Rheology of Melts and Solutions Part 1: Viscosity and Its Measurement

by Clifford K. Schof, Schof Associates

This article deals with the rheological behavior of polymer melts and polymer solutions and considers how these materials relate to coatings. It begins with the measurement of dilute solution viscosity, including the intrinsic viscosity number (intrinsic viscosity) and related parameters. Polymer melts and the usefulness of melt rheology techniques to characterize melt coatings and flow are discussed. Methods for the measurement of concentrated solutions are presented, including uniaxial viscometry and rolling ball techniques.

INTRODUCTION

You may wonder what an article on melts and solutions is doing in a paint and coatings journal. The solution aspect is not difficult to explain because we often deal with resins in solution, and leisters, varnishes, and stains essentially are solutions. Also, more and more paint components will be incorporated as solutions in paint manufacturing by dispensing measured amounts of solutions and dispersions into containers becomes commonplace. In addition, dilute solution viscosities are useful for characterizing polymers. Regarding resins, readers will know that powder coatings melt and flow on baking, but they may be surprised to learn that many other coatings also behave like polymer melts. For example, high-solids coatings show considerable flow even after all solvent is lost, particularly at elevated temperatures.

The analytical aspects of all this come with the techniques used to measure rheological behavior and the questions that the results should answer. Does the paint of component meet specifications? Does the paint have the correct rheological characteristics for the application? Why is the paint experiencing flow problems? Why is the appearance not up to standard? What are the characteristics of the polymers and oligomers in the resin?

DILUTE POLYMER SOLUTIONS

Although the movement to environmentally compliant technologies has reduced the use of moderate to high molecular weight polymers in paints, characterization of polymers by dilute solution viscosity is of interest to the coatings industry. The reason for working with very low polymer concentrations is that they yield intermolecular interactions and allow measurement of polymer-polymer interactions. Viscosity values can be used to determine molecular weights and to establish whether a solvent is a good one or poor one for the polymer in question.

Measurements are usually made in glass capillary viscometers. In this method, a liquid drains through a fine bore tube and the viscosity is determined from the flow time and the tube dimensions.1 The basic glass capillary design is that of Ostwald: a U-tube with two reservoirs built by a bellows or a bell, as shown in Figure 1. The liquid is added to the viscometer, pulled into the capillary by suction, and then allowed to drain by gravity back into the lower reservoir. The time that it takes for the liquid to pass between two marked marks, one above and one below the upper reservoir, is a measure of the viscosity. In U-tube viscometers, the effective pressure head and, therefore, the flow time, depend on the volume of liquid in the instrument. Hence, the conditions must be the same for each measurement. Cleanliness is critical for accurate and precise results. The viscometer must be cleaned thoroughly after each series of measurements. ASTM standards D 445, "Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)," D 446, "Standard Specification and Operating Instructions for Glass Capillary Kinematic Viscometers," and D 2872, "Standard Practice for Dilute Solution Viscosity of Polymers," provide valuable information on glass capillary viscometers and their use.

VISCOITY RELATIONSHIPS

A key viscosity parameter for polymer characterization is the limiting viscosity number of intrinsic viscosity, [η]. It is related to the molecular weight of the polymer, and it is calculated by extrapolating to zero concentration of one or both of two parameters: the viscosity number (reduced viscosity) and the logarithmic viscosity number (inherent viscosity). These quantities and their means of calculation are outlined below.

The viscosity ratio or relative viscosity, nrel, is the ratio of the viscosity of a polymer solution to the viscosity of the pure solvent in capillary viscometers measurements, the relative viscosity (dimensionless) is the ratio of the flow time for the solute (S) to the flow time of the solvent (S1).

nrel = T1/T2 = n2/n1 (dimensionless)

The specific (ηsp) viscosity is defined as

ηsp = (In n2/n1) = n2 - 1 (dimensionless)

The viscosity number or reduced (red) viscosity is defined as

η = n2 - 1)C (units = m2/kg or dl/g)

The logarithmic viscosity number or inherent (inh) viscosity is

ηinh = ln(n2/C) (units = m2/kg or dl/g)

where C is the concentration of polymer in convenient units, traditionally g/100 cm3 but kg/m3 in SI units. The viscosity number and logarithmic viscosity number vary with concentration, but each can be extrapolated (Figure 2) to zero concentration to give the limiting viscosity number (intrinsic viscosity). Usually, measurements at four or five concentrations are needed.

