The dynamics of surface tension

Resolving measurement problems in wetting of complex coatings.

Victor P. Janule.

Unexpected application problems can occur with coatings because their surface tension may vary in a complex manner over a short period of time. The causes of these problems can be identified by measuring the variation of surface tension versus surface age by a differential maximum bubble pressure (DMBP) technique.

The relationship between surface tension and surface energy is critical to coating performance and determines the degree to which coating formulators achieve positive spreading coefficients, so that the coatings flow out properly. High viscosities, high solids content and other formulation characteristics may adversely affect accurate measurement of both static and dynamic surface tensions.

Multiple surfactant combinations and solvents containing surfactants can result in complex dynamic surface tension curves, which can then adversely affect coating performance, but only under specific coating application conditions. How can we mitigate these problems and achieve accurate surface tension measurement?

Fingerprinting the formulation

Each coating formulation has a unique "molecular fingerprint" based on the tangential intermolecular forces that keep the formulation together, and expressed in milliNewtons/metre or dynes/centimetre. This parameter is the fluid surface tension, the intermolecular force of attraction between adjacent molecules, expressed in force per unit width.

If a coating formulation changes at the molecular level, then the surface tension will change. Unlike water-based surfactant formulations, coatings tend to be viscous, have a high solids content, and by nature have high adhesion, making measurement more problematic.

Pure fluids and most solvents have a single "static" or "equilibrium" surface tension value. If a formulation contains surfactant(s) then it will have a "dynamic" surface tension characteristic which varies as the age of the surface varies. This relationship is a kind of "fingerprint" covering the time that the process allows surfactant molecules to migrate to newly created air/fluid interfaces where they lower the surface tension.

Dynamic surface tension controls coating application

Surface tension dictates whether a coating will wet, spread over or retract from a solid substrate. Most formulations exhibit both an adhesive force that is a measurement of the affinity of the coating for the substrate, and a cohesive force that is a measure of the degree of self-adhesion of the coating.

The spreading coefficient is the difference between work of adhesion and work of cohesion. If work of adhesion is the greater of the two, then spontaneous spreading occurs. If work of cohesion is the greater, then retraction, a surface defect, occurs. Understanding the principles and relationships of surface tension and surface energy (wetting tension) is vital in order to control transfer and adhesion.

Surfactants act as "migrant workers" in coatings

Surfactants are used in most coatings to lower the surface tension to below the surface energy of the substrate to be coated and thus obtain a positive spreading coefficient that enhances wetting, spreading, and adhesion.

At the instant a coating is deposited on a substrate, at zero time of new surface generation, the concentration of surface active molecules at the interface is the same as in the bulk solution. The surfactant molecules then diffuse to and adsorb at the newly created fluid/substrate interface and the fluid/air interface. They will next try to line up with their hydrophobic ends pointed at the interface, causing a compressive force to act on the surface, reducing surface tension.

The concentration and nature of the surfactant determines by how much the surface tension can be reduced, but the speed at which diffusion takes place influences how fast wetting will occur. Wettability, and ultimately "coatability", is influenced by the combined physical and chemical properties of the constituents.

Fast migration is critical to good performance

It takes anywhere from several seconds to several minutes for surface tension to reach equilibrium. This is why the relevant parameter in designing coatings is dynamic surface tension rather than static (equilibrium) surface tension. Selection of surfactants and types is based on specific needs, and often mixed surfactants are used which may result in complex dynamic surface tension fingerprints.

In general, surfactants with a lower molecular mass (short hydrophobic tail) diffuse more rapidly to interfaces. Most surfactants at higher concentrations exert strong molecular attractions between adjacent molecules, creating strong surface films, whose strength determines the surface properties of the surfactant solutions.

Surfactants that diffuse slowly may not lower surface tensions sufficiently within coating application time constraints and may be partially responsible for defects. A surfactant that migrates rapidly from high concentrations (low surface tension) to low concentrations (high surface tension) can mitigate surface defects by eliminating surface tension gradients.

Formulators will sometimes mistakenly increase surfactant concentration in order to reduce gradients, rather than using a better surfactant. Surfactants should ideally have both low equilibrium and low dynamic surface tension values; low enough so coatings are applied to substrates at process speeds with desirable viscosities. Ideally, the surfactant should perform more than one function.

Surface tension measurement - the dynamic method

The Differential Maximum Bubble Pressure (DMBP) method of surface tension measurement is unaffected by surface foam or surface contamination because measurements are made in the body of the fluid. Two probes of dissimilar orifice sizes bubble into a fluid where the differential pressure of the formed bubbles is measured, which is directly proportional to the surface tension.

While classical methods measure only equilibrium surface tension, DMBP tensiometers measure both equilibrium and dynamic surface tension, as the user can choose the bubble rate, which corresponds to the surface age; the time during which surfactant molecules migrate to the gas/fluid interface. DMBP tensiometers are calibrated using two fluid standards of known surface tension values. This method complies with ASTM test method D 3825-90 [3].

