.3% of the values will be outside the control limits when the process is in control.

For control charts, s is traditionally estimated by dividing the moving range average by 1.13 (instead of using the standard definition).^{14,16} The moving range average (mr-bar) is simply the average of all the moving range values. For the moving range chart, the upper control limit (UCL) is 3.27 times mr-bar and the lower control limit (LCL) is zero (which reflects the situation when consecutive measurements are exactly identical).^{14,16}

Determination of Special Cause

The most common feature of a process showing stability is the absence of any recognizable patterns. Based on various references,^{2,4,17,18} violation of at least one of the following six rules in the individual chart is suggested as the criteria for determining when the process is out of control (i.e., special cause exists).

1. All points should lie between the upper and lower control limits.^{2,4,17,18}
2. Cyclical or recurring patterns should be absent.^{17,18} A violation of this rule implies the process distribution is not random.
3. All points should not lie too close (within $\pm 1.5\sigma$) of the center line. A violation of this rule does not mean that the process is out of control, but instead that the control limits, as calculated, are no longer applicable because either the process has changed (improved or become more precise), or simply that the initial control limit calculation was incorrect.¹⁷

4. No seven consecutive points should show a monotonically rising or falling trend.^{17,18} A trend may indicate a steady change (e.g., progressive buildup of polymeric film on the inner walls of a capillary die).
5. No seven (Burr² recommends about 10 instead of 7) consecutive points should lie on the same side of the center line.^{4,17} A violation of this rule indicates a change in the process average.
6. No 10 out of 11 (or 12 out of 14) consecutive points should lie on the same side of the center line.⁴ A violation of this rule also indicates a change in the process average.

Instead of rules 5 and 6, some statisticians prefer the "Western Electric Rules"¹⁹ (no two out of three consecutive points more than 2σ away from average and no four out of five consecutive points more than 1σ away from average).

For the moving range chart, only rule 1 above applies. A violation of rule 3 will result in all points lying close to LCL for the moving range chart. When the control chart indicates that the process is out of control, a corrective action plan should be initiated to investigate the origin of the special cause and appropriate action taken to eliminate it, thus bringing the process back in control. The exact nature of the corrective action plan depends upon the process. For example, for capillary rheometry, this can be systematic calibration/verification as discussed below.

EXPERIMENTAL

Rheometers

The two capillary rheometers discussed are an Instron Capillary Rheometer Model 3211 and a Vimeg Capillary Rheometer. The die used for the Instron had the following dimensions: length, $L = 25.5$ mm and diameter, $D = 0.767$ mm, with $L/D = 33.3$, and entrance angle = 90° . The die used for the Vimeg had the following dimensions: $L = 15$ mm and $D = 1$ mm, with $L/D = 15$, and entrance angle = 180° .

The oscillatory rheometer used is a Bohlin Controlled Stress Melt (CSM) Rheometer. The parallel plate mode was used to make the measurements, with a gap of 1 mm and a stress of 400 Pa. The sample was compression molded in the form of a cylindrical disk and checked against a bright light source to ensure that no air bubbles were present. These steps are essential to ensure that the melt

sample between the parallel plates will be uniformly homogeneous and free of any entrapped air bubbles (which would lead to errors on the low side). The direct use of pellets (instead of compression molded disks) to make measurements is discouraged because it increases the probability of having entrapped air bubbles in the melt sample.^{11,13,20}

Material

The high-density polyethylene (HDPE) monitor material (90A) used for the Instron Capillary Rheometer and Bohlin CSM Rheometer has a melt index (2.16 kg) of 7.3 and a density of 962 kg/m³. The HDPE monitor material (91C) used for the Vimeg Capillary Rheometer is more viscous and has a high load melt index (21.6 kg) of 11.4 and density of 944 kg/m³. Both monitors were specially prepared and blended to make the resin as homogeneous and uniform as possible. All measurements are made at 190°C.

