

GETTING *Personal* WITH *Characterization*

Using particle size, zeta potential and rheological data to formulate stable personal care products.

Developing desirable, high performance personal care products that are capable of market success is an exacting task.

Everyday commodities such as face and body washes, body lotions and toothpaste must meet stringent end-use performance targets, reproducibly delivering both the required functionality and the aesthetics that will appeal to consumers. Achieving this performance at a competitive cost is, of course, essential. Many personal care products are suspensions, complex mixtures that might include particulate abrasives, insoluble solids to give opacity, visual cues and excipients or actives that confer, for example, moisturizing benefits and/or antibacterial properties. Suspension stability is a critical attribute of such products, as this underpins the consistency of performance; but, it can be difficult to achieve. In this article, we look at how particle sizing, rheological analysis and zeta potential measurement can help. In combination, these techniques lend extensive support to the formulation process, accelerating the development of better products.

GOALS FOR FORMULATION

Particle size of the suspended phase is a prime candidate for manipulation during the formulation of a suspension-based personal care product. Particle size can influence, for example, dissolution rate, appearance and abrasiveness, all of which may be critical in defining performance. However, particle size and size distribution also affect rheology, which, in turn, controls aspects of performance, such as customer perception, ease of use and stability. This network of interactions makes the formulation process a complex optimization challenge, with stability often especially difficult to engineer.

The goal for stability is that the dispersed phase should remain in a suspended state for the lifetime of the product, under all relevant conditions, or materials should

redisperse easily if settling does occur. Both settling and/or sedimentation introduce the risk of non-homogeneity in a product, potentially compromising performance. The particle size of the dispersed solid, the viscosity of the continuous phase and the rheology of the suspension can all be manipulated towards improving stability; in addition, it can be extremely useful to measure and control a further variable, zeta potential.

THE MECHANICS OF SUSPENSION STABILITY

The factors that contribute to dispersed-phase stability may be classified as either kinetic or thermodynamic in origin. Kinetic factors are those relating to the speed of movement of the particles. For example, increasing the viscosity of the suspending medium supports greater stability because it slows down particle movement, thereby reducing the potential for aggregation and sedimentation. Thermodynamic stability, by contrast, derives from steric and electrostatic effects, and is controlled by manipulating particle-particle interactions, through size or shape modification, for example, or by altering the electrostatic charge. Zeta potential quantifies the magnitude of the electrostatic repulsion or attraction between particles and can therefore provide useful information to support such modifications.

Submicron particles in a suspension tend to remain dispersed as a result of Brownian motion. However, for larger particles, the effect of gravity becomes significant if there is an appreciable difference in density between the dispersed and continuous phases. The ratio of gravitational to Brownian forces, which is a function of particle size, can therefore be used to predict the likelihood of sedimentation (see equation 1: a is the particle radius, $\Delta\rho$ is the density difference between the dispersed and continuous phases, g is acceleration owing to gravity, k_B is the Boltzmann constant and T is the temperature).¹

$$a^4 \Delta\rho g / k_B T$$

A ratio of more than one would suggest that some degree of sedimentation is likely; a ratio of less than one indicates a stable system. However, this equation does not take into account the possible impact of particle-particle interactions. If small particles flocculate upon collision, then the system may become gravity dominated, with an attendant increase in the likelihood of sedimentation, an effect that is predictable from equation 1.

In an electrically charged suspension, DVLO (Derjaguin, Landau, Verwey and Overbeek) theory suggests that two particles will only approach one another and adhere if they have sufficient thermal energy to overcome the repulsive forces separating them.^{2,3} Zeta potential, the potential at the slipping plane between the particle and associated double layer and the surrounding solvent (Figure 1), quantifies the magnitude of this repulsion and the impact of strategies used to modify it, such as altering the pH. Particles within a suspension that exhibit a large negative or positive zeta potential will tend to successfully repel each other whereas low zeta potential values increase the likelihood of flocculation. The dividing line between stability and instability is generally taken as ± 30 mV, with zeta potentials outside of these limits indicating a stable system.^{4,5} This assumption is, however, dependent on particle properties.^{1,2}

This means that zeta potential measurement can provide detailed insight into electrostatic dispersion mechanisms. Rheological measurements, by contrast, support the optimization of kinetic stability. Together, these techniques enable a thorough understanding of all of the factors influencing suspension stability, so promoting secure dispersion control. The following case study demonstrates how zeta potential and rheological data can

be used to develop stability in a suspension of particles of defined particle size.

