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

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This article deals with the rheology 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 limiting viscosity number (intrinsic viscosity) and related parameters. Polymer melts and the usefulness of melt rheology techniques to characterize molten coatings and follow cure are discussed. Methods for the measurement of concentrated solutions are presented, including rotational 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 letdowns, varnishes, and clears essentially are solutions. Also, more and more paint components will be incorporated as solutions as paint manufacturing by dispensing 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 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 or 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 oligimers 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 still is of interest to the coatings industry. The reason for working with very low polymer concentrations is that they reduce 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. The basic glass capillary design is that of Ostwald: a U-tube with two reservoir bulbs separated by a capillary, 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 etched 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 2857, “Standard Practice for Dilute Solution Viscosity of Polymers”

Figure 1—Ostwald glass capillary viscometer.
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, $[\eta]$. It is related to the molecular weight of the polymer. It is calculated by extrapolation to zero concentration of one of the other 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, $\eta_{rel}$, is the ratio of the viscosity of a polymer solution to the viscosity of the pure solvent. In capillary viscometer measurements, the relative viscosity (dimensionless) is the ratio of the flow time for the solution ($t$) to the flow time for the solvent ($t_0$),

$$\eta_{rel} = \frac{t}{t_0} = \frac{\eta}{\eta_0} \quad \text{(dimensionless)}$$

The specific (sp) viscosity is defined as

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_{rel} - 1 \quad \text{(dimensionless)}$$

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

$$\eta_{red} = \eta_{sp}/C = (\eta_{rel} - 1)/C \quad \text{(units = m}^2\text{/kg or dL/g)}$$

The logarithmic viscosity number or inherent (inh) viscosity is

$$\eta_{inh} = (\ln \eta_{rel})/C \quad \text{(units = m}^3\text{/kg or dL/g)}$$

where $C$ is the concentration of polymer in convenient units, traditionally g/100 cm$^3$ but kg/m$^3$ 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

$$\eta_{sp} = k_1 \eta_c + k_2 \eta_c^2$$

which becomes the Huggins equation:

$$\eta_{sp}/C = [\eta](1 - k_h \eta_c)$$

where $k_h$ 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 $\eta_{sp}/C$ versus $C$ 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 0.5–1 in poor solvents. Huggins constants can be found in reference 5. Excellent summaries of equations, techniques, and references relating to the viscosity of dilute polymer solutions are also available, as is information on dilute polymer solutions that are shear thinning.
POLYMER MELTS AND CONCENTRATED SOLUTIONS

When powder, high-solids, or electrodeposition coatings are baked or measurements are made on them at elevated temperatures, they are not thought of as polymer melts, but that essentially is what they are. It is not necessary to know this to be able to make viscosity measurements, but such 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 rheology 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 MW 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, but capillary extrusion techniques probably are the most common. Since such instruments rarely are found in coatings laboratories, rotational viscometers having heating capabilities are more likely to be used for molten paint films. Oscillatory shear measurements are useful for measuring the elasticity of polymer melts and also 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. Squeeze film flow is an interesting technique that is suitable for processibility testing of polymer melts and might have applications for molten coatings.

Polymer melts generally are Newtonian at very low shear rates, then show decreasing viscosity with increasing shear rate. A high shear rate 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 non-Newtonian. This is illustrated in Figure 3, where solutions of a styrene-butadiene-styrene block copolymer are Newtonian and viscous at low shear rates, but become shear thinning at high shear rates, dropping to relatively low viscosities beyond 10 s⁻¹. The shear rate at which the break in 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 at 25 °C are toluene 0.59 mPa·s (= cPs), o-xylene 0.67 mPa·s, and cyclohexane 2.20 mPa·s. Therefore, it is not surprising that solution A has the highest viscosity, but the differences between B and C obviously are due to more than the differences in solvent viscosities.

There must also be differences in the polymer-solvent interactions.

Powder coating melts are Newtonian until near gelation as are most solventborne clearcoats. The low viscosity during the flash is followed by an even lower viscosity well into the bake, which is why clear is so vulnerable to dirt and other contamination. The fact that viscosity does increase, often sharply, during crosslinking means that viscosity measurements of a coating at elevated temperatures can be used to follow the cure process. Although cure in a viscometer is not identical to cure in an oven, it still is a very useful technique for comparing formulations and chemistries, evaluating catalysts, and establishing root causes of problems. Plots of viscosity versus time at the bake temperature give curves such as those for an automotive clearcoat with and without catalyst that are shown in Figure 4. The original coating cured slowly and the viscosity had only reached about 3500 Ps (350 Pa·s) after 11 minutes. The catalyzed coating cured more rapidly and the viscosity was headed for infinity after six minutes.

Since the cured coating usually does an excellent job of gluing the parts of the viscometer together, only cone/plate or plate/plate sensors should be used and the parts should be separated while the coating still is hot and molten. Ideally, measurements should be made with an oscillatory rheometer, but viscosity also can be followed at a given speed on a conventional rotational viscometer. However, slip-stick behavior may occur as the coating cures, which produces peculiar saw-toothed traces. There are several ways of preparing specimens:

- The coating can be applied to a panel, then flashed and scraped before placing in the viscometer. This method replicates the drying of a coating and seems to be more realistic than other methods, but precision studies have shown that there is variability in both the spraying and scraping processes.

- The paint can be sprayed directly onto a plate that has been removed from the viscometer and then is returned for measurements after the appropriate flash time. One problem is that the cone up-down position must be pre-set for the plate, but there is no way to be sure that the plate height is exactly the same as before.