The specific viscosity also can be represented by

ηsp = [η] + k [η]3

which becomes the Huggins equation:

ηsp/C = [η] (1 + k' [η])

where k' is the Huggins viscosity constant, a commonly used dilute solution viscosity number or index. It is easily determined from the slope of a plot of ηsp/C vs. C such as the lower plot in Figure 2. The Huggins constant may be thought of as a measure of the "goodness" of the solvent for the polymer with values around 0.3 in good solvents and 0.5 in poor solvents. Huggins constants can be found in reference 5 along with constants for another semi-empirical equation relating viscosity and concentration, that of Schult and Blackwood.5

The Huggins equation and Huggins constants can be used to determine values for [η]. The latter gives an equation:

[η] = 1 + 4k ηinh/1 + 1/2 C

can be used for single-point determinations (calculations from a single viscosity measurement at a known concentration). The general validity of single-point methods has been questioned, but they can be very useful, especially for making corruptions, in even simpler method is to approximate [η] by the logarithmic viscosity number of a single sufficiently dilute solution, such as 0.1 or 0.2 g/100 cm3.

[η] = ηinh = ln(n2/C)

The limiting viscosity number depends on the polymer, solvent, and temperature, but under a given set of conditions it is related to the molecular weight by the Mark-Houwink relation, η = KMη. Where K and a are constants and M is the molecular weight of the polymer. Tables of K and a are available for a large number of polymers and solvents. Excellent summaries of equations, techniques, and references related to the viscosity of dilute polymer systems are also available, as is information on dilute polymer solutions that are shear thinning.12
Rheology of Melts and Solutions Part 1: Viscosity and Its Measurement

by Clifford K. Schoff, Schoff Associates*

This article deals with the rheological behavior of polymer melts and polymer solutions and considers how these materials relate to coatings. It begins with the measurement of dilute solution viscosity, including the definition of viscosity number (intrinsic viscosity) and related parameters. Polymer melts and the usefulness of melt rheological techniques to characterize melt coatings and follow cure are discussed. Methods for the measurement of concentrated solutions are presented, including instrument calibration and roll-fall techniques.

INTRODUCTION

You may wonder what an article on melts and solutions is doing in a paint and coatings journal. The solution aspect is not difficult to explain because we often deal with resins in solution, and leadwaxes, varnishes, and clearcoat essentially are solutions. Also, more and more paint componentst will be incorporated as solutions in paints manufactured by dispersing metered amounts of solutions and dispersions into containers becomes commonplace. In addition, dilute solution viscosities are useful for characterizing polymers. Regarding melts, readers will know that powder coatings melt and flow on baking, but they may be surprised to learn that many other coatings also behave like polymer melts. For example, high-solids coatings show considerable flow even after sufficient solvent is lost, particularly at elevated temperatures.

The analytical aspects of all this come with the techniques used to measure rheological behavior and the questions that the results should answer. Does the paint of component meet specifications? Does the paint have the correct rheological characteristics for the application? Why is the paint experiencing flow problems? Why is the appearance not up to standard? What are the characteristics of the polymers and/or oligomers in the resin?

DILUTE POLYMER SOLUTIONS

Although the movement to environmentally compliant technologies has reduced the use of moderate to high molecular weight polymers in paints, characterization of polymers by dilute solution viscosity is still of interest to the coatings industry. The reason for working with very low polymer concentrations is that they render intermolecular interactions and allow measurement of polymer-solvent interactions. Viscosity values can be used to determine molecular weights and to establish whether a solvent is a good one or poor one for the polymer in question.

