Application note | V291

Rheometers

Investigating the shear flow and thixotropic behavior of paints and coatings

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Keywords

Rheology, paints, coatings, thixotropy, shear recovery, shear thinning

Figure 1: HAAKE MARS iQ Rheometer with Peltier plate temperature control for use with parallel-plate and cone-and-plate geometries.

Introduction

Paints and coatings are intricate blends of various components such as pigments, binders, solvents, and other additives like anti-foaming, curing, and dispersing agents (to name a few). Each component or additive has a specific role in determining the overall quality of the paint as well as its performance both during and after application such as adhesion, leveling, strength, gloss, stability, durability, impact resistance, etc. Paints are considered highly-structured particle dispersions and as a result, they commonly display complex flow behavior.

Over its lifetime, paint will be exposed to a wide range of shear rates and shear environments. During storage and transport, paint will experience low levels of shear (<1 s^{-1}) and in order to prevent phase separation, the paint is expected to have a high, solid-like viscosity and even display a yield stress. During processing, the pumpability and energy required for mixing and transport directly correlates with its viscosity at medium-to-high shear rates (10 to 1000 s^{-1}). Finally, during application (brushing, rolling, spraying, etc.), the paint will be subjected to high shear rates (>100 s^{-1}) where it is expected to behave as a relatively low viscosity, free-flowing liquid.

As a result, a simple single-point viscosity measurement cannot fully capture the complex flow behavior of paint. Thus, paint needs to be evaluated using a full suite of rheological tests in order to truly examine its overall performance. Here, we assessed the rheological behavior of a commercial paint product with the Thermo Scientific™ HAAKE™ MARS™ iQ Rheometer using three fundamental tests: stepped shear rate viscosity profile, thixotropy loop, and shear recovery. These specific test methods can help simulate how the paint is processed and applied but can also help further optimize and evaluate final product formulations.

Material and methods

Commercially available water-based wall paint was examined using the HAAKE MARS iQ Rheometer with mechanical bearing (Figure 1). The Peltier plate temperature module was used to control temperature at 20 ± 0.1 °C. Samples were tested using the 60 mm diameter parallel-plate geometry. Due to the automatic lift and precise gap control of the MARS iQ measuring head, the gap height was set and maintained at 0.3 mm during all measurements. The smaller gap height not only reduced the required amount of sample volume (~0.9 mL), but it also allowed for higher shear rates to be obtained while limiting sample migration or ejection from between the plates during testing.

Three common test methods were employed to investigate the rheological behavior of the paint: 1) stepped shear rate profile, 2) thixotropy loop, and 3) three-step shear recovery (please refer to our previous application note[1] for more details on how to setup these test methods using the Thermo Scientific™ HAAKE™ RheoWin™ Software). The stepped shear rate profile was employed to measure the viscosity of the paint over four orders of magnitude in shear rate. The shear rate was increased in a stepwise fashion from 0.1 to 4000 s^{-1} holding each shear rate constant until the torque response changed by less than 2%. The sample was then considered to have reached steady state, and the instrument moved to the next shear rate in the pre-determined window of shear rate values. The instrument continued to step through the entire predetermined range of shear rates, waiting for the sample to reach steady state at each shear rate (this is a time-independent measurement). The measured viscosity (η) was then plotted as a function of input shear rate (γ).

The thixotropy loop experiment includes a controlled rate (CR) ramp from low to high shear rates, followed by a shear rate hold at the highest shear rate, and then an identical CR ramp back to the starting shear rate.[2] Here, the shear rate was ramped from 0 to 100 s^{-1} over 100 s and then held constant at the maximum shear rate of 100 s^{-1} for 30 s. The shear rate was then reduced back to zero over the same 100 s time period. The hysteresis area between the ramp up and the ramp down curves was calculated to quantify the thixotropic behavior of the material. A non-thixotropic or non-shear history-dependent material would exhibit identical viscosity curves for the ramp up and ramp down and thus, would have no hysteresis area. Conversely, the larger the hysteresis area the more a material is considered thixotropic and dependent on its shear history. Since the hysteresis area depends strongly on the input experimental parameters, like the shear rate range and shear time, the hysteresis area is not an absolute measure for thixotropy nor is it considered a true material property. However, different materials can be compared to one another if they are examined using the same thixotropy procedure with identical test settings. Rheological models can also be fit to the thixotropy loop data in order to calculate additional material properties. Here, the commonly used Casson model was applied to calculate the yield stress of the paint sample. One major disadvantage of the thixotropy loop experiment is that it cannot provide information on the recovery time of a material after being exposed to a high shear rate.

The three-step shear recovery test, on the other hand, is used to monitor how the viscosity of a material changes over time after being exposed to high shear. During the first step, a relatively low shear stress (τ) of 8 Pa was applied for 30 s, and the sample's initial viscosity was measured while keeping its internal structure intact. Next, the sample was exposed to a relatively high shear rate of 100 s^{-1} for 30 s in order to fully break down its microstructure. Then the applied shear was immediately reduced back to a constant stress of 8 Pa, and the change in viscosity of the sample was observed for 90 s. The third and final step is used to monitor how much and how quickly a sample recovers after shearing. The first and third steps can be performed using a low applied shear rate (using the CR mode), however, when applying even a low shear rate, the sample cannot be considered fully at rest, and consequently its microstructure and apparent recovery will be influenced. Thus, it is strongly advised that the first and final steps are performed using the stress control mode. Overall, the resultant sample viscosity was displayed as a function of time across all three steps.