- A few drops of paint from the can are applied to the plate on the viscometer. Usually, the plate temperature is then ramped to the bake temperature, although the plate can be preheated. This method may seem unrealistic since it does not allow much solvent to escape, but it works well.

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**Figure 4**—Viscosity-time plots for two versions of an automotive clearcoat. The circles describe the cure of the original, noncatalyzed clear. The triangles show the cure of the catalyzed version. Measurements were done with an oscillatory viscometer.
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, but useful parameters include the time of the viscosity upturn, the time at which the curve goes vertical (if this happens), the slope of the line or curve, and the time when the maximum viscosity is achieved.

The limiting low shear or zero-shear viscosity \( \eta_0 \) of molten polymers and concentrated solutions can be related to their weight-average molecular weight, \( M_w \), by the following relations: \( \eta_0 = K M_w \) for low molecular weight and \( \eta_0 = K M_w^{0.4} \) for high molecular weight.\(^{22-24}\)

The transition between the 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 MW),\(^{25}\) again above paint resin MW. However, in highly concentrated oligomeric solutions such as high-solids coatings, relatively high dependencies of viscosity on molecular weight and solids occur even at low molecular weights.\(^{26,27}\) This is probably due to hydrogen bonding that causes the stringing together of short chains or the formation of a loose network, thereby increasing the effective chain length.

Something similar to this has been seen with the formation of viscosity-building needle-like structures by low molecular weight materials.\(^{28}\) Although the viscosity-molecular weight relationships noted here really only hold for narrow molecular weight distribution polymers, they still can be useful with broader distributions such as those found in resins for coatings.

Melt viscosity measurements of resins are useful for quality control, problem solving, and making batch-to-batch comparisons. For example, a high temperature ICI-type high shear viscometer (ASTM D 4287, "High Shear Viscosity Using a Cone/Plate Viscometer") is a useful QC or process tool for the manufacture of resins. Hot resin can be taken from a kettle and its viscosity measured immediately. If the viscosity has reached a specified level, the batch is finished and the reaction can be stopped. Testing hot resin avoids the tedious process of having to cool and dissolve the resin specimen, then measure the viscosity of the solution. An indication of the usefulness of this technique is the fact that when an ICI-type cone/plate viscometer was lent to a resin plant for a resin cooking trial, the instrument never came back.

Melt viscosity measurements also may be used for comparison of resin batches in cases where a high molecular weight tail or the presence of gel is suspected in a batch, but gel permeation chromatography (GPC) has not indicated an unusual molecular weight. Filtration prior to the GPC measurement often removes high MW polymer (especially in poor solvents) and gel, thereby skewing the results. The melt viscosity measurements are done after solvent has been driven from the resin (preferably by heating under vacuum) and usually are done with a high temperature cone/plate viscometer. Batches that have been tested have shown substantial melt viscosity differences when high molecular weight material was 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 cups work better for Newtonian clearcoats and resin solutions than they do for shear thinning pigmented paints, but they still have poor precision. For this reason, cups should be restricted to process control and not used for setting product specifications. Rotational viscometers (particularly those with adequate temperature control) are much better instruments for the measurement of rheological behavior.\(^{7,29,30}\) Most research viscometers have excellent temperature capabilities and allow oscillatory, as well as controlled shear and stress, measurements. However, much less expensive viscometers usually are sufficient for formulation and problem-solving work. The small sample adapter (SSA) that turns a Brookfield viscometer into a concentric cylinder instrument and inexpensive cone/plate viscometers work well for measurements on clearcoats and resin solutions as well as on pigmented formulations. Figure 5 shows viscosity-solids data for waterborne and solventborne clearcoats measured with a Brookfield low shear cone/plate viscometer. If we look at the curves from right to left, we see the effects of dilution on viscosity. The solventborne clear drops steadily in viscosity, but the waterborne clear first increases in viscosity, then decreases. The latter behavior is common in dispersion-type waterborne resins and clear.

Another useful technique is rolling ball viscosity.\(^{29,31-33}\) This is an old (1930s or earlier) method that involves rolling a small ball bearing (usually 6 mm, \( \frac{1}{4} \) 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 ill-defined because the ball often slides and rolls, but the technique can be very helpful in problem solving.

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Figure 5—Low shear viscosity (1 s\(^{-1}\)) versus solids for a waterborne clearcoat (●) and a solventborne clear (■).
Plots of rolling ball viscosity versus time are useful for comparing batches or formulations that show differences in leveling, crater resistance, volatile entrapment, etc. Examples of such plots are illustrated in Figure 7, which gives data for a solventborne clearcoat and shows the effect of (1) 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 latter instrument, the TNO Rolling Ball Viscometer, uses 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 enamel during the flash and bake. Rolling ball has even been used to measure viscosities of powder coatings on panels during heating.

Another version involves rolling a large steel ball down an inclined plane onto a wet painted panel being baked on a precision hot plate. The reciprocal of the distance rolled 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. 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 letdown solutions. It is important to match paste and letdown viscosities. Good pigment dispersions are easily spoiled (floculated) by attempts to mix them with letdowns 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 well be necessary to formulate so that part of the letdown 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 may appear daunting, but references 2, 13, 29, 30, and 41–46 offer good places to start.

Part 2 of this article will deal with viscoelasticity of concentrated solutions, surface flows in coatings, the effect of temperature on melt and solution viscosity, and how solvents affect rheology.

**References**


(6) Schulz, G.V. and Blaschke, F., J. Prakt. Chem., 158, p. 130 (1941) and 159, p. 146 (1941).


(38) ASTM Method D 3121, "Tack of Pressure-Sensitive Adhesives by Rolling Ball," ASTM International, West Conshohocken, PA.


