Introduction

A wide variety of products are liquid dispersions. This is because aqueous based dispersions have advantages, for example lower viscosity compared to solutions of comparable solute concentration and water is more acceptable than organic solvents. One of the most important requirements for these products is that the dispersed phase remains stable, and does not settle for many months and in some cases for a few years. Manufacturers need to produce stable products; not only will an unstable product be costly to the manufacture, in some cases like medicine, it can be harmful to the patient. Some stability tests that are currently in use take a very long time and accelerated aging tests may not be reliable. If stability testing is not properly carried out, there is the risk of producing an unstable product. Therefore, formulators urgently need to have a rapid stability screening test for liquid dispersions.

Rheologists and colloid scientists have made remarkable progress in understanding the relationships between the rheology of liquid dispersions, polymer solutions, complex fluids, and their physical chemistry, structure, and morphology. Specifically, major advances have been made in relating the rheology of dispersions to aggregation rate of particles. Floc models and theories, like the Rouse, DLVO for charge-stabilized colloids, Poisson-Boltzmann equation, et al have developed over the years. At best these theories are only semi quantitative, due to their simplifying assumptions. For additional reading see references [1-5].

Experimentalist have benefited from these theories because it aids in designing the appropriate rheological tests and assists in analyzing the results. Most revealing is that liquid dispersions are complex arrays of particles, called flocs, that are attracted by nearest neighbor van der Waal’s forces and hydrodynamic interactions. Dispersions are rheologically complex fluids that have combined viscous and elastic behaviors, which can be described by a viscoelastic spectrum – an oscillatory frequency sweep. A complete spectrum must cover all the relaxation times, such that the frequency dependence of the material functions, storage and loss moduli, extend well into the terminal plateau regions of the spectrum. Steady shear rate measurements are also valuable for determining the hydrodynamics of dispersions.

The stability of a particle dispersion will depend upon the balance of the repulsive and attractive forces which the particles experience as they approach one another. In order to maintain dispersion stability, the repulsive forces need to dominate. Formulators use several approaches to stabilize particles dispersed in liquids. The most common methods of aqueous stabilized particles are steric, electrostatic and network structures. More recently it has been reported that incorporating nanoparticles into colloids improves stability [6]. Electrostatic stabilization affects particle interactions due to the distribution of charged species in the system and can be influenced by various factors such as the pH and/or the concentration and type of electrolyte present. These variables will strongly influence the dispersions’ rheology and stability. Properly balancing the attractive and repulsive forces is the primary means of achieving a stable suspension. The significance of the electrostatic interaction between colloidal particles can be assessed by measuring the zeta potential of the sample. The magnitude of the measured zeta potential is an indication of the electrostatic repulsive force that is present and can be used to predict the long-term stability of the product [7]. The effect of the pH or ionic strength of the medium or the concentration of an additive on the zeta potential and rheology of the sample can give information to help maximize the stability of a formulation.

For experimental rheology to play a significant role in predicting particle stability of liquid dispersions, the measurement technique must be sensitive to extremely small viscoelastic differences or structural and physiochemical changes of the dispersion. This effectively allows investigation of the sample at rest.

Experimental and discussion of results

This note presents a case study on two very similar dispersions, designated as samples A and B. Sample A settles faster than sample B, but both samples settle so slowly that it will take several months before any shelf life differences are noticeable. It is the objective of this note to show how rheology can test and identify stability differences.

Both samples are charge-stabilized colloids with 25wt. % of dispersed particles. The following
measurements were made: oscillatory single frequency time sweeps, amplitude sweeps and frequency sweeps covering a temperature range from 5 to 35°C.

Finally, master curves are prepared to extend the material functions towards the storage modulus (G'∞) plateau region of their viscoelastic spectra. It is critical to extend the high frequency region beyond the typical upper limit of a rotational rheometer for analysis of dispersion stability (see also Lionberger and Russel [8] and Shikata and Pearson [9]). This will be discussed in more detail later. To generate master curves, it is important to know that a sample has not changed phase within the measuring temperature range. This is identified by inspecting the master curve and ensuring the shift factor works equally well on both the storage and loss moduli.

The first test to perform on an unknown sample is the oscillatory single frequency time sweep, to determine the time required for the sample to reach and maintain stability. This time will allow for possible structure rebuild from sample loading, and will indicate any effects of appreciable solvent evaporation. For samples A and B it took three minutes to reach a constant G' value. No further testing should be performed if the sample does not attain a steady value.