Results and discussion

As expected, the investigated commercial paint sample exhibited significant shear thinning behavior, displaying nearly a three order of magnitude reduction in viscosity across the explored shear rate range of 0.1 to 4000 s^{-1} (Figure 2). Initially, the paint had a relatively high viscosity of 200 Pa·s, and its viscosity continued to decrease as the shear rate was increased, displaying a final viscosity of 0.5 Pa·s. Paints are complex particle dispersions that commonly display shear thinning behavior. Shear thinning occurs due to shear-induced orientation and disaggregation of particles in the flow direction. The alignment and further dispersion of particles causes a decrease in internal friction, resulting in an overall reduction in viscosity with increasing shear rate.

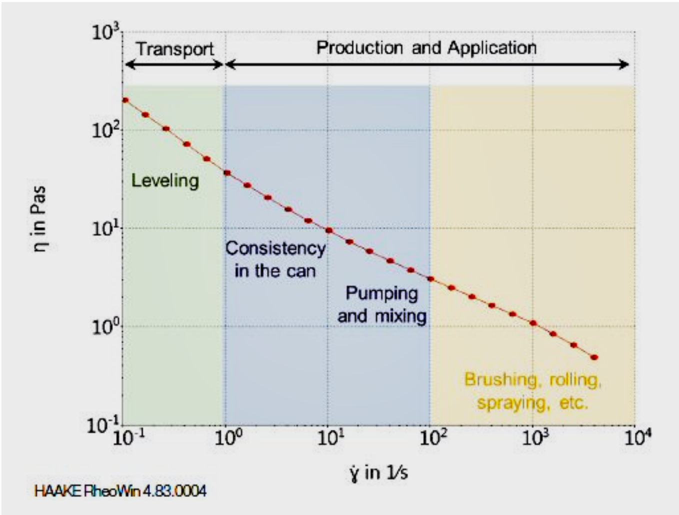

Figure 2: Paint viscosity as a function of applied shear rate. The different material behaviors and shear regimes from transport to production and application are displayed on the plot.

The shear thinning behavior of paint is crucial to its performance and products are formulated with this ideal flow behavior in mind. When exposed to low shear conditions (mainly due to gravity), as those experienced during transport and storage, having a high viscosity helps maintain product consistency and keep particles from settling out of suspension (i.e., phase separation). Also, a higher viscosity at low shear helps prevent the paint from running or streaking after it has been applied to a vertical surface like a wall. However, contrastingly, under the intermediate shear conditions during processing, the paint should be readily flowable and exhibit a medium-to-low viscosity making it easy to mix, pump, transport, etc. Under high shear application, the paint should be even lower in viscosity making it relatively effortless to be applied using brushes and rollers, and should even have the ability to be sprayed through a nozzle. Studying the paint behavior over a broad, shear-rate range is essential for assessing its true quality across its entire lifespan from storage to final usage.

Understanding paint viscosity in response to applied shear is only part of the picture when it comes to product performance. One major question is how does a specific paint recover after being exposed to an elevated shear rate? For instance, after the paint has been applied to a wall does it remain as a low-viscosity liquid or does it reverse back to a high-viscosity material under the low-shear forces of gravity? If the paint remains as an easily flowable liquid for too long, it can drip down the wall leaving droplets or streak marks after the paint has fully cured. However, if it recovers too quickly, the paint will be susceptible to showing brush or roller marks resulting in an uneven or textured final surface coating. The thixotropy loop and shear recovery tests are essential for uncovering and gauging these time-dependent behaviors.

During the thixotropy loop experiment, the paint sample again displayed shear-thinning behavior (Figure 3). However, very little difference between the shear rate ramp-up and ramp-down curves was observed, resulting in a relatively small calculated hysteresis area of ~12 Pa/s. A zero or near-zero hysteresis area indicates that a specific paint recovers almost instantly after being exposed to an applied stress or strain, suggesting that it will be devoid of sagging and droplet formation after application. In addition to calculating the hysteresis the software was also able to extract the apparent yield stress of the paint sample by fitting the measured data with the Casson model. The calculated yield stress for the paint was 35 Pa. The yielding behavior of paint is important for assessing sagging when applying paint to a vertical wall[3] or for predicting shelf-life stability (i.e., its ability to resist phase separation during storage).

