ADVANCED RHEOLOGY

Viscoelastic Effects in Coating

Whilst slurries and coating colours are normally thought of as liquids (by responding to stress by flowing), they sometimes exhibit some properties of solids. This is known as viscoelasticity, and means that instead of flowing, the material stores some of the applied stress and releases it when the stress is removed. Interactions between thickeners, such as CMC, protein or starch, and pigments in coating colours induce viscoelasticity. This is usually seen as structuring of the suspensions at low shear rates. This structure has to be broken down mechanically in order to make the colour flow, hence the material exhibits a **yield stress.**

Figure 1: Strain sweep output for kaolin - starch coating colour.

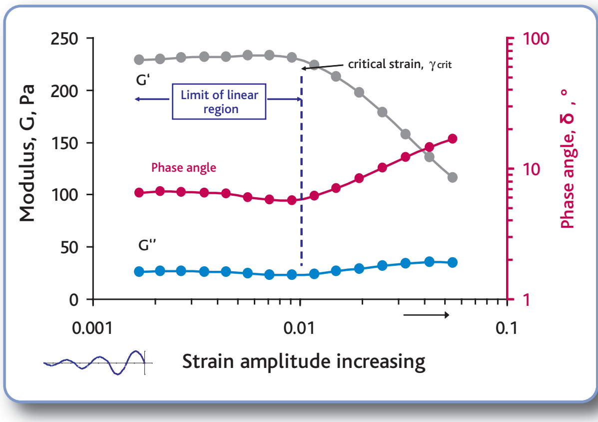
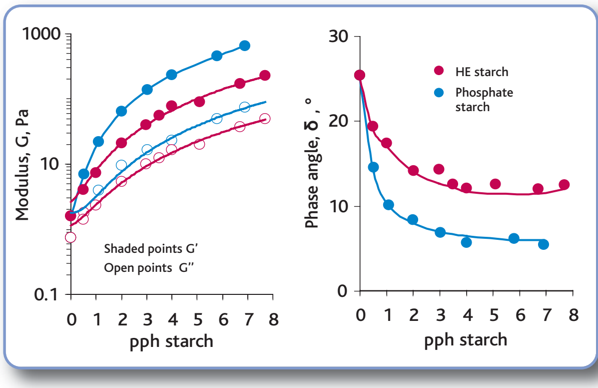


Figure 2: Effect of starch on the viscoelasticity of kaolin - based coating colours.



Measurements of the elastic properties of coating colours can be made using oscillatory shear on the Paar Physica or Bohlin Gemini rheometers, for example. The suspensions are subjected to a sine wave deformation at very small amplitudes. The phase difference between the applied strain and measured stress (the **phase angle, δ**), is a measure of the overall elastic or viscous nature of the sample. A phase difference close to zero indicates strongly elastic behaviour, as opposed to 90°, which indicates purely viscous behaviour. These measurements also give information about the amount of energy stored elastically (the **storage** or **elastic modulus, G´**) and that lost through flow (the **loss** or **viscous modulus, G˝**). A typical output from the instrument is shown in Figure 1. The modulus values remain constant until a critical strain amplitude is reached, when the structure starts to be broken down. Comparisons are always made in the flat portion of the graph, known as the **linear viscoelastic region.** Most coating colours containing thickeners have phase angle values between 5 and 15°, and so are elastic in character.

In general, pigments have relatively minor effects on the viscoelastic character of coating colours. High aspect ratio kaolins usually give stronger structures than GCCs, and fines deficient (narrow p.s.d.) pigment designs give weaker structures. The major influence, however, comes from the interaction between pigments and any added thickeners. Imerys has researched this in depth in order to understand how the formulation environment can be optimised to suit different pigment designs, basepaper characteristics and application conditions.

PCC

GCC

KAOLIN

Co-binders like CMC or starch increase the elastic modulus as a result of flocculation of the pigment. The loss modulus also increases, but to a lesser extent, because the thickener raises the viscosity of the water phase. Figure 2 shows the influence of two different starch derivatives on the viscoelastic response of a kaolin-based formulation. It is clear that the phosphate starch has the strongest interaction with the kaolin, judged by its effect on the elastic modulus and phase angle.

This effect on the loss modulus can help to dissipate energy at the nip exit of the metered size press (MSP), and so reduce misting. Figure 3 illustrates this with data from a pilot coating trial where the pigments were kept constant and only the thickener amount and type was changed.