Calibration/Verification

An important issue is how often calibration should be done, especially in light of the earlier discussion regarding overcontrol. If a measurement system is under statistical control, then calibration should be done only when it goes out of control (violation of any of the six rules listed above), when a system change occurs (e.g., a heater is replaced), or when a new system is being put in place. A distinction is made here between verification and calibration. Verification only means certain parameters (e.g., temperature) are measured to ensure that they are not outside permissible tolerances. Verification of nominal values (e.g., of temperature, etc.) may be done as often as desired because no changes are made to the measurement system (i.e., no dials are tweaked). Calibration means that changes are made that may affect the measured values.

The calibrations/verifications for capillary rheometers were done in accordance with ASTM 3835-93a.¹² These included calibrating/verifying the load cell, crosshead speed, temperature, and various instrument dimensions (piston diameter, piston land length and diameter, barrel diameter, and capillary orifice length and diameter). These dimensions are involved in the apparent viscosity and/or apparent shear-rate calculations. For example, the die orifice diameter should be verified by frequent checks with a "go/no-go" gauge.¹² This should be done when the die is initially at room temperature before installation, and not when the die is hot. The use of the

go/no-go gauge alerts the user whenever the die is dirty or a polymeric film is building up on the inside surface (which is probably the most common source of error). Because the apparent shear rate is inversely proportional to the cube of the capillary diameter, the percentage error in apparent shear-rate calculation is three times that in the capillary diameter (but in the opposite direction). Also, the wall shear stress is directly proportional to the capillary diameter. Hence, the percentage error in apparent viscosity measurement is four times that in the die orifice diameter.

The cross-head speed needs to be verified because the shear-rate calculation depends upon it. This was done by attaching a flag of known length to the crosshead. A 12.7-mm long flag was used for all speeds less than 0.19 mm/s, a 25.4-mm long flag was used for speeds between 0.19 and 0.64 mm/s, and a 50.8-mm long flag was used for all speeds above 0.64 mm/s. When the crosshead moves downward, the flag triggers a photoelectric switch on and then off, that in turn, turns a clock on and off (capable of measuring up to $\frac{1}{60}$ th of 1 s). The speed is then calculated by simply dividing the known flag length by the time taken by the crosshead to traverse that distance. Use of a more sophisticated apparatus (e.g., use of laser, more sophisticated electronics, etc.) may be desirable but was not available for use in this study. It may also be desirable to correct, if necessary, for any systematic errors due to diffraction of light around the edges of the flag by looking at the difference between the on-off and off-on transitions. A long flag will minimize the effect of such errors. Alternatively, the flag can be designed to give the difference between two on-off transitions (or vice versa) and thus have these errors cancel each other.

The temperature readout on the display of capillary rheometers is from a thermocouple attached to the metal barrel and the actual polymeric melt temperature could be different. Hence, it is important to periodically calibrate the temperature readout by measuring the actual temperature of the polymeric melt. Because the melt viscosity follows the exponential Arrhenius dependence on temperature, the error depends upon the temperature at which the measurement is made and also upon the sensitivity of the viscosity to temperature. For example, HDPE²¹ has an activation energy of about 27 kJ/mol and hence an error of 1% in temperature measurement at 190°C will lead to an error of 2.9% in viscosity calculation. Similarly, polypropylene²² has an activation energy of about 40 kJ/mol and

hence an error of 1% in temperature measurement at 230°C will lead to an error of 4.5% in viscosity calculation.