In order to examine a samples true, undisturbed recovery behavior, applying small stresses in step 1 and 3 is recommended. Shear recovery tests simulate the effects of gravity acting on paint after being applied better than any of the above applied shear rate experiments. Initially, at an applied shear stress of 8 Pa, the paint displayed a relatively large and constant viscosity of ~10,000 Pa·s (Figure 4). Then under an applied shear rate of 100 s^{-1}, the viscosity dramatically reduced to a constant value of 3 Pa·s. When the applied shear was reduced back to a constant stress of 8 Pa, the viscosity of the paint instantly increased to >100 Pa·s and then continuously and more gradually increased over time. At the end of the 90 s recovery period, the paint had fully recovered to its initial unsheared, resting viscosity. The full and relatively quick recovery of the paint correlates well with the results obtained from the above thixotropy loop experiment. In general, a delayed recovery improves the leveling behavior of a coating, avoiding unwanted brush or roller marks. However, if the recovery is too slow the paint tends to sag and form droplets. Thus, striking the proper balance between too slow vs. too fast of a recovery is a critical formulation metric when evaluating the performance of paints and coatings.

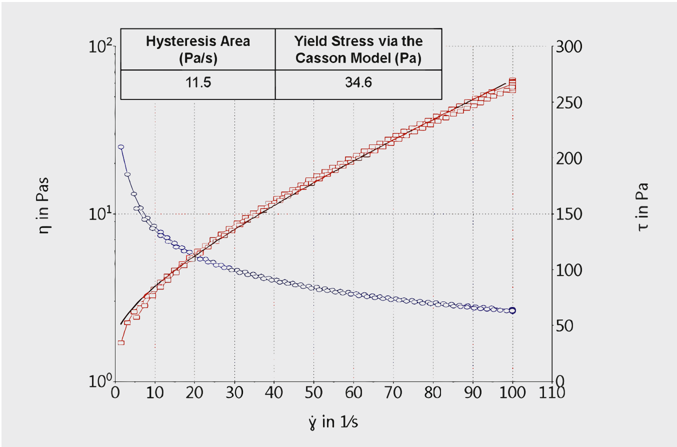

Figure 3: Paint viscosity (circles; left y-axis) and resultant shear stress (squares; right y-axis) as a function of input shear rate for the thixotropy loop test. The Casson Model fit is plotted as a solid line and the calculated yield stress and hysteresis area are displayed inset on the plot.

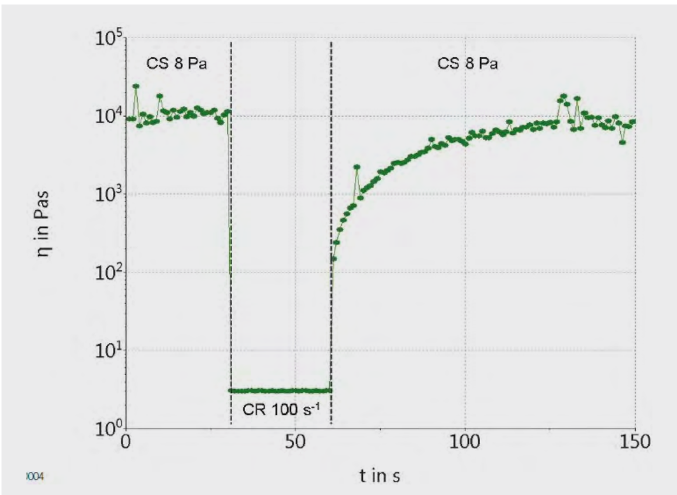

Figure 4: Paint viscosity as a function of time for the three-step shear recovery test: 1) controlled stress (CS) at 8 Pa, 2) controlled rate (CR) at 100 s^{-1}, and 3) CS at 8 Pa.

Conclusions

The HAAKE MARS iQ Mechanical-bearing Rheometer proved to be a fully equipped rheometer that goes beyond the capabilities of a standard viscometer. The automatic lift of the measuring head allowed for using small gap heights (<1 mm) and small sample volumes (<1 mL), as well as accessing high-shear rates (>1000 s^{-1}) without the influence of secondary flows. As a true rheometer, the HAAKE MARS iQ Instrument was able to fully assess the complex rheological behavior of the paint sample.

The viscosity of the paint was measured over four orders of magnitude in shear rate allowing the full flow curve of the paint to be evaluated from the low-shear transport and storage regimes to the high-shear application environment. The thixotropic behavior of the paint was also measured, allowing for a more comprehensive evaluation of the paint's flow behavior. In addition, the controlled stress (CS) mode of the HAAKE MARS iQ Rheometer was employed to evaluate the real shear recovery of the paint, while the sample was considered at rest without disturbing its microstructure using an applied rotation rate during the recovery period. This study demonstrates that the HAAKE MARS iQ Rheometer is fully capable of assessing the complete rheological behavior of paints and coatings required for new product development and quality assurance.

References

1. Meyer F., 2014, Application Note V274 – Investigating the thixotropic and shear recovery behavior of paints and coatings using the Thermo Scientific HAAKE Viscotester iQ Rheometer, Thermo Fisher Scientific, 1–5.
2. Barnes H. A., 1997, Thixotropy – a review, J. Non-Newtonian Fluid Mech., 70, 1–33.
3. Schramm G., 2004, A practical Approach to Rheology and Rheometry, 2nd Edition, Thermo Electron Karlsruhe, 143–144.