The next test is the amplitude sweep. The purpose of this test is to determine the linear viscoelastic region (the amount the sample can be strained with out changing its structure). The strain where G' begins to decrease is the critical strain. If the intrinsic structure of a sample is to be measured by rheology, it must be tested below this critical strain. A series of amplitude sweeps was made ranging in temperatures from 5 to 35°C and frequencies from 1 to 50Hz. Figure 1 shows the amplitude sweeps of both samples tested at 25°C and 1Hz. The critical strain is 0.22 strain units for both samples. Very slight differences in the material functions, storage and loss moduli, are observed.

Next is the frequency sweep. This test is of primary interest because G' is directly related to the interparticle forces. From the theory developed by Bergenholtz et al [10], the relationship between the high frequency plateau modulus and the interaction potential is given by the Zwanzig and Mountain formula [11]. The following equation relates the high frequency storage modulus, G'∞, to the interaction potential between the particles:

\[
G'_\infty = \frac{\phi}{4\pi} \int_0^\infty g(r) r^2 \left( 1 - e^{-d\psi(r)/kT} \right) dr
\]

where a is the particle radius, \( \phi \) is the volume fraction of the particles, \( g(r) \) is the radial distribution function and \( \psi(r) \) is the interaction potential between the particles. At high frequencies when the time scale of Brownian motion relaxation times of the particles is long compared the frequency time scale, i.e. for high Deborah Number, the storage modulus is a reflection of the interaction potential between the particles. So to predict a more stable dispersion we are looking for a high G' value at high frequencies (typically above 100 Hz).

Frequency sweeps at each temperature were performed at a strain of 0.1 strain units, to keep within the linear viscoelastic region. The significance of this test is to determine the characteristic relaxations of the flow units, particles and flocs alike and their complex interactions. A comparison of the frequency dependence of the material functions for samples A and B is shown in Figure 2. These plots are identical at 25°C. The viscoelastic functions are dominated by the rheology of the discrete floc flow units where both the storage and loss moduli (G' and G'' respectively) approach a limiting slope on a log-log scale, defining the terminal region. An exception is when the flocs associate forming a network structure, in which case G' plateaus at diminishing frequencies.

For samples A and B, it is necessary to perform tests that will reveal floc-floc interactions. These results are found in the plateau region of the viscoelastic spectrum where Brownian relaxations are diminished. For floc units subjected to low frequencies,
self-diffusion due to Brownian translational movement dominates and prevents a disordering due to shear planes. It is conceivable that the time scale to establish rest state ordering of the flow units is in the range of milliseconds or less for low viscosity aqueous dispersions. Therefore, in order to determine the net effect of attractive-repulsive forces it is necessary to determine the value of the storage modulus in the higher frequency plateau region (in the range of 200Hz for these samples). This can only be achieved by applying a time-temperature superposition algorithm to calculate master curves for both samples A and B. Horizontal shifts of the temperature-frequency data using 35°C for the reference temperature reveals the key reason why the dispersed phase of sample A will settle faster than for Sample B.

Figure 3 shows the master curve for sample B and Table 1 lists comparative data.

Observe in Table 1 that the low frequency data is nearly identical for samples A and B. As the frequency increases, larger differences in the storage moduli occur. At 200Hz the storage modulus $G'$ of sample B is 48.59Pa compared to Sample A’s value of 39.97Pa. This means that sample B has a higher effective interaction potential charge than sample A, from the Zwanzig and Mountain formula.

Steady rate sweep measurements were also performed as shown in Figure 4. The behavior of the two samples is nearly the same over the entire shear rate range from 0.1 to 500s$^{-1}$. The Cox-Mertz relationship (relating shear rate to oscillatory frequency) does not necessarily hold for dispersions because the flow unit structure produced in oscillatory and steady shear fields is not the same.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$G'$ (Pa) Sample A</th>
<th>$G'$ (Pa) Sample B</th>
<th>$G''$ (Pa) Sample A</th>
<th>$G''$ (Pa) Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.029</td>
<td>0.029</td>
<td>0.503</td>
<td>0.524</td>
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<tr>
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<td>17.39</td>
<td>16.93</td>
<td>20.70</td>
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<tr>
<td>200</td>
<td>39.97</td>
<td>48.59</td>
<td>7.41</td>
<td>9.89</td>
</tr>
</tbody>
</table>

Table 1 Master Curve Results
Conclusion
Experimental rheology is capable of rapidly identifying the important material functions that control the stability of liquid dispersions providing the viscoelastic spectrum covers the high frequency plateau region. This can be accomplished by producing valid master curves. To ensure validity of the analysis, it is necessary to make all measurements in the linear viscoelastic region well below the critical strain.

References
7. Further information on the measurement and use of zeta potential can be found at http://www.malvern.com/

Figure 4: Steady shear measurements (O – Sample A, + - Sample B)