The calibration of the dynamic oscillatory rheometer was done in accordance with ASTM 4440-93 and ISO 3219-1977(E).^{13,20} The temperature value on the readout display is usually from a thermocouple attached to the base of the metal fixtures (parallel plates or cone-and-plate). The actual temperature of the polymeric melt is usually lower than this temperature. This difference is greater at higher temperatures. The difference is especially significant when the polymeric melt is heated by forced gas convection (it can be as much as 5–15°C at high temperatures in the range of 250–400°C). As discussed above in the case of capillary rheometers, the consequent deviation of the viscosity measurement from the correct viscosity value can be considerable. Heating by electric resistance heaters may give better thermal stability and lower temperature offset. The true melt temperature was verified by actually inserting a calibrated thermocouple into the sample while it was held between the parallel plates. The resulting offset was input into the computer software operating the rheometer to correct for the temperature lag. It is recommended that anyone using oscillatory rheometers determine the temperature offset between the display reading and the actual melt temperature and thereby report the corrected temperature. This becomes especially important when comparing data from different equipment. Other calibrations (like torque and angular displacement) on oscillatory rheometers are usually done by the manufacturer.

RESULTS AND DISCUSSION

Control Charts

Monitor samples are tested twice a week at the Solvay Center on Monday and Wednesday mornings. Two numbers (magnitude and phase angle) are required to completely describe a complex variable like complex viscosity and, in general, it would be desirable to maintain control charts on both these quantities. (Alternatively, any pair of relevant parameters, e.g., G' and G'' , could also be chosen). However, due to our special interest in the magnitude of complex viscosity, control charts are maintained using only the magnitude of the complex viscosity measured at 0.015, 1, and 15 Hz for the Bohlin rheometer. For the capillary rheometers, control charts are maintained for the apparent viscosity measured

at apparent shear rates of 100 and 1000 s⁻¹ in the Instron and at 10 and 100 s⁻¹ in the Vimeg. For brevity, only representative control charts for the apparent viscosity measured at an apparent shear rate of 100 s⁻¹ (referred to as μ_2) using the capillary rheometers and the magnitude of the complex viscosity measured at a frequency of 1 Hz using the oscillatory rheometer will be discussed here. The results for all control charts are summarized in Table I. The control limits are calculated by using the first 31 data points (26 for the Bohlin) and then these control limits are subsequently used to monitor the performance of the rheometer. For the sake of completeness, all data points are shown in the control charts.

Instron Capillary Rheometer

Historically, the centerline and standard deviation for μ_2 had been, respectively, 685 and 28.3 Pas (Fig. 3). A complete calibration was done as part of the process of revamping the entire measurement system and the crosshead speed and temperature were corrected. As a result, the centerline shifted up to 713 Pas and the standard deviation was reduced to 22 Pas. This is reflected in the moving range chart (Fig. 4) where the UCL is reduced from 104 to 81 Pas. The standard deviation of the apparent viscosity (both the absolute value and as percent of average) decreases as the apparent shear rate increases (Table I). That is, the measurements become more precise as the shear rate is increased. This is reflected by the error bars in Figure 5. This is true for the Vimeg as well (and for all capillary rheometers that use a load cell and/or pressure transducer). The reason is that as the shear rate increases, the magnitude of the force/pressure measured generally increases as well, improving the precision. A similar increase in the magnitude of the force/pressure measured is also obtained when a more viscous resin is used; hence, the relative standard deviation for the Vimeg is much lower than that for the Instron (Table I). The relative standard deviation (or RSD) is defined as $100*(s)/\text{average}$.

Vimeg Capillary Rheometer

On the individual μ_2 control chart (Fig. 6), the encircled 37th point is above the UCL (special cause). This is reflected by the corresponding point on the moving range chart (Fig. 7) being above its UCL. The reason for this was investigated by a systematic calibration and was determined to be polymeric film buildup on the inside surface of the die.

Table I Apparent Viscosity and Magnitude of Complex Viscosity Measurements (Pa.s) at 190°C

Rheometer	Monitor	Apparent Shear Rate or Frequency	No. Data Points ^c	Average	Standard Deviation	RSD ^b (%)
Bohlin	90A	0.015 Hz	26 ^a	1034 ^a	27 ^a	2.61
Bohlin	90A	1 Hz	26 ^a	862 ^a	26 ^a	3.02
Bohlin	90A	15 Hz	26 ^a	505 ^a	17 ^a	3.40
Instron	90A	100 s ⁻¹	31	713	22	3.09
Instron	90A	1000 s ⁻¹	31	264	2.6	0.98
Vimeg	91C	10 s ⁻¹	31	8755	73	0.83
Vimeg	91C	100 s ⁻¹	31	2227	12	0.54
Vimeg	91C	200 s ⁻¹	31	1425	6	0.42

^a These values correspond to averaged [(ascending + descending)/2] data from successive measurements on different samples.

