Insight into non-linear rheology of highly filled non-Brownian suspensions

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ABSTRACT

Yield stress fluids finding application in a wide range of industries are examined here using novel approaches to investigate non-linear viscoelasticity. This contribution focusses on front side metallization pastes used to print circuits on photovoltaic cells and explores how these learnings can be transferred to other application areas, in particular to food processing and food perception. Aspects of shear as well as extensional viscosities are explored as both deformation modes are important features in these processes.

INTRODUCTION

Highly filled dispersions exhibiting a yield stress and subsequent strong shear thinning find wide industrial applications ranging from metallization pastes in electronics and communication to personal hygiene, drilling muds in petroleum industry and food products. In most cases the yield stress is a desired feature that imparts important processing behaviour or lends the products their distinct consumer perception quality. In other cases, the yield stress poses a challenge for processing and should be managed accordingly. Highly filled suspensions in viscoelastic media are particularly challenging from a rheological characterization perspective. To understand how these materials behave one needs to study various linear but also non-linear viscoelastic material functions as well as short time recovery behaviour. These suspensions are notorious for slip, elastic flow instabilities, non-homogeneous flows (shear banding) and they are thixotropic.

Slip, elastic flow instabilities and shear banding need to be mitigated in good rheological experimentation, however may also provide valuable information about material behaviour. The thixotropic nature of these materials poses yet another characterization challenge. Its impact on the measurement needs to be understood, appropriately managed, and it also is important with regards to material behaviour.

This paper presents examples that are taken from work on metallization pastes and food products and demonstrates how novel analysis schemes are implemented to shed new light on the rather complex material behaviours that can be observed and how these relate to formulation on one and to processing on the other hand.

A yield stress is a prominent characteristic of many fluids of industrial relevance a few of which are shown in Fig. 1. In the processes illustrated the fluid is subjected to a complex deformation field where shear and extension may act simultaneously or in sequence and recovery from high shear may play an important role in how the material sets in a certain shape. In screen printing in particular the material is worked under the repetitive action of a squeegee, first to spread the paste across the

Figure 1: Applications of yield stress fluids in photovoltaics, foods and as drilling muds

screen to obtain even coverage and then to press it through the screen onto the substrate. The first is referred to as the flooding step, the second as material transfer.

Once material transfer is complete, the mask lifts off the substrate to leave the patterned material behind. This step is referred to as "snap-off" even if the relative linear speed at which the mask separates from the printed paste is comparatively slow (1-10mm/s). After the snap-off the material settles into its final shape (levelling).

As can be seen from this description, the sequence of process steps subject the material to different deformation modes at quite different deformation rate ranges. While shear viscosity and overcoming a yield stress is important to flooding performance, the viscosity at high shear, extensional viscosity and slip are important during material transfer. During snap-off the deformation is mostly extensional and slip will facilitate a clean separation of the mask from the printed feature. The time scales of thixotropic recovery will then govern how much the printed feature retains its shape or levels.

This in turn makes it clear that a correlation of rheology to the definition of the printed feature must address the various modes of deformation, deformation rates and time scales, as well as time scales of thixotropic recovery. Furthermore, slip is an important performance attribute of these fluids and cannot be treated as a "rheological nuisance", but rather needs to be quantified.

This leads us to the main questions to be answered with regard to the rheology-process correlation:

- How does yield stress, shear viscosity and shear thinning impact the various steps of the process?
- What role does extensional viscosity play during material transfer and snap-off?
- What role does slip play during any of the processing steps?
- Which are the relevant time scales that rheological responses should be measured on, i.e., are steady state properties relevant or should one consider transient properties?

These questions directly translate into measurement challenges.

- How can the yield stress be measured unambiguously? How can shear viscosity be measured accurately without the influence of uncontrolled artefacts (slip, particle bridging, edge instabilities, shear banding, fracture etc.)?
- Can the extensional viscosity of a yield stress fluid be measured at deformation rates relevant to the process?
- How can slip be quantified meaningfully?
- Can measurements of transient properties reveal material responses on time scales <100ms?

