# Determination and Assessment of the Rheological Properties of Pastes for Screen Printing Ceramics

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ABSTRACT

Understanding the rheological properties of pastes is critical for optimizing the production of ceramic parts central to clean energy technologies by screen printing. At this stage, measurements are largely based on flow curves and yield stress measurements but oscillatory rheology and shear start-up experiments are now being looked at, to provide more insight into the paste rheology. This paper discusses recent results in the use of combined rheological methods to characterize pastes for screen printing.

## INTRODUCTION