^b RSD, relative standard deviation = 100* (standard deviation)/(average).

^c Number of data points used to calculate the average and standard deviation.

This was deduced from the fact that the go side of the go/no-go gauge no longer passed through the capillary orifice. When appropriate corrective action was taken (the die was cleaned in an oven), the values came back within the control limits. Without the benefit of SPC, erroneous data (on the high side) would have been inadvertently reported for measurements made on this rheometer. As discussed above, at 100 s⁻¹, the Vimeg makes more precise measurements than the Instron (Table I) and hence errors due to die buildup are more easily detected. A monotonically rising trend was observed from points 51–57 (violation of rule 4 discussed above). The cause was investigated but could not be unambiguously determined. However, it may be spec-

ulated that the monotonic rise could be due to steady buildup of polymeric film on the inside surface of the die. Note that because the buildup was gradual, no corresponding out-of-control signal is obtained on the moving range control chart (Fig. 7). This illustrates the need for both the individual and the moving range control charts.

The encircled 68th point on the moving range chart (Fig. 7) gives an out-of-control signal. This corresponds to the substantial difference in the magnitudes of the 68th and 69th measurements (even though both these measurements are within the control limits of the individual chart). This implies that although both the measurement values lie within the normal variation expected, their relative spread is too great. A system-

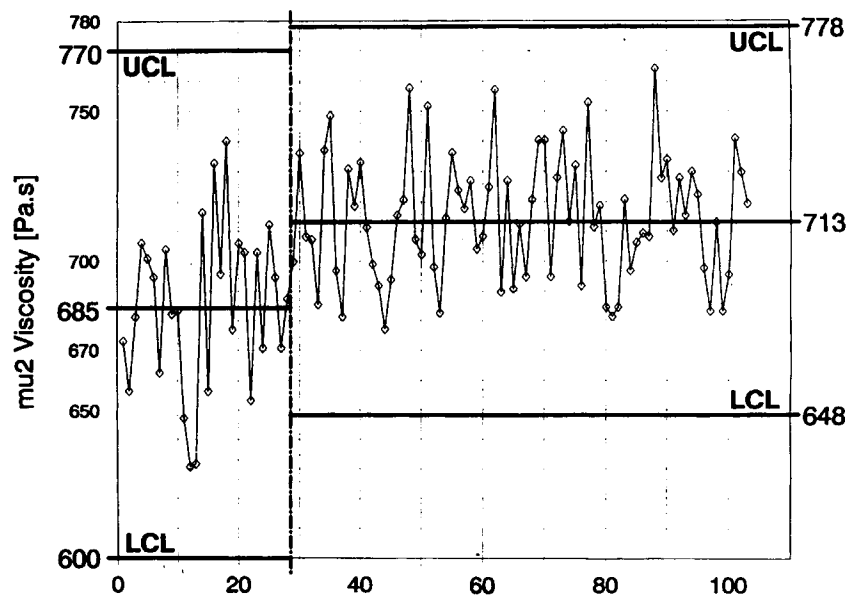


Figure 3 Individual control chart for the apparent viscosity at an apparent shear rate of 100 s⁻¹ (μ_2) in the Instron Capillary Rheometer.

