APPLICATION NOTE

Predicting the Stability of Dispersions with a Yield Stress

Introduction

Assessing the long-term stability of a dispersion or emulsion can be both a tedious and time-consuming process; however, it is essential to ensure a product meets quality standards. Formulators often achieve stability through a combination of effects; minimizing interfacial tension, increasing steric or electrostatic repulsion of the dispersed phase and/or by increasing the viscosity of the continuous phase. For dilute dispersions, the combined effect of these factors can often be reflected in the zero shear viscosity, which can give an indication of the rate at which droplets will coalesce and separate, or dispersions will settle. For systems that are more concentrated, formation of a network structure through dispersed phase interaction or particle/droplet jamming may occur. In this case, stability will be largely related to the strength of the network structure, which can be quantified by the yield stress.

For stability, the yield stress must be greater than the stress imposed by the dispersed phase under the influence of gravity. This can be estimated from the following equation:

$$\sigma = \frac{4(\rho_D - \rho_C)rg}{3}$$

Equation 1

 ρ_D = density of dispersed phase ρ_C = density of continuous phase g = acceleration due to gravity r = radius of dispersed phase

There are a number of experimental tests for determining yield stress. One of the quickest and easiest methods is to perform a shear stress sweep and determine the stress at which a viscosity peak is observed. Prior to this viscosity peak, the material is undergoing elastic deformation. This peak therefore represents the point at which the elastic structure breaks down (yields) and the material begins to flow.

For a system to be stable, the yield stress must be sufficient to withstand the stresses imposed by the dispersed particles, but also additional stresses likely to be encountered during product transportation for example.

This application note shows methodology and data for evaluating the stability of two shower gel (bodywash) products against their capability to suspend bubbles as a product requirement.

Experimental

- Two commercial shower gel products were evaluated; one containing surfactant only and the other containing surfactant and an associative thickener.
- The latter product has been specifically formulated to be able to suspend bubbles in the bottle whilst the product is on the shelf (note - to eliminate the influence of the bubbles on the rheological behaviour, the bubbles in this sample were removed by centrifugation prior to testing).
- A particle stress calculator was used in the rSpace software to calculate the stress imposed by a dispersed particle on the surrounding medium, with particle properties as user inputs (see Equation 1).
- Rotational rheometer measurements were made using a Kinexus rheometer with a Peltier plate cartridge and a cone and plate measuring system¹, and utilizing standard pre-configured sequences in rSpace software.
- A standard loading sequence was used to ensure that both samples were subject to a consistent and controllable loading protocol.



- All rheology measurements were performed at 25°C.
- A shear stress ramp was performed, and the data was analyzed using a peak analysis to determine the yield stress.
- The magnitude of the product yield stress is then compared with the imposed stress calculated from the properties of dispersed particulates to assess long term stability of the system.

Results and Discussion

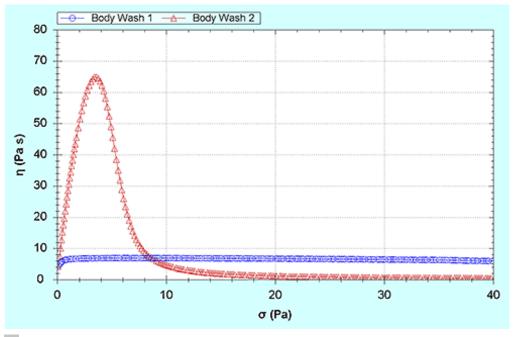
Figure 1 shows the viscosity against stress curves for the two shower gel samples in the stress ramp test. Data for Bodywash 2 shows a clear viscosity peak in the stress ramp test, while data for Bodywash 1 is relatively flat. This implies that Bodywash 2 is exhibiting strain hard-ening associated with a yield stress while Bodywash 1 is behaving like a liquid with a zero shear viscosity.

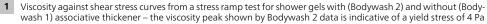
In some instances, viscoelastic liquids may show a slight peak in viscosity even though they do not possess a true yield stress. In this case, user discretion may be required or alternatively confirmation using an alternative test such as a creep test or shear rates test to confirm the presence of a zero shear viscosity².

The measured yield stress for Bodywash 2 was 4 Pa.

Using Equation 1, we can predict that the stress imposed by a 100 μ m diameter air bubble would be approximately 0.65 Pa, hence a yield stress of 4 Pa should be sufficient to suspend the bubble phase, although additional stresses encountered during transport and potential reduction in network strength due to increased temperature also need consideration.

Since Bodywash 1 does not have a yield stress, an accurate value of zero shear viscosity is needed to evaluate stability, such as analysis from a creep test. Data from this test showed the zero shear viscosity to be 8 Pas and from this figure, a bubble rise rate of approx. 6 cm a day was predicted for a 100 μ m bubble. This is clearly unacceptable to maintain long-term stability of the dispersed system, and the incorporation of a yield stress would be necessary to give the required long term stability and shelf-life for a bubble-suspending product.







Conclusion

Two shower gel products were compared using a yield stress ramp test. Bodywash 2, which contains an associative thickener, was shown to have a yield stress capable of suspending gas bubbles. Bodywash 1, which contains no additional thickener, had a zero shear viscosity that was insufficient to promote long-term stability.

The test therefore offers a fast and convenient way of predicting suspension stability for a given particle size and density.

References

1. White Paper – Understanding Yield Stress Measurements, NETZSCH-Gerätebau GmbH

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that a parallel plate geometry can also be used – with this geometry being preferred for dispersions and emulsions with large particle sizes. Such material types may also require the use of serrated or roughened geometries to avoid artefacts relating to slippage at the geometry surface.