Last, but not least, this view allows extensions into other application areas where different material classes are considered, subjected to a different process; however, we will demonstrate how similarities in the way these materials are processed justifies using similar rheometric techniques and more importantly exploit the analogies for the interpretation of the observations. In this very sense, one can extend this discussion to, say, the swallowing process and perception of food stuffs.

EXPERIMENTAL

Front side photovoltaic (PV) silver pastes were studied in rotational, capillary and extensional rheometry. Rotational rheometry was performed on an ARES-G2 using roughened 25mm parallel plates. To achieve uniform deformation history and symmetric loading, samples were deposited using a doctor blade set to 500µm and a slow, controlled rate compression to attain a gap of 250-300µm. Strain sweeps were collected from $5x10^{-3}$-100% strain to measure yield and flow strains (resp. stresses).

Steady state shear experiments were conducted on a Dynisco LCR7001 capillary rheometer with custom made dies of L/D of 60 and 2mm diameter to assure that neither slip, nor particle bridging would affect measurements. This way steady state viscosity over shear rates of 50-1000s^{-1} are accessible.

Extensional rheometry was performed on the CaBER in an altered experimental protocol. The extension of the paste sample was observed under the initial separation of the plates called the strike period. Different separation speeds were examined by setting strike times between 20 and several hundred ms. The change in filament diameter was recorded using high speed videography and the forces acting on the filament were recorded using the normal force sensor in the bottom plate of the CaBER.

RESULTS

Fig. 2 shows the two pastes of interest which have nearly identical linear moduli, however they differ in the strain and stress at which the linear regime ends and where G'=G", i.e. the flow condition.

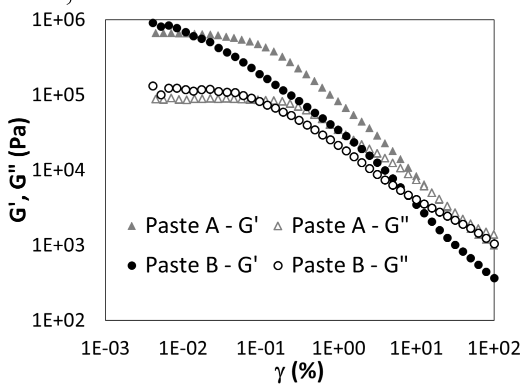

Figure 2: Viscoelastic moduli of two model PV silver pastes as a function of strain amplitude

The oscillatory nature of these tests has a few implications. At strain amplitudes outside the linear regime, G' and G" are increasingly incomplete representations of the stress response. The values of G' and G" are furthermore obtained at steady alternance, meaning that they reflect static, time averaged properties of the material. In most processes, however, materials are subjected to a series of rather short and therefore transient events. Fortunately, the oscillatory stress response can be reinterpreted as transient moduli according to Rogers.[1,2]

This allows the non-linear information to be interpreted without loss of information and importantly, it provides insights into fluidization and reformation processes, their kinetics and the acting viscoelasticity of the fluid under defined straining conditions. One can thus obtain measures of the speed of yielding and reformation by examining the transient moduli at the flow condition (G'=G" represented by grey line in Fig. 3) in a single experiment.

In this example, yielding and reformation distinctly differ in regards to how fast these processes occur. This is shown in Fig. 3 where the trace of the deltoids left/above the flow condition represent the fluid state of the material. The duration to pass from one apex to the next are summarized in Tab. 1. From that one can see that the time paste A spends in fluidized form is significantly shorter than for paste B.