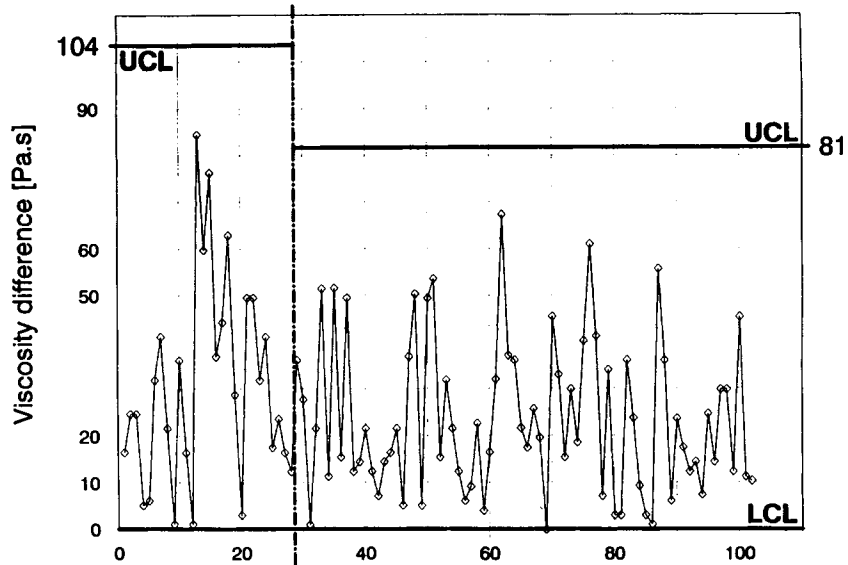


Figure 4 Moving range control chart for the apparent viscosity at an apparent shear rate of 100 s^{-1} (μ2) in the Instron Capillary Rheometer.

atic calibration/verification was done but no cause could be found. Further investigation determined that, during this time, the regular technician was on vacation and these measurements were made by an untrained technician with poor experimental skills, which resulted in consecutive measurements varying widely (or greater standard deviation). Without the benefit of SPC, this would not have been detected. This illustrates how the consistency and reliability of measurements depends not only on the instrument, but

also on the person making the measurement. SPC monitors the entire measurement system (which incorporates all these factors). This also illustrates again the need for both the individual and the moving range control charts.

Oscillatory Rheometer

In keeping with the recommendation for duplicate measurements,¹³ oscillatory measurements are made

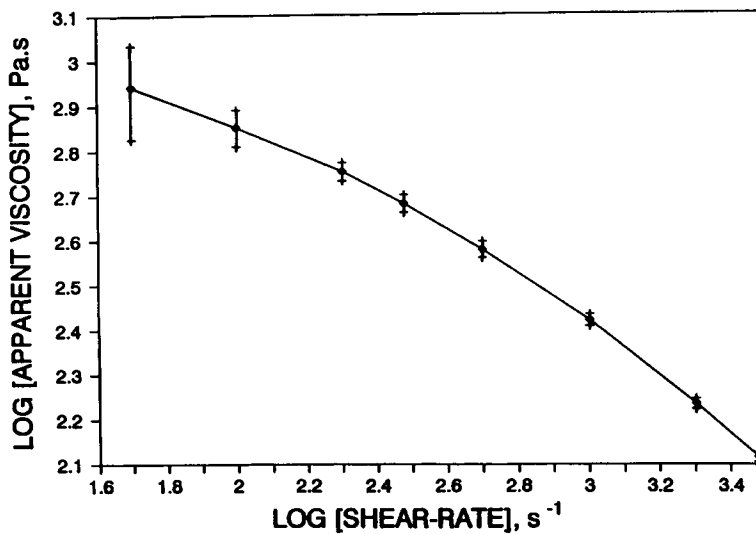


Figure 5 The dependence of the apparent viscosity on the apparent shear rate of HDPE monitor 90A at 190°C measured using the Instron Capillary Rheometer (error bars also shown).