CASE STUDY: DEVELOPING A STABLE SUSPENSION OF MICROCRYSTALLINE SILICON DIOXIDE

Figure 2 shows how changing pH affects the zeta potential of a suspension of silica particles with an average particle size of 3.7 μm . These data were gathered using a Malvern Zetasizer Nano S in conjunction with an MPT2 autotitrator. From the starting point of a dilute dispersion of the material in deionized water, the autotitrator was used to steadily decrease the pH up to an end-point of 1.0, using standard solutions of HCl. Although this suspension has a negative zeta potential in excess of 30 mV across a wide pH range, it is, in fact, unstable at neutral pH, and forms a compact sedimented layer upon standing. Returning to equation 1, it is relatively easy to explain why. Inputting the relevant values produces a result of 45, suggesting that gravitational forces are highly dominant and sedimentation is likely. In this type of gravitationally dominated system, even substantial electrostatic interactions are insufficient to provide stability ... and kinetic stabilization must therefore be induced.

INCREASING VISCOSITY

As previously suggested, the kinetic stability of a suspension can be improved by increasing the viscosity of the continuous phase. Stokes' law, which states that sedimentation velocity is inversely proportional to the shear viscosity of the continuous phase, describes this effect and suggests that doubling the viscosity will halve the rate of sedimentation.⁶ However, Stokes' law is only applicable for dilute suspensions in which particle interactions are minimal. Settling of concentrated suspensions is complicated by the interactions between neighbouring particles and the fact that a high particle loading leads to an increase in overall density and viscosity.

An alternative way to induce kinetic stability is to give the system a yield stress by introducing a network structure. Systems with a yield stress do not flow until the applied shear exceeds a certain value. Network structures can be achieved by gelling the continuous phase through the introduction of suitable additives, or alternatively by reducing the repulsion between particles to promote flocculation

in the system, a strategy that at first sight can seem counterintuitive when attempting to increase stability.

PROMOTING A NETWORK STRUCTURE

The data displayed in Figure 2 show that zeta potential reduces, towards the isoelectric point (the point where zeta potential is zero), as the pH is decreased. This means that lower pH systems will be more prone to flocculation. The effect of this pH-induced flocculation on suspension viscosity can be determined from Figure 3, which displays shear viscosity as a function of shear rate for concentrated silica dispersions of varying pH. All rheological data were measured using Kinexus Pro and Gemini 2 rotational rheometers (Malvern Instruments).

The suspension with a pH of 3.9 exhibits a zero shear viscosity plateau; that is, at low shear rates, the viscosity becomes constant, a behaviour that is associated with samples that are liquid-like under very low shear conditions. By contrast, the curves measured at a lower pH do not exhibit this feature, suggesting that at very low shear these suspensions may be more solid-like. Extended testing to lower shear rates would be a way to confirm this.

To probe the nature of the induced structure, a three-step shear rate test was done. Viscosity was measured at a low shear rate, then at a high rate and then under the original conditions (data not