Table 1: Durations of transition between Apexes of the deltoid

Apex	Paste A	Paste B
	[ms]	[ms]
1-2	23	35
2-3	196	219
3-1	92	66

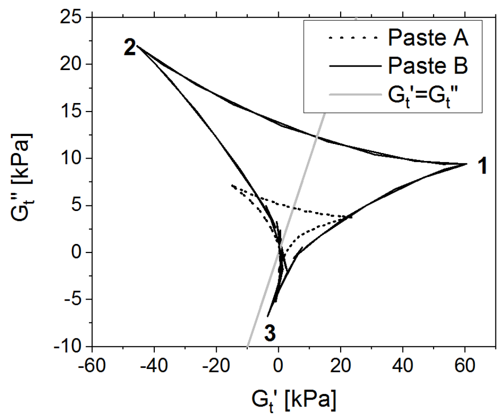

Figure 3: Transient moduli of Paste A and B obtained at 10rad/s represented in a Cole-Cole diagram along with the flow condition G'=G" represented by the black line. Apexes of the deltoid are numbered 1-3.

Furthermore, significantly different speed of yielding and recovery is found for the two samples investigated (Tab. 2). This provides a direct measure of the time it takes to break down the paste structure and thus how easily it is fluidized to allow material transfer through the mask. At the same time, this experiment provides insight into how fast the material regains solid characteristic and thus will sustain gravitational and surface forces which act to level features of the printed line.

Extensional deformation is arguably as important as shear and thus, extensional viscosity measurements were performed on a CaBER instrument using a modified procedure as described above. Extensional viscosity and strong non-linear effects (i.e. extensional strain hardening) give rise to tack and stringiness. These have adverse effects during both, material transfer through the screen (mixed shear and extensional flow) as well as the snap-off step where stringiness leads to undesired peaks and valleys on the printed line.

Table 2: Speed of Yielding and Recovery

Paste	Yielding speed [MPa/s]	Recovery speed [MPa/s]
A	1.8	0.12
B	5.4	0.35

As can be seen in Fig. 4, the extensional viscosity is higher and shows a weaker rate dependence than the shear viscosity, indicating significant strain hardening. Differences between the two samples manifest at low strain rates (<10s^{-1}), likely where stresses are on the order or below the yield stress of the material.

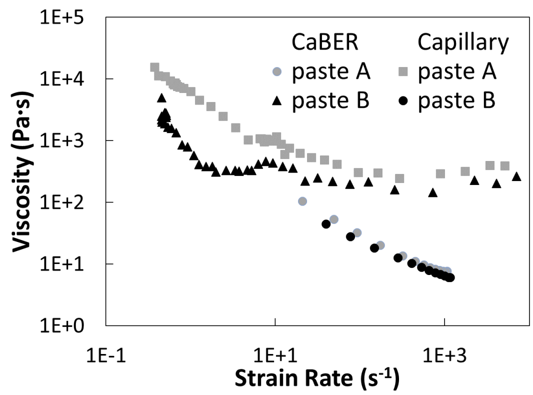

Figure 4: Extensional viscosity of paste A and B compared to shear viscosity obtained from Capillary rheometry

The difference observed in the low rate behaviour is also due to the presence of significant wall slip for paste B compared to paste A as can be seen in Fig. 5. The observation of slip at and below the yield stress of the material is expected.[3]

One can define a vertical and horizontal (Hencky) strain according to

$$\varepsilon_Z = ln\left(\frac{L}{L_0}\right) \qquad (1)$$

$$\varepsilon_D = 2ln\left(\frac{D_0}{D}\right) \qquad (2)$$

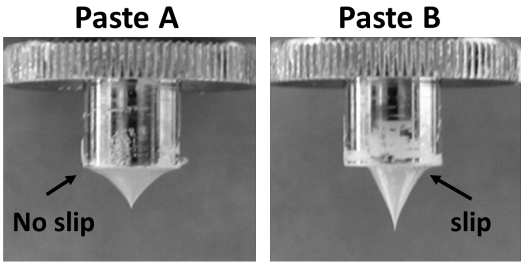

Figure 5: Observation of wall slip for paste A and B at a separation speed of 1mm/s

This allows the discussion of these effects in a parametric representation, direct comparison of the three samples and the effect of increasing separation speed on the results. The use of these parameters provides an intuitive representation as it directly relates how much vertical movement is necessary to induce thinning of the filament.