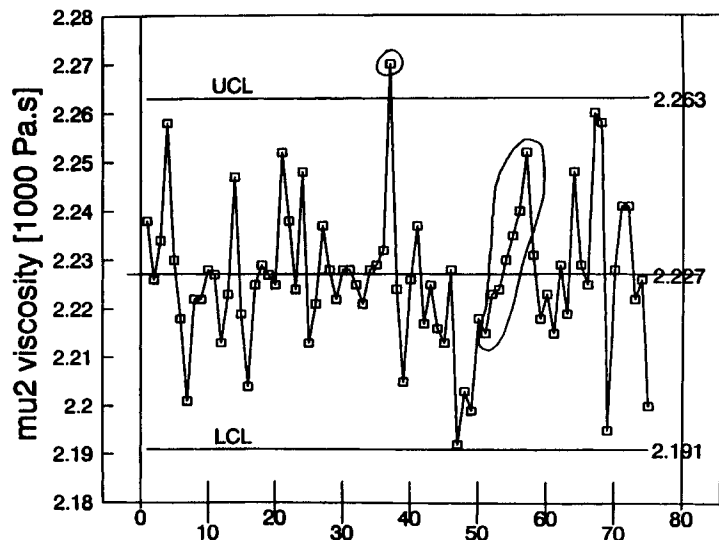


Figure 6 Individual control chart for the apparent viscosity at an apparent shear rate of 100 s^{-1} (μ_2) in the Vimeg Capillary Rheometer.

both in the ascending and descending sweep on the same sample. The magnitudes of these values are then averaged and the averaged magnitude is taken to be the magnitude of the complex viscosity measurement. The centerline for the magnitude of the complex viscosity measured at a frequency of 1 Hz was initially 997 Pas (Fig. 8) with a standard deviation of 51 Pas (only 13 data points before calibration were available and hence this calculation of the standard deviation would have wide confidence limits). As part of the process of revamping the entire measurement system,

temperature and torque calibration was done. As a result, the centerline shifted down to 862 Pas and the standard deviation fell to 26 Pas. The absolute values of the differences between the magnitudes of the complex viscosity (for the revamped system only) are shown in Figure 9. The absolute value of the difference between the values measured in the ascending and descending sweeps made on the same sample and the absolute value of the difference between the averaged viscosity values of successive samples are shown. The average of the latter differences (30 Pas) is greater

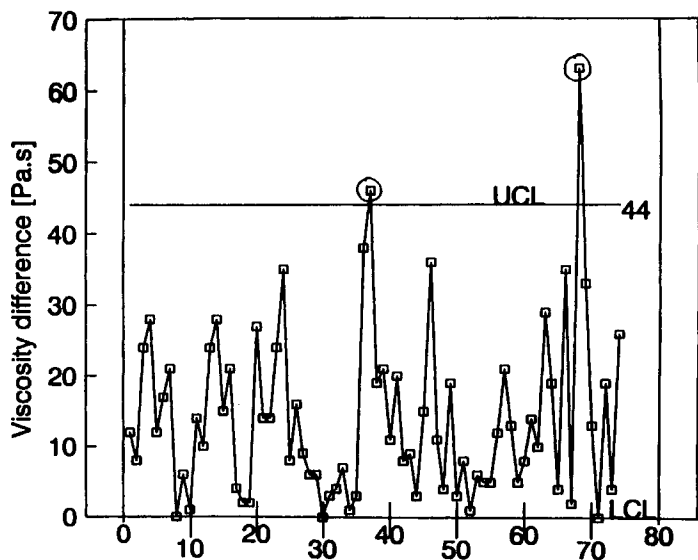


Figure 7 Moving range control chart for the apparent viscosity at an apparent shear rate of 100 s^{-1} (μ_2) in the Vimeg Capillary Rheometer.