Measurements are usually made in glass capillary viscometers. In this method, a liquid drains through a fine bore tube and the viscosity is determined from the flow time and the tube dimensions. A basic glass capillary design is that of Osmond: A U-tube with two narrowbore tubes separated by a card with an eyelet, as shown in Figure 1. The liquid is added to the viscometer, pulled into the upper reservoir by suction, and then allowed to drain by gravity back into the lower reservoir. The time that it takes for the liquid to pass between two marked marks, one above and one below the upper reservoir, is a measure of the viscosity. In U-tube viscometers, the effective pressure head and, therefore, the flow rate, depend on the volume of liquid in the instrument. Hence, the conditions must be the same for each measurement. Cleanliness is critical for accurate and precise results. The viscometer must be cleaned thoroughly after each series of measurements. ASTM standards D 445, "Viscometric Flow Apparatus for Transparent and Opaque Liquids and the Calculation of Dynamic Viscosity," D 6446, "Standard Specification and Operating Instructions for Glass Capillary Kinematic Viscometers," and D 2875, "Standard Practice for Dilute Solution Viscosity of Polymers," provide valuable information on glass capillary viscometers and their use.

VISCOSITY RELATIONSHIPS

A key viscosity parameter for polymer characterization is the limiting viscosity number or intrinsic viscosity, \( \eta_\infty \). It is related to the molecular weight of the polymer. It is calculated by extrapolation to zero concentration of one of the other two parameters: the viscosity number (reduced viscosity) and the logarithmic viscosity number (inherent viscosity). These quantities and their means of calculation are outlined below.

The viscosity ratio or relative viscosity, \( \eta_r = \eta_\infty / \eta_0 \), is the ratio of the viscosity of a polymer solution to the viscosity of the pure solvent. In capillary viscometers measurements, the relative viscosity (dimensionless) is the ratio of the flow time of the solvent (S) to the flow time for the solvent (L), \( \eta_r = t_S / t_L \). The specific (sp) viscosity is defined as \( \eta_s = (\eta - 1) / \eta_0 \), where \( \eta_0 \) is the intrinsic viscosity constant, a commonly used dilution solution viscosity number or index. It is easily determined from the slope of a plot of \( \eta_s / \eta_0 \) versus concentration, such as the lower plot in Figure 2. The Huigens constant may be thought of as a measure of the 'goodness' of the solvent for the polymer with values around 0.5 in good solvents and 0.3–1 in poor solvents. Huigens constants can be found in reference 5 along with constants for another semi-empirical equation relating viscosity and concentration, that of Schulz and Blackley.

The Huigens equation and Huggins constants can be used to determine values for \( \eta_s \) and \( \eta_\infty \). The latter gives an equation:

\[
\eta_\infty = \eta_0 (1 + K \eta_0) ^{-1/2}
\]

which becomes the Huggins equation:

\[
\eta_s / \eta_0 = (1 + K \eta_0) ^{-1}
\]

where \( K \) is the Huggins viscosity constant, a commonly used dilution solution viscosity number or index. It is easily determined from the slope of a plot of \( \eta_s / \eta_0 \) versus concentration, such as the lower plot in Figure 2. The Huigens constant may be thought of as the "goodness" of the solvent for the polymer with values around 0.5 in good solvents and 0.3–1 in poor solvents. Huigens constants can be found in reference 5 along with constants for another semi-empirical equation relating viscosity and concentration, that of Schulz and Blackley.

The Huggins equation and Huggins constants can be used to determine values for \( \eta_s \) and \( \eta_\infty \). The latter gives an equation:

\[
\eta_\infty = \eta_0 (1 + K \eta_0) ^{-1/2}
\]

where \( K \) is the Huggins viscosity constant, a commonly used dilution solution viscosity number or index. It is easily determined from the slope of a plot of \( \eta_s / \eta_0 \) versus concentration, such as the lower plot in Figure 2. The Huigens constant may be thought of as a measure of the 'goodness' of the solvent for the polymer with values around 0.5 in good solvents and 0.3–1 in poor solvents. Huigens constants can be found in reference 5 along with constants for another semi-empirical equation relating viscosity and concentration, that of Schulz and Blackley.