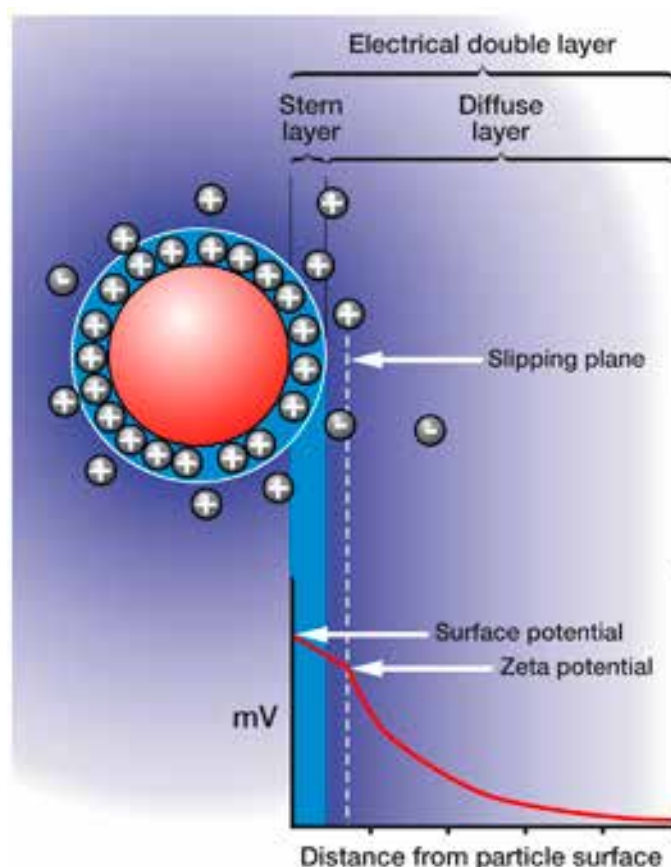


Figure 1: Zeta potential is the potential difference at the slipping plane.

shown). The time taken for the suspension to regain its low shear viscosity was measured and found to be very short, suggesting that any structure-conferring network breaks down at high shear but then is almost instantaneously rebuilt once shear is reduced. These results suggest that the interactions induced by decreasing the pH are strong enough to produce a structure that resists the effects of Brownian motion but sufficiently weak to be broken down under the application of shear.

In fact, flocculation can occur via two different mechanisms, depending on the electrostatic properties of the system. Here, the colliding particles exhibit the mechanism of adhering strongly to form an open structure that favours network

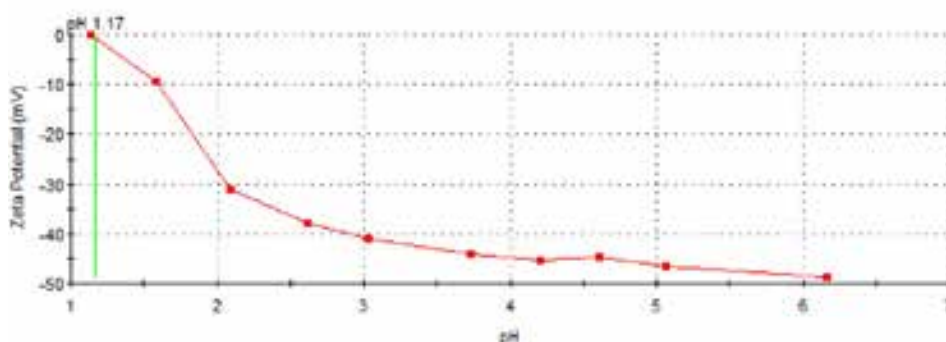


Figure 2: Zeta potential and isoelectric titration data for a standard silica sample.

formation. By contrast, more weakly flocculating systems are able to rearrange themselves on a local scale to form dense flocs that tend to sediment.^{1,6} These behaviours may be fully rationalized using DVLO theory but, generally speaking, a greater reduction in zeta potential favours the development of a network structure.

MEASURING THE YIELD STRESS

Measuring yield stress, the stress required to initiate flow, is a useful way of quantifying the impact of structure in a fluid. In a final series of rheological tests, the yield stress of each of the suspensions was therefore measured by performing a shear stress sweep to identify the stress at which a peak in viscosity is observed. The results are shown in Figure 4. The two low pH samples show a peak in viscosity, indicating a yield stress. A higher value of yield stress for the lowest pH system suggests that the structural strength developed is higher under these conditions, a finding consistent with the lower zeta potential. The absence of a yield stress in the high pH sample indicates that there is no network structure in this sample, a result in agreement with the viscosity curve data, which shows a zero shear viscosity plateau.

These data confirm that reducing the pH has successfully induced structure in

the sample; but, the question remains as to whether this structure is sufficient to impart sufficient stability. Equation 2 enables estimation of the stress imposed on its surroundings, by a particle, within a particulate gel. Here, ρ_D is the density of the dispersed phase and ρ_C is the density of the continuous phase.