Classical curves: surface tension changes smoothly

A "classical" dynamic surface tension curve is a relatively smooth and decreasing curve that would give the highest surface tension possible for this formulation if extrapolated

to zero time (zero surface age). The curve decreases steadily into the equilibrium zone as the surface age is increased. Equilibrium is reached when the surface tension reaches its lowest attainable value, as illustrated in Figure 1.

Measurement speeds are limited by dead time

The limitation on how fast bubbles can be created in specific coatings is determined primarily by the "dead time": the time in which the bubble breaks down after it reaches maximum bubble pressure, departs from the orifice, the coating flows into the area it has left, and capillary action occurs.

Many published dynamic curves are inaccurate because the limitations that "dead time" brings to dynamic surface tension curves were ignored. Figure 2 is an example of two dynamic curves that have some invalid data, due to calibration and/or testing where bubble rates were too fast (to the left of the vertical lines), and bubble rates almost reached oscillating jet mode. For an accurate dynamic curve, the values would continue to increase with decreasing surface age (dotted lines).

The bubble interval has two time components: surface age and dead time. The maximum bubble rate that can generate an accurate dynamic surface tension curve is affected not only by the rheology of the fluids tested, but also by the surface age limits of the calibration fluids. The choice of probe orifice size and physical probe tip configuration are also factors.

DMBP tensiometers allow users to reach surface ages approaching the millisecond range in water and about one third of this for alcohol. The surface ages may be quite similar, although the flow settings are quite different.

The same volumetric flow will generate more than three times the bubble frequency in alcohol as in water, due to alcohol's much lower surface tension. Testing of standard calibration fluids shows that for deionised water calibration there is often no upper limit for DMBP tensiometers. However, for alcohol, the limit is 35% of the Mass Flow Controller setting, as compared to water.

Determining the limiting bubble rate

As bubble rates are increased, the uncalibrated surface tension value will increase. When the surface tension no longer increases or starts to decrease, this is the fastest that the bubble rate can be set for this specific probe set.

What, therefore, can be done to improve on surface age limitations? Orifices with a sharper tip or smaller radius reduce the dead time. Inverted probes are another possibility, allowing the buoyancy of the bubble to lift it from the orifice faster than with downward facing probes.

Multiple surfactants create complex fingerprints

When multiple surfactants are present, dynamic surface tension curves can become "complex", as illustrated in Figure 3. These curves can occur when certain combinations of surfactants or a solvent containing surfactants are used. Here, the dynamic surface tension undergoes several transitions. One surfactant migrates quickly to the air/fluid interface to lower the surface tension and then another one arrives and supplements or displaces the faster migrating molecules.

These more complex characteristics explain why some coatings may have some process-time related zones of performance that contradict initial expectations. It is important to recognise the differences between the flawed dynamic curves in Figure 2 and the perfectly good complex dynamic curve in Figure 3, and what causes each to occur.

High viscosities also give measurement errors

As the viscosity of the coating increases, the hydrodynamic resistance of the fluid against the moving bubble increases significantly. This causes a measurement error sometimes referred to as the "viscosity effect". Though negligible for coatings of low viscosity, it can be several tens of mN/m for highly viscous coatings.

For mildly viscous fluids (up to around 500 centipoise), using an inverted probe can reduce the viscosity effect since the buoyancy of the bubble lifts it off the orifice more rapidly. Shorter dead times and higher bubble rates can also be achieved with inverted probes. Also, if the calibration fluids have exactly the same viscosity as the tested coating, the viscosity effect can be cancelled out during calibration.

Single probe tensiometers require correction factors to deal with the viscosity effect. Even if correction values are used, each test sample must be measured accurately for viscosity in order to apply correction factors. The DMBP method mitigates this problem area. In the differential method, surface age rates are set by the user and can be set differently for each orifice. Since each probe sees the same viscosity, this method lends itself to viscosity compensation.

The Stokes solution - cancelling out viscosity effects

Stokes Law, applied to both orifices, results in a simple relationship between the orifice radius and surface age of each bubble. Surface ages are adjusted to cancel out the viscosity effect by setting each orifice in inverse relationship to the radii of the two orifices. Stokes Law is applied as follows:

[formula one see PDF file page four]

where:
μ = viscosity at both orifices
σ = surface tension of the liquid
r_1 = radius of the small orifice
r_2 = radius of the large orifice
τ_1 = surface age of the small orifice
τ_2 = surface age of the large orifice

This relationship then gives the surface ages in inverse relationship to the radii:

[formula two see PDF file page four]

This problem is solved by setting up the correct viscosity compensation ratio using these Stokes' Law relationships. A software program then captures every maximum differential bubble pressure and logs the surface tension values. By running the tensiometer for several minutes and collecting about fifty to one hundred values in a data file, the user picks out the lowest values corresponding to viscosity compensated readings.

Probe materials affect calibration drift

The function of coatings is to coat and adhere to substrates, which implies they can cause problems of coating and plugging of the probes used to measure surface tension. Judicious choice of probe materials and probe sizes go a long way towards mitigating this problem. Table 1 illustrates some sample surface energy values for various materials.