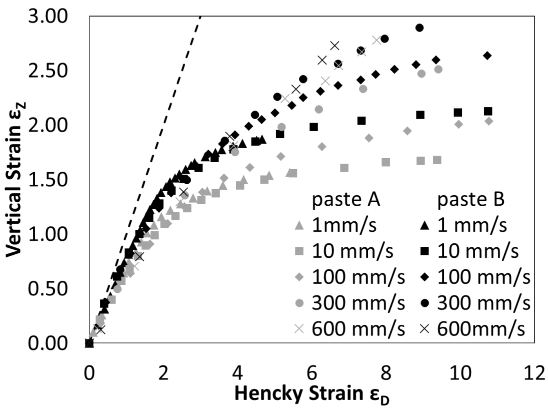

Figure 6: Vertical vs. Hencky strain at various separation speeds for paste A (grey) and B (black).

Fig. 6 shows the differences between paste A and B more clearly and also reveals the onset and magnitude of strain hardening effects observed at the higher separation speeds (>100mm/s). The softer paste B (lower yield stress) appears to be stringier, i.e. a higher vertical strain is required to attain the same Hencky strain. Conversely it appears that paste B shows less strain hardening and therefore less tack than paste A.

DISCUSSION

This contribution demonstrates how various measurements in shear and extension can reveal important information about steady state and transient properties on process relevant deformation and time scales. Of particular significance to the screen printing process is insight into the kinetics of the yielding and reformation behaviour of these pastes. This information thus provides direct insight into the processes that allow the paste to fluidize and thus transfer through the mask and subsequently solidify so that the printed feature can retain its shape.

Extensional viscosity and kinematic information is accessible using the CaBER with a modified measurement protocol. This experiment reveals information about the stringiness and tack (extensional thickening and rate dependent extensional viscosity). Tack is an important aspect of material transfer through the mask as it is a mixed shear and extensional flow. During snap-off the flow field is predominantly extensional and stringiness leads to peaks and valleys in the printed line.

To assess which paste leads to better printing outcomes from rheological measurements one has to consider all the properties described here as they have bearing on the various steps of the process. The ideal paste would combine the various material responses and response time scales as well as phenomena like slip advantageously for an optimized performance. Ultimately modelling efforts with input from these measurements would provide a direct connection to the performance in screen printing.

A yield stress just high enough to require some additional squeegee pressure to induce material transfer through the mesh when it is intended (and not prematurely before the mask seals against the substrate) combined with lower shear viscosity and tack is desired. While paste B exhibits higher stringiness it makes up for it by significant wall slip. This allows clean separation of the paste from the mask during snap-off. The time paste B spends in the fluid state after snap-off is larger compared to paste A and thus the peakiness that may have resulted from the materials stringiness can level. However, the material also regains its solid like character quicker than paste A, therefore allowing the shape of the printed line to be close to the intended shape.

One can now muse how this approach and insight can be transferred to other processes. For that consider the processes that a yield stress fluid such as peanut butter undergoes in the mouth as it is ingested. The deformations in the mouth happen on similar time scales as those described in the process above and the process involves a sequence of steps where shear, mixed flow or predominantly extensional flow fields act on the food stuff and break it down to a fluid.

From the fluids perspective, a lot of food stuffs are yield stress fluids, often suspensions of solids in a viscous or viscoelastic matrix. In that regard, one would try to understand very similar concepts as for instance not only the yield stress but how the material yields. The viscosity of the food stuff in fluid form will determine the time scales required to travel from the mouth to the oesophagus, and given the mixed and increasingly extensional flow field, it is important to understand both, shear and extensional properties of the fluid.