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

Note that equation 2 is derived on the assumption that gravitational forces act across the whole surface of a spherical particle. If the gravitational force is considered to act on a normal plane, then using the cross-sectional area of the sphere, the stress imposed becomes $\sigma = (\rho_D - \rho_C)rg$. The use of both derivations can be found in published literature.

Substituting appropriate values for the silica suspension used here, into equation 2, indicates that the largest particles present, those around 10 μm in diameter, would impose a stress of approximately 0.01 Pa. This figure is well below the yield stress exhibited by the low pH suspensions, so these systems should be stable under quiescent conditions. However, this

thermodynamic stability will only be maintained if the stress imposed on the structure does not exceed the yield stress. If higher stresses were applied during transportation, for example, or during use, then the weak network structure could break down ... allowing the particles to sediment.

IN CONCLUSION

For suspension-based personal care products, particle size, zeta potential and rheology are all important characteristics. Manipulating them successfully enables the formulation of products that meet performance targets, and is especially critical when engineering the suspension stability that underpins the consistency of that performance. The combined application of analytical strategies that measure these parameters therefore promotes knowledge-driven formulation towards a stable product that reliably meets end-use and manufacturing goals. Because particle size, rheology and zeta potential are interconnected, and in combination impact suspension behaviour in so many ways, their measurement and understanding is an essential foundation for those looking to control suspension performance to meet the diverse and demanding needs of consumers.

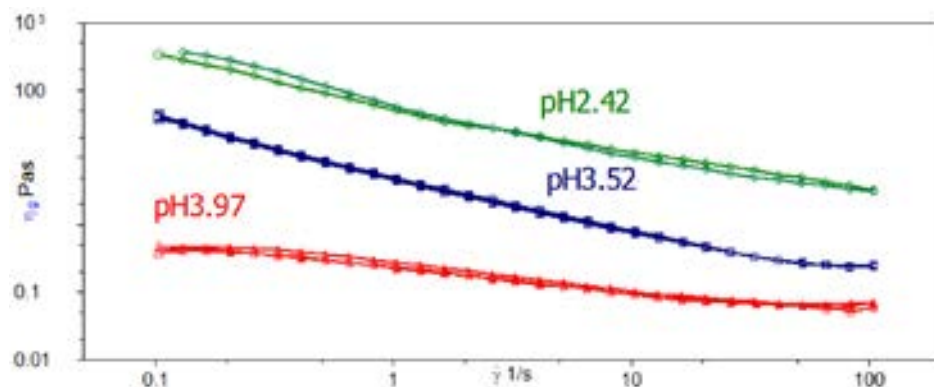


Figure 3: Flow curves for concentrated silica dispersions of varying pH.

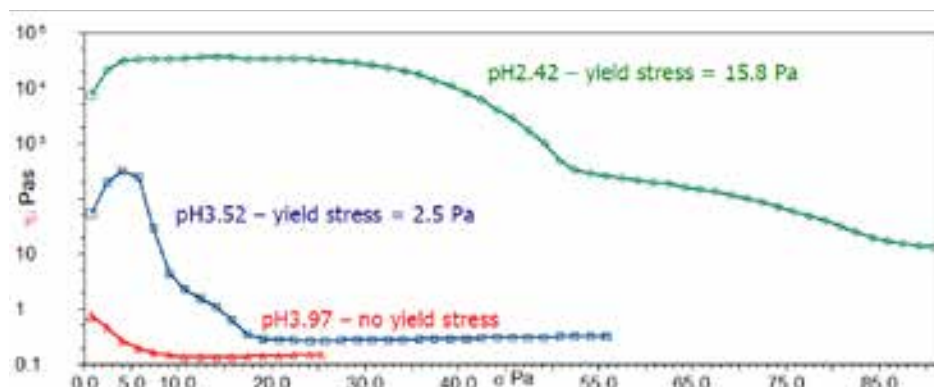


Figure 4: Yield stress measurements for samples prepared at different pH values.

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