The Huggins equation and Huggins constants can be used to determine values for \( \eta_s \) and \( \eta_\infty \). The latter gives an equation:

\[
\eta_\infty = \eta_0 (1 + K \eta_0) ^{-1/2}
\]

where \( K \) is the Huggins viscosity constant, a commonly used dilution solution viscosity number or index. It is easily determined from the slope of a plot of \( \eta_s / \eta_0 \) versus concentration, such as the lower plot in Figure 2. The Huigens constant may be thought of as a measure of the 'goodness' of the solvent for the polymer with values around 0.5 in good solvents and 0.3–1 in poor solvents. Huigens constants can be found in reference 5 along with constants for another semi-empirical equation relating viscosity and concentration, that of Schulz and Blackley.

The Huggins equation and Huggins constants can be used to determine values for \( \eta_s \) and \( \eta_\infty \). The latter gives an equation:

\[
\eta_\infty = \eta_0 (1 + K \eta_0) ^{-1/2}
\]
POLYMERS AND METHODS
When powder, high-solids, or electrodeposition coatings are baked or measured, they are not thought of as polymer melts, but that's exactly what they are. It is not necessary to know this to be able to make viscosity measurements, but knowledge can help explain problems and certain kinds of behavior. There has not been a lot published on the viscosity behavior of coatings at elevated temperatures, but the theory of molten polymers has been studied in great detail and we can build on the results of that research.

Melt viscosity is a function of temperature, polymer molecular weight (and molecular mass distribution), and polymer structure. Melts exhibit elastic as well as viscous properties.

A number of experimental methods have been applied to measure the melt viscosity of polymers[1,2] but capillary extension techniques probably are the most common. Since such instruments rarely exist in coatings laboratories, most optical viscometers, having heating capabilities are more likely to be used to measure melt viscosities. However, shearthinning measurements are useful for measuring the elasticity of melt polymers[3,4] and also of molten paint films. Some research viscometers permit the measurement of normal stress effects resulting from elasticity. Controlled stress methods also can be useful for evaluating melts and coatings. Square film flow is an interesting technique that is suitable for the processing testing of polymer melts[5] and might have applications for modern coatings.

Polymer melts generally are Newtonian at very low shear rates, then show decreasing viscosity with increasing shear rate. A high shear rate of Newtonian region may exist, but heat generation and polymer degradation at high shear rates usually obscure it. Depending on the concentration, the solvent, and the shear rate of measurement, concentrated polymer solutions may give wide ranges of viscosity and appear to be Newtonian or not. Newtonian. This is illustrated in Figure 3, where solutions of a styrene-butadiene-styrene block copolymer and Newtonian viscosity at high shear rates, but become shear-thinning at high shear rates, dropping to relatively low viscosities beyond 10³ s⁻¹. The shear rate at which the batch behavior occurs depends on the concentration and on the solvent. Note that the viscosity also depends on which solvent was used to dissolve the polymer. The viscosities of the three solvents are 100 mPa·s, xylene 0.59 mPa·s (°C/P), and toluene 0.46 mPa·s. Therefore, it is to be expected that solution A has the highest viscosity, but the differences between the two solvents and C obviously are due to more than the differences in solvent viscosities.

There must also be differences in the polymer-solvent interactions. Powder coated melts are Newtonian until near gelation[6,7] or are most solvobornene clear. The triangles show the curve of the catalyzed version. Measurements were done with an oscillatory viscometer.

Clearcoats Viscosity vs. Time at 140°C (280°F)

<table>
<thead>
<tr>
<th>Clearcoat</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>6000</td>
</tr>
<tr>
<td>Uncatalyzed</td>
<td>6000</td>
</tr>
<tr>
<td>Catalyzed</td>
<td>6000</td>
</tr>
<tr>
<td>Time (sec)</td>
<td>0 100 200 300 400 500 600 700</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>600</td>
<td>700</td>
</tr>
<tr>
<td>700</td>
<td>800</td>
</tr>
</tbody>
</table>

As long as comparisons are made under the same circumstances. The curves in Figure 4 are examples of this kind of experiment. Viscosity values must not be taken as absolute translation, their parameters include the time of the viscosity measurement, the time at which the viscosity measurement is taken (if this time is long), the slope of the linear curve, and the time when the maximum viscosity is achieved.