PTFE ("Teflon") may be an ideal probe material, with a surface energy below 20, which would be non-wetting to most coatings, but is problematic from a calibration and contamination standpoint. Calibration fluids such as alcohol, and other surfactant-containing coatings, take time to flush off PTFE completely, and this is critical to avoid cross-contamination. Stainless steel probes may be a better choice. They are practically indestructible, non-wetting to most coatings, and can be electro-polished for better surface smoothness.

The main problem with any small orifice probe that a coating can wet is that capillary action during dead time allows the

coating to build up inside the orifice, quickly reducing the radius and thus throwing the tensiometer out of calibration. A slightly larger orifice allows some initial, but less serious, build-up to occur inside the tip. Longer time periods result before the instrument is thrown out of calibration. What is lost in measurement resolution is more than compensated for by the longer time allowed to obtain an accurate reading.

Understanding the test method is the key to success

Many problems in coating applications can be resolved by measuring their surface tension before they are used. Transfer, spreading and adhesion can be improved by choosing surfactant and additive combinations that provide the best dynamic surface tension profiles for specific applications.

To accurately establish dynamic surface tension profiles, certain problems that are inherent in coatings with high adhesion and high viscosity must be resolved. Because many coatings are adhesive, contain solids or pigments, and have moderate to high viscosity it is advantageous to understand how an instrument can be set up to minimise plugging problems, dead time limitations, and viscosity effects.

References

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Results at a glance

- The surface tension of coatings plays a key role in determining how they will flow out during application.
- The surface tension of surfactant-containing coatings changes during application, since the surfactants take a measurable time to migrate to newly formed surfaces.
- In particular, complex dynamic changes can occur when different surfactants diffuse at different rates, leading to unexpected application problems.
- Changes in surface tension can be measured using a differential maximum bubble pressure (DMBP) technique.
- Understanding and resolving some known measurement problems allows coatings performance to be characterised under all possible application conditions before use.

The author:

-> Victor P. Janule is founder and president of Chem-Dyne research corporation, SensaDyne instruments division, Mesa, Arizona, USA. He pioneered the commercialisation of the maximum bubble pressure tensiometer. He holds a BS degree in electrical engineering from the University of Wisconsin and an MBA from Ohio University.

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$$\Delta\sigma = \frac{3\mu r_1}{2\tau_1} \qquad \Delta\sigma = \frac{3\mu r_2}{2\tau_2}$$

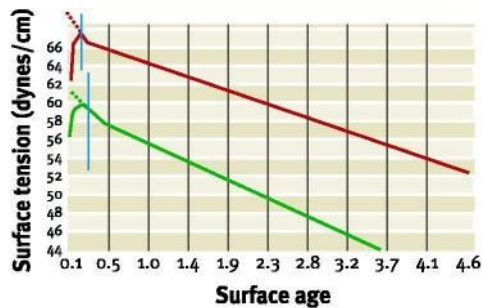ECJ_Janule_Fig4_07/08_05
formula one

$$\frac{3\mu r_1}{2\tau_1} = \frac{3\mu r_2}{2\tau_2} \Rightarrow \frac{r_1}{\tau_1} = \frac{r_2}{\tau_2}$$
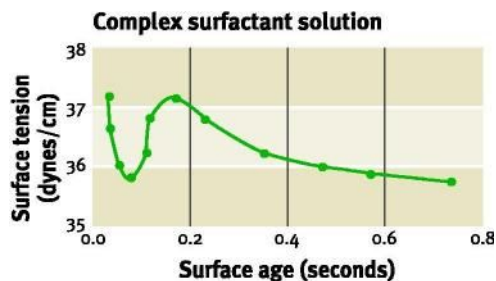
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formula two
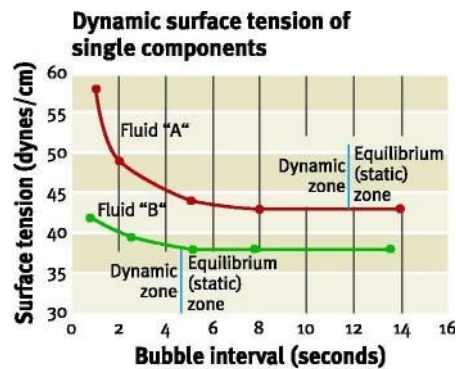
ECJ_Janule_Fig1_07/08_05
Figure 1: Classical dynamic surface tension curves for single components, showing a smooth increas in surface tension as surface age decreases

ECJ_Janule_Fig2_07/08_05
Figure 2: Dynamic surface tension curves, showing inaccurate data generated at high bubble speeds (to left of vertical lines) and realistic values (straight dotted lines)

ECJ_Janule_Fig3_07/08_05
Figure 3: Complex surface tension curve resulting from the presence of surfactants with different migration and surface tension characteristics

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Table 1: Surface energies of sample materials which can be used in surface tension probes

Material	Surface energy (dyne/cm)
Ceramics	> 56 (around 80)
Steel	55
Mild Steel	52
Copper	50
Polyester	44
Copper-nickel alloy	38
Neoprene	36
Aluminium-chrome alloy	36
Chromium	34
Nickel	32
Stainless steel	31
Polyurethane	30
Silicone rubber	< 30
PTFE ("Teflon")	< 30 (around 18)