One example where we have successfully implemented this idea were samples for dysphagia treatment. For the treatment of dysphagia (a condition where the timing of the swallowing reflex is slowed) thickening agents such as natural gums are used to increase the viscosity in a way that will allow the retarded swallowing reflexes of the patient to be sufficient to swallow the fluid without aspiration.

These gum solutions are typically semi-dilute and are therefore considerably lower in viscosity compared to the pastes discussed above. This poses a significant challenge for extensional viscosity measurements under controlled strain rate conditions. However, the idea of kinematic curves as in Fig. 6 and Fig. 7 provided a wealth of insight into stringiness. It even allowed an estimate of the extensional viscosity of these samples by equating the surface with viscous forces at the maximum of the kinematic curve.

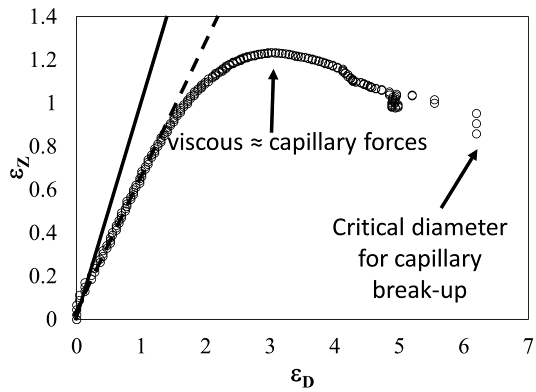

Figure 7: Kinematic curve of a gum solution used for dysphagia treatment illustrating ideal (solid line) and non-ideal behaviour (dashed line), viscous-capillary balance and critical diameter for filament break.

Fig. 8 shows the extensional viscosity of two test solutions sample 1 and 2 normalized to reference sample. While the extensional viscosity of the test fluids at lower strain rates is comparable to the reference, significant enhancement of extensional viscosity is observed at higher strain rates ($>1s^{-1}$). This means that these solutions resist fluid break-up into drops

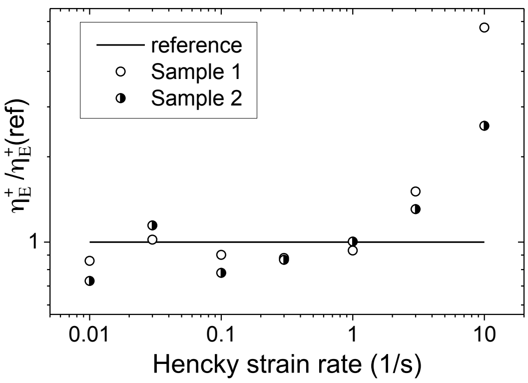

Figure 8: Extensional viscosity of two test solutions sample 1 (open circle) and sample 2 (half-filled circle) normalized to reference solution (solid line)

with 2.6 (sample 2) and 5.7 (sample 1) times the force. This stringiness or cohesiveness of the fluid is an important feature in preventing aspiration as it allows the fluid to move as a single volume and impede break-up into separate drops that could move down both openings of the oesophagus. Both, the proper timing of the fluid transfer from the mouth to the oesophagus (premature or delayed arrival of the fluid) and the cohesiveness of the fluid are important features of solutions for dysphagia care that need to be independently quantified through shear as well as extensional viscosity measurements. The appropriate swallowing models can inform about what the ideal conditions are and from that recommendations can be derived for the formulation of improved dysphagia care fluids.

CONCLUSIONS

In this contribution, we have demonstrated why both, shear and extensional viscosity measurements are of importance to applications of PV silver paste in screen printing. In particular, we demonstrated how new analysis schemes can access time scales relevant to the process and how kinematic information obtained from extensional measurements can inform about tack and stringiness, important attributes of the property profile of a differentiated paste. Furthermore, we demonstrate how these techniques and learnings can be transferred to other applications, namely the study of hydrocolloids used as viscosity modifiers in food applications.

ACKNOWLEDGMENTS

We would like to thank Simon A. Rogers for discussions and Nicolas J. Alvarez for discussions and support with experiments.

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