The limiting low shear or zero-shear viscosity, γ₀, of molten polymers and concentrated solutions can be related to their weight-average molecular weight, M_w, by the following relations: γ₀ = K M₀, for low molecular weight and γ₀ = K M₀⁻¹ for high molecular weight. The transition between these two forms of behavior occurs at a critical molecular weight, M_c, which is above the molecular weight of most paint resins. Viscosity-solids relationships also show a break in behavior due to chain entanglement above a certain molecular weight (ranging from 3,800 to 36,000 g/mol) with 10² to 10³ million. However, in highly concentrated oligomeric solutions such as high solids, low molecular weight materials with high viscosity (on molecular weight and solids by solution method). Generally, the melt viscosity measurements are done after solvent has been driven from the resin (preferable by heating under vacuum) and usually are done with a high temperature cone/plate viscometer. Ratchets that have been tested haven't shown significant melt viscosity differences when high molecular weight materials were present (later separated and identified by other techniques).

Measurement of the Viscosity of Concentrated Solutions

Concentrated solutions can be characterized via a wide range of viscometers. Probably the most common device used in the coatings industry is the efflux cup. Viscosity cup work better with Newtonian clearcoats and resin solutions than they do for shear thinning pigmented paints, but they will have poor precision. For this reason, cups should be restricted to process control or for benchmarking product specifications. Rotational Viscometers (particularly those with adequate temperature control) are much better instruments for the measurement of rheological behavior that is not shear thinning. Most resin viscometers have excellent temperature capabilities and allow oscillatory, as well as controlled shear and strain, measurements. However, much less expensive viscometers usually are sufficient for formulation and problem-solving work. The small sample adapter (STA) that turns a Brookfield cone/plate viscometer into a concentric cylinder instrument and disposable cone/plate viscometers work well for measurements on clearcoats and sticky solutions as well as on pigmented for materials. Figure 5 shows viscosity solids data for waterborne and solventborne clearcoats measured with a Brookfield lowrance cone/plate viscometer. If we look at the curves from right to left, we see the effects of dilution on viscosity. The solventborne clearcoat drops steadily in viscosity, but the waterborne clearcoat increases in viscosity, then decreases. The latter behavior is common in dispersion-type waterborne resins and clays.

Another useful technique is rolling ball viscometry[8,9] and this is an older (1950s or earlier) method that involves rolling a small ball bearing (usually 6 mm, ¼ inch in diameter) down a wet painted panel on an inclined plane (Figure 6). The viscosity, which can be thought of as a surface viscosity is inversely proportional to the velocity of the ball. The system can be calibrated with standard oils or other fluids of known viscosity, but that is not necessary for comparison work. The geometry is so well known that there are tables and rules, but the technique can be very helpful in problem solving.
Plots of rolling ball viscosity versus time are useful for comparing batchers or formulations that show differences in leveling, crater resistance, volatility, etc. Examples of such plots are illustrated in Figure 7, which gives data for a solvent-bearing lacquer and alcohol effect on) adding a flow agent and (2) replacing a portion of the solvent with a slower solvent. The addition of the slower solvent allowed the surface to stay open longer to release more volatiles. This solved a popping problem.

Rolling ball viscosity also has been measured under bake conditions with the inclined plane in an oven and with a different apparatus employing a stationary ball and a moving substrate. The instrument, the TNO Rolling Ball Viscometer, was a turntable similar to that of a phonograph record player. Data from this device are presented in Figure 8, which shows rheological behavior of a high-solids system during the flash and bake. Rolling ball has even been used to measure viscosities of powder coatings on panels during baking.

