Parallel Superposition Studies on Paint Using An ARES-G2 Rheometer

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ABSTRACT

Paints are commonly applied under certain shear conditions. Typically, the flow behavior and the viscoelastic properties of paints have been investigated separately. To study the viscoelasticity of paint materials at the application shear conditions, a combined steady shear and oscillatory motions must be applied to the sample simultaneously. It is a challenge to use a controlled stress rheometer to perform this type of analysis because two individual closed loops (i.e., controlled rate and strain) are needed at the same time. However, the ARES G2 rheometer is a pure controlled strain rheometer, and, so, its motor can apply accurate shear rates and oscillatory strains simultaneously. The ARES G2 is the ideal rheometer for performing parallel superposition studies on viscoelastic fluids such as paints.

INTRODUCTION

Testing by parallel superposition rheology has been used to analyze the viscoelastic properties of dispersions, suspensions, and polymer melts [1-5]. In superposition experiments, the steady shear and oscillatory motions are applied to a sample in the same direction simultaneously. The basic idea of this technique is to analyze the nonlinear condition of the material, resulting from steady-state shear flow, by applying a linear perturbation at selected frequencies [6-8]. The observed parallel superposition moduli depend not only on the microstructure at the shear rate under consideration but also on its evolution with shear.

The interpretation of superposition rheology data is still under further investigation since the viscoelastic superposition response on a microscopic level is rather complex. However, from a practical standpoint, this analytical technique is very powerful since it provides valuable information regarding the material's viscoelasticity under nonlinear perturbation. Most of the reported parallel superposition studies have been conducted at a controlled shear rate with a superimposed small oscillatory stress. This was due to the limitation of using control stress rheometers. However, in this research, we used the ARES G2 rheometer together with the APS temperature control system to study the viscoelastic properties of different paints under certain shear conditions. The tests were conducted at controlled shear rates and oscillation strains. The TA Instruments ARES G2 rheometer is a pure controlled strain rheometer. Its drive motor is designed to deliver the most accurate frictionless rotational motion over wide ranges of angular displacements and speeds. No feedback loop is needed for controlling both the strain and shear rate. With the separate motor and transducer (SMT) design, the force/torque rebalance transducer (FRT) measures the pure torque/force signal that comes only from the sample. The Advanced Peltier System (APS) is a powerful temperature control system on the ARES G2 rheometer, which can be used in combination with cone-plates, parallel plates, and Couette systems with different types of rotors.

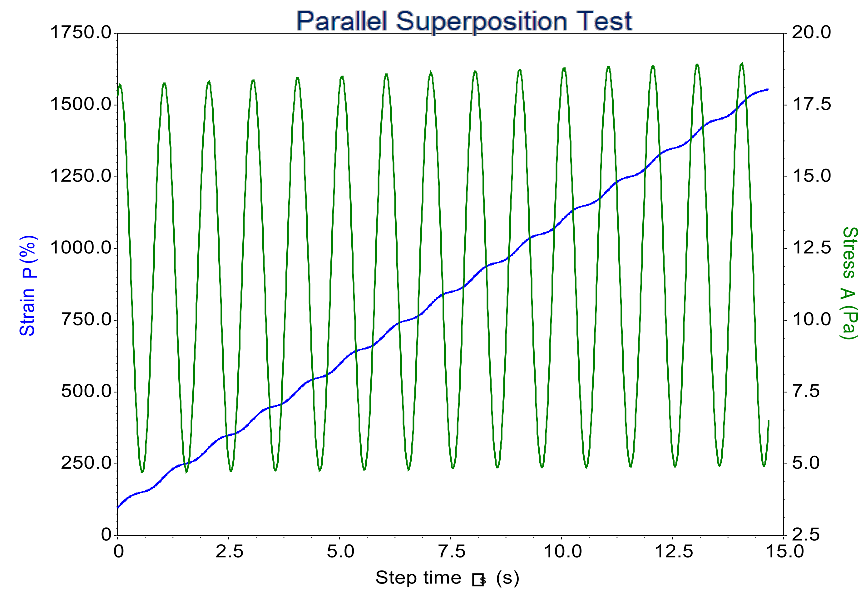

Figure 1 Parallel superposition stress and strain parameters

In the ARES G2 superposition measurements, the total sample shear strain is defined as the sum of a steady shear component, γ_{steady}, and an oscillatory component, γ_{osc}:

$$Y(t) = Y_{steady}(t) + Y_{osc}(t)$$

If one assumes a constant shear rate for steady flow and conventional sinusoidal deformation for the oscillation, one gets the following:

$$\Pi(t) = \Sigma_m t + \Theta \sin(\omega t)$$

$$\Sigma(t) = \Sigma_m + \omega\Theta \cos(\omega t)$$

Then, the stress can be expressed as a sum of the steady state

$$A(t) = A_m + A_{osc}(t)$$

The steady shear stress, A_m, is independent of the oscillatory component of the deformation and is, simply, $\Gamma(\Sigma)\Sigma$. The oscillatory stress, A_{osc}, can be expressed in the usual fashion, so one has the following:

$$A(t) = \Gamma(\Sigma)\Sigma + B\sin(\omega t + \delta)$$

The corresponding parallel complex shear modulus, $G_{\parallel}^{*} = B/\Theta$, can be separated into two components, The in-phase component, $G_{\parallel}'$, and the out of phase component, $G_{\parallel}''$, with δ being the phase angle between the oscillatory shear stress and the oscillatory shear strain:

$$G_{||}' = (B/\Theta)\cos(\delta) \qquad G_{||}'' = (B/\Theta)\sin(\delta)$$

EXPERIMENTAL

The parallel superposition analyses were performed using an ARES G2 rheometer with APS temperature control system and a Couette geometry with a DIN rotor. The paint samples were obtained from two different vendors. The steady flow tests were conducted under 25°C at shear rates from 0.011/s to 500 1/s. Dynamic time sweeps, strain sweeps, and frequency sweeps were performed with superimposed steady flow at different shear rates.

RESULTS AND DISCUSSIONS

Figure 2 shows the steady state flow test results on 2 paint samples. Both of these paints exhibit shear thinning behavior. Overall, the blue paint has a slightly higher viscosity than the red paint in the low shear rate region but a much higher viscosity in the high shear rate region.