In general, elasticity is regarded as detrimental to coating runnability. In blade metering, it has been implicated in the formation of blade deposits and scratching, for example. In metered size press coating, it is thought to exacerbate orange peel mottle.

Extensional Viscosity

The majority of rheology measurements are made in shear deformation. However, many coating processes involve the coating being stretched, or extended. Examples are colour flowing into a blade nip, filamentation at the exit of the MSP nip, and stretching of the falling film during curtain coating. The parameter of importance here is the extensional viscosity, which we can measure using an orifice attachment on the ACAV capillary viscometer. Again, pigments have a relatively small effect, and the primary influence is the thickener chemistry. The example in Figure 4 shows how an interactive thickener can increase the ratio of extensional to shear viscosity (known as the Euler number).

Ultra High Shear Measurements

The most critical part of the coating process is the high shear rate metering stage. In order to provide rheological measurements which are useful in this part of the process, capillary viscometers such as the ACAV A2 are often used. However, the timescale under the blade is extremely short (about 10µs) compared with the much longer time the colour is sheared in a 50mm capillary. We prefer to use an attachment which has a narrow slit geometry. This has a gap of 75 µm and a length of 0.5mm, closer to the blade dimensions. By passing a coating colour through the slit two or three times, shear instability can be detected as an apparent increase in viscosity with each pass. This is caused by deposits forming in the gap, which reduce the flow rate. These would cause runnability problems such as streaks in blade coating. In the example shown in Figure 5, the trigger is an excess of dispersant, showing that adding too much dispersant may actually induce runnability problems.

Figure 3: Rheological prediction of misting on MSP

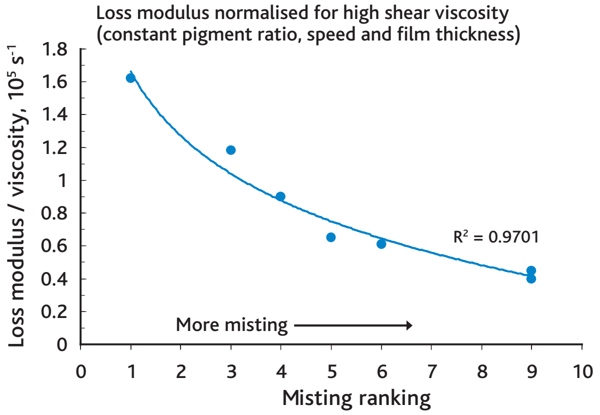


Figure 4: Influence of thickener type on extensional viscosity

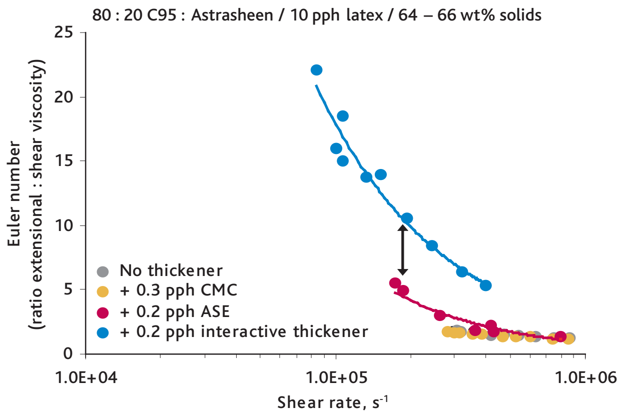
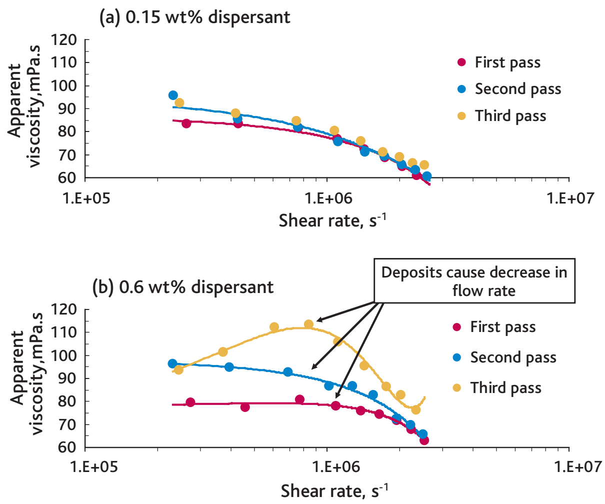


Figure 5: ACA slit shows effect of dispersant dose on shear stability. Kaolin + dispersant, 10 pph latex, 0.3 pph CMC, 59 wt% solids.



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