Another variety of devices rolling a large steel ball down an inclined plane onto a wet painted panel being baked on a precision hot plate. The reciprocating distance traveled by the ball can be taken as proportionate to the viscosity. This is a modification of a method used for determining the tack of pressure sensitive adhesives. The hot plate version of the method can be difficult, messy, and frustrating and the beginning and end of bakes often result in ball bearings flying across the lab, but it is possible to learn a lot about different formulations. However, it does not work with fast drying coatings.

One aspect of the rheology of concentrated solutions that seems to have been ignored in the literature is the viscosity of leaded solutions. It is important to match paste and leaded viscosity. Good pigment dispersion is easily spoiled (floculated) by attempts to mix them with leaded systems that are substantially different in viscosity. This situation has become worse with high-solids coatings and the demand for very high-solids pastes that turn out to have excessively high viscosities and often do not have enough vehicle to adequately stabilize the pigment particle. It may be necessary or formulative so that part of the leaded solution is in the pigment paste to balance viscosities.

**COMMENTS AND CONCLUSIONS, PART 1**

Melts and solutions are only part of the total picture of coatings, but knowledge of their behavior is useful in formulation, manufacturing, and problem solving. Certainly, control of their rheology and the ability to characterize their behavior is important. The body of literature concerning these materials is very large and many appear daunting, but references 2.13, 2.20, 30, and 45 are good places to start. Part 2 of this article will deal with the mechanics of concentrated solutions, surface flows in coatings, the effect of temperature on melt and solution viscosity, and how solvents affect rheology.

**References**


Plots of rolling ball viscosity versus time are useful for comparing batchers or formulations that show differences in leveling, craze resistence, volatile egress, etc. Examples of such plots are illustrated in Figure 7, which gives data for a soberr保姆derer concentrate and allows the effect of adding a flow agent and (2) replacing a portion of the solvent with a slower solvent. The addition of the slower solvent allowed the surface to stay open longer to release more volatiles. This solved a popping problem.

Rolling ball viscosity has also been measured under bake cidevices with the inclined plane in an oven4 and with a different apparatus employing a stationary ball and a moving substrate.4-7 The latter instrument, the TNO Rolling Ball Viscometer, is a turntable similar to that of a phonograph record player. Data from this device are presented in Figure 5, which shows rheological behavior of a high-solids coated during the flash and bake.6 Rolling ball has even been used to measure viscosities of powder coatings on panels during baking.6

The variety of processes involving a large steel ball down a moveable inclined plane onto a wet paint panel being baked on a precision hot plate. The reciprocation of the distance traveled by the ball can be taken as proportional to the viscosity. This is a modification of a method used for determining the tack of pressure sensitive adhesives.44 Hot plate apparatus of the method can be difficult, messy, and frustrating, and the beginning and end of bakes often result in ball bearings flying across the lab, but it is possible to learn a lot about different formulations. However, it does not work with fast drying coatings.

One aspect of the rheology of concentrated solutions that seems to have been ignored in the literature is the viscosity of ledown solutions. It is important to match paste and ledown viscosity. Good pigment dispersion is usually spoiled (fluorocarbon by attempts to mix them with ledowns that are substantially different in viscosity. This situation has become worse with high-solids coatings and the demand for very high-solids pastes that turn out to have excessively high viscosities and often do not have enough vehicle to adequately stabilize the pigment particles. It may be necessary to formulate so that part of the ledown solution is in the pigment paste to balance viscosities.

COMMENTS AND CONCLUSIONS, PART 1

Melts and solutions are only part of the total picture of coatings, but knowledge of their behavior is useful in formulation, manufacturing, and problem solving. Certainly, control of their rheology and the ability to characterize their behavior is important. The body of literature concerning these materials is very large and many appear daunting, but references 2, 13, 29, 30, and 45-48 offer good places to start. Part 2 of this article will deal with the practicality of concentrated solutions, surface flows in coatings, the effect of temperature on melt and solution viscosity, and how solvents affect rheology.

References


August 2007

76

JCT CoatingsTech.

www.coatingstech.org