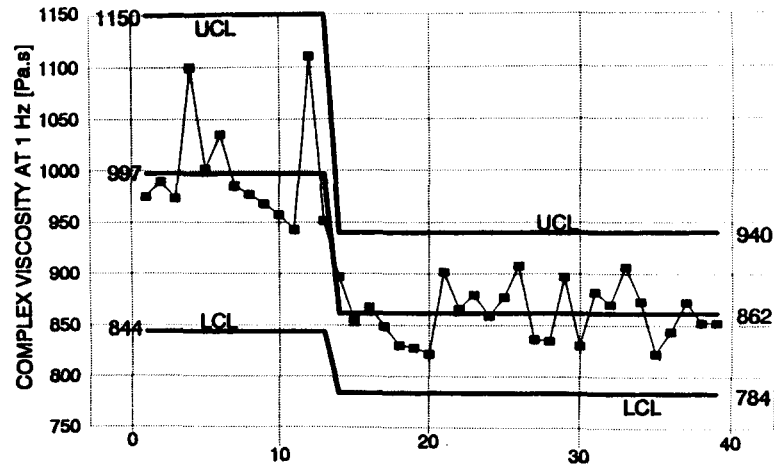


Figure 8 Individual control chart for the magnitude of the complex viscosity at a frequency of 1 Hz in the Bohlin CSM Rheometer (the value plotted is the average of the ascending and descending sweep).

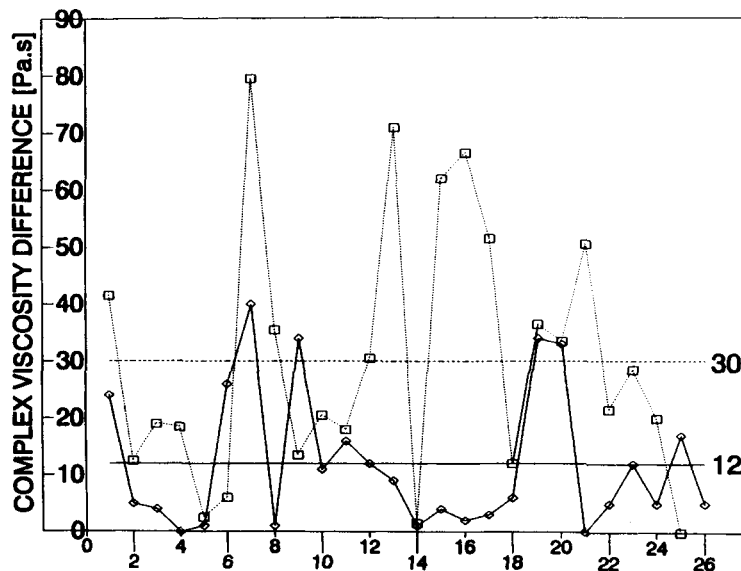


Figure 9 The absolute value of the complex viscosity difference at 1 Hz for the revamped system of the Bohlin CSM Rheometer: (□) difference between successive averaged measurements on different samples; (◇) difference between ascending and descending sweeps on the same sample.

than that of the former (12 Pa.s) because the latter measurements are made on different samples, and hence are expected to show greater variability than values measured on the same sample. This is because measurements made on the same sample are not subject to variation resulting from sample preparation, trimming of the melt between the plates, etc. This issue is discussed in detail by Bafna²³ and that discussion is not repeated here. Contrary to the trend shown by capillary rheometers, the precision improved as the frequency was reduced (Table I). This is because the Bohlin is a controlled stress rheometer, and as the

frequency is reduced (for a given constant stress level), the magnitude of the angular deflection increases (improving the precision). The opposite is seen when constant strain is used for making oscillatory measurements.^{24,25} This is also discussed in detail by Bafna.²³

CONCLUSIONS

The application of SPC to rheological measurements has been demonstrated. With the help of case studies on capillary rheometry and dynamic oscillation, it

has been shown how SPC, coupled with careful calibration and maintenance of rheometers, can demonstrate significant improvement in the accuracy and precision of rheological measurements. This improvement is evident on examination of the various control charts discussed and the narrowing of their control limits. This study illustrates how SPC can easily and routinely detect a special cause (like dirty die or burnt-out heater), thereby assuring that erroneous data will never be inadvertently reported.

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