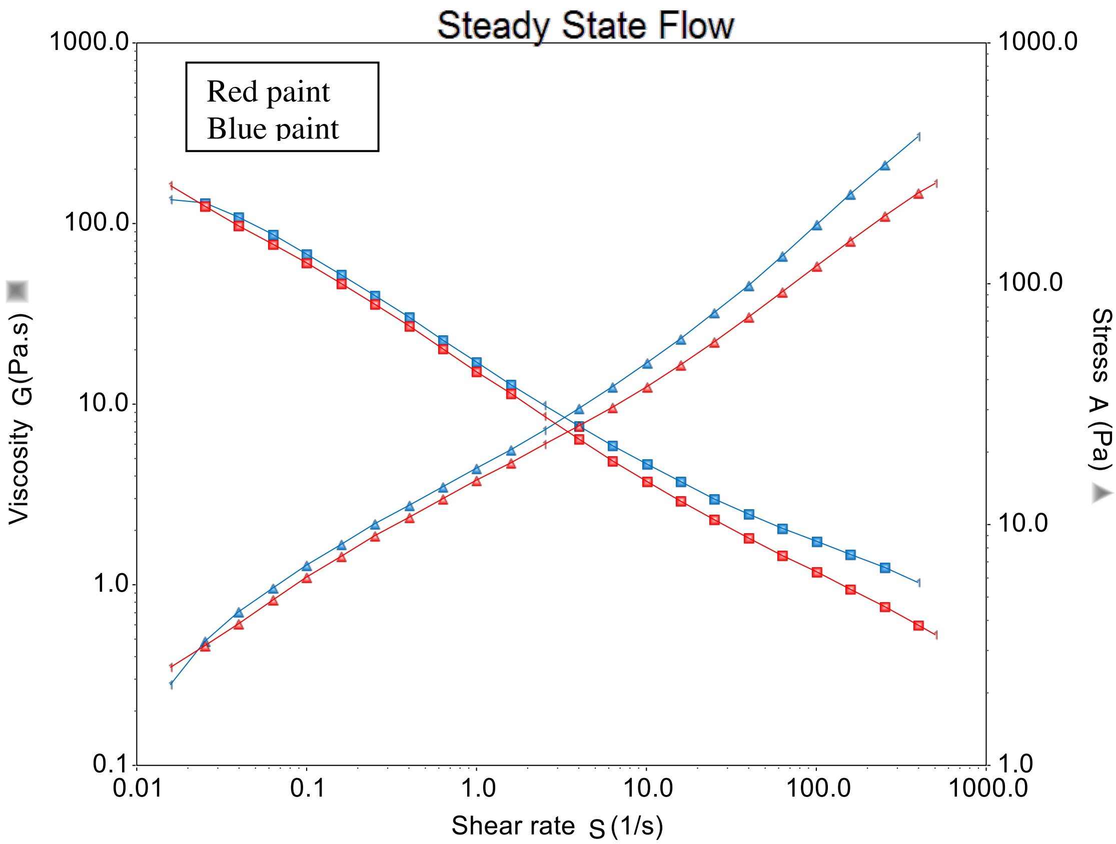

Figure 2 Steady rate sweep tests at 25°C

Figure 3 shows the strain sweep results of the red and blue paint. The strain sweep tests were performed at frequency of 1 Hz under no shear and also at shear rate of 1.0 1/s. Both paints exhibit a lower storage modulus, G', and a broader linear viscoelastic region when sheared at 1.0 1/s, relative to zero shear rate testing. The red paint shows a more significant decrease in its storage modulus than does the blue paint. This phenomenon can also be observed in the time sweep results. Figure 4 shows the time sweep results under different superimposed shear rates. The tests were performed at frequency of 1 Hz and with an oscillatory strain that was in the linear region of the material. With no additional steady shear, the red paint shows a higher modulus compared with the blue paint. But under shear conditions, the modulus of the red paint drops significantly with increasing shear rates. At a shear rate of 10 1/s, the G' of the red paint is about one decade lower than that of the blue paint. These test results show that even though these 2 paints exhibit similar shear viscosity under application conditions, their viscoelastic properties can be very different. The lower G' may cause the sample to lose structure, which may lead to phase separation. This parallel superposition testing allows one to investigate the elasticity and micro-structure of the materials in a sensitive way.

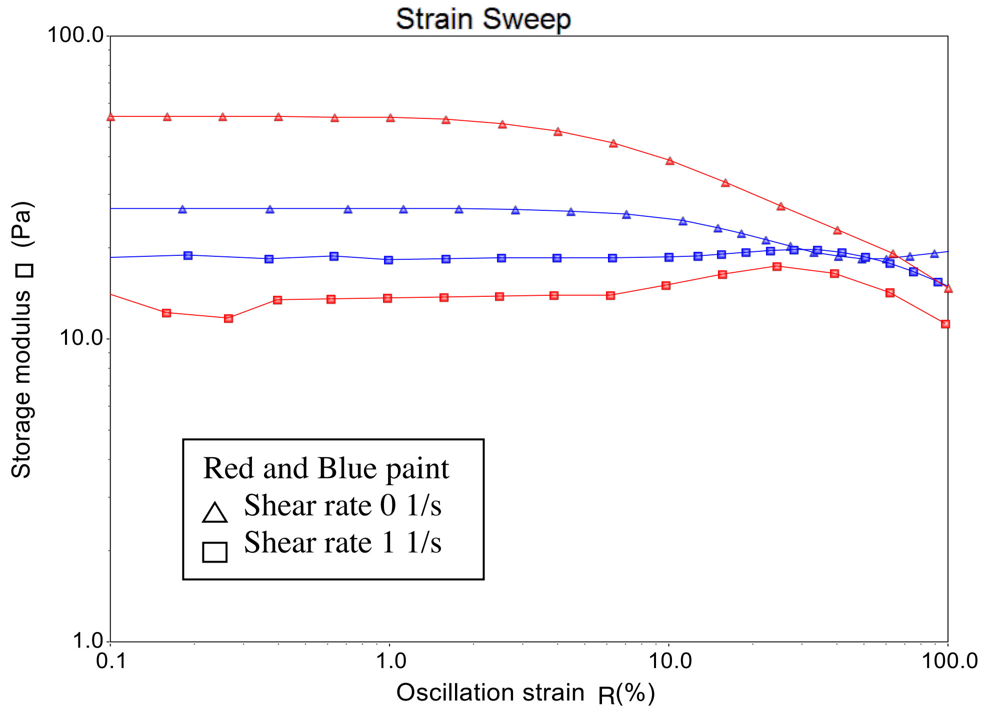

Figure 3 Strain sweeps at 25˚C and shear rates of 0 and 1 1/s

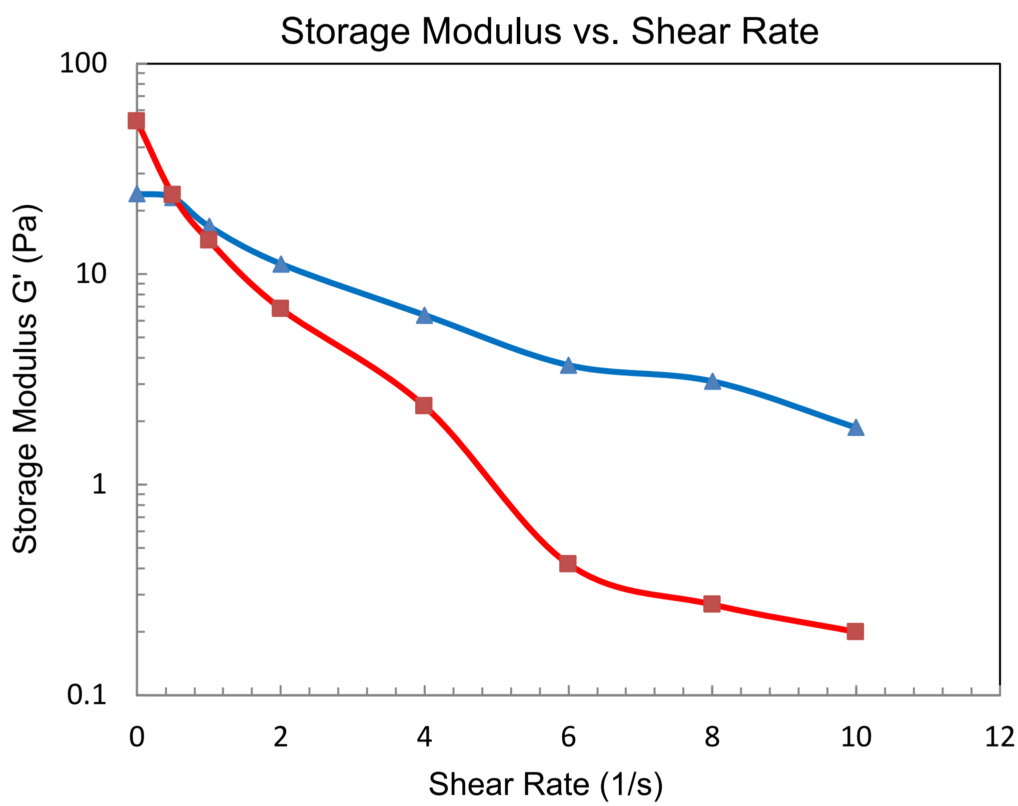

Figure 4 Dynamic time sweeps at different superimposed shear rates

Figure 5 shows the results of frequency sweeps under different shear conditions. The experiments were conducted at 25˚C with an oscillatory strain that is within the linear region of the material. Without applying any steady shear to the sample, the storage modulus (G') of the red paint was higher than that of the blue paint throughout the measurement frequency range. The G' values of both paints decreased with decreasing frequency. However, under additional shear conditions, the G' of the red and blue paints show similar values at higher frequencies, but the G' of the red paint decrease more significantly at lower frequencies compared with the blue paint. The major difference in the modulus between the red and blue paints under shear is observed in the low frequency range. The G' of the red paint was below detectable levels at frequency below 2.5 rad/sec.

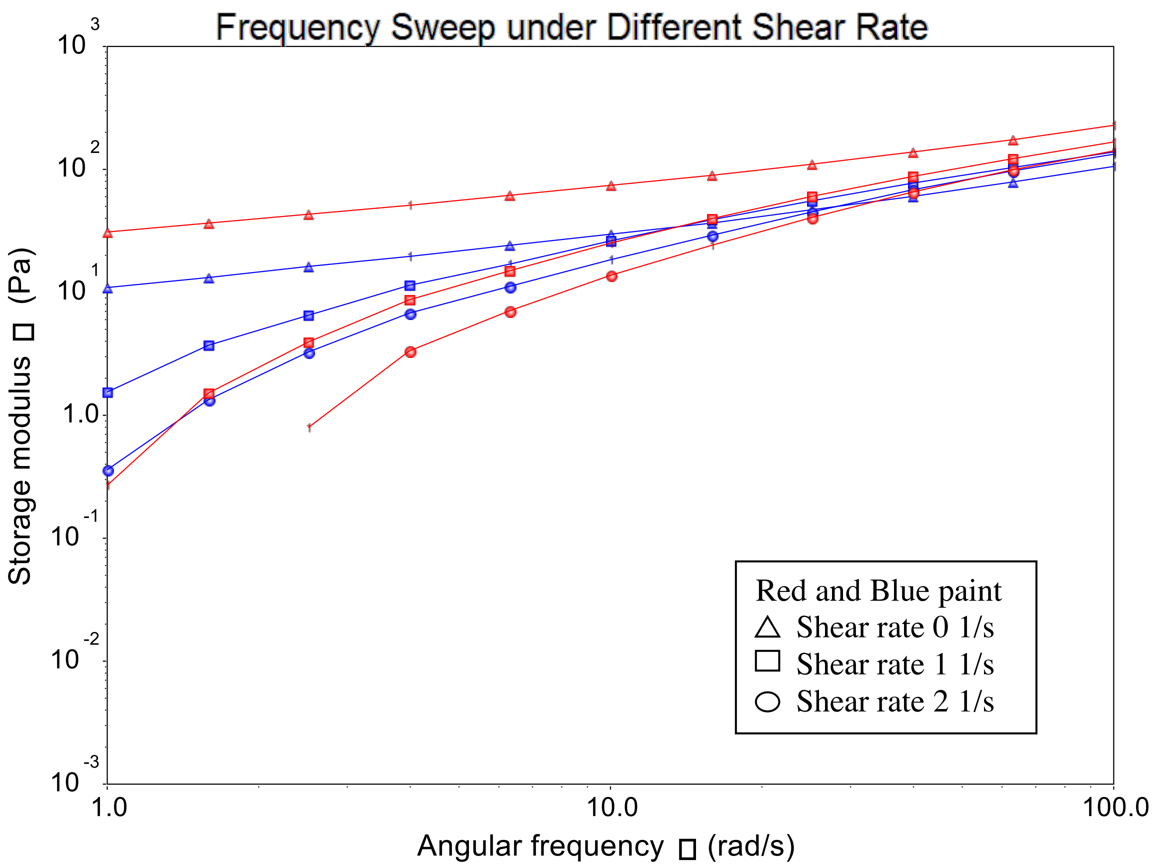

Figure 5 Dynamic frequency sweeps at different superimposed shear rates

CONCLUSIONS

The TA Instruments ARES G2 rheometer, with Trios software, is capable of performing parallel superposition experiments. The available superimposed test modes including dynamic time sweep, strain sweep, frequency sweep and temperature ramp/sweep. Parallel superposition analysis is a powerful technique for analyzing the viscoelastic properties of materials under shear conditions. Traditional shear viscosity measurements were not able to distinguish major differences between the red and blue paint samples. However, under parallel superposition analysis, these two paints show obvious differences in terms of viscoelastic moduli at application shear conditions. The red paint shows higher storage modulus (G'), compared with the blue paint, with no additional steady shear. However, its G' decreases significantly under shear conditions. Therefore, under application shear conditions, the G' of the red paint shows much lower values compared with that of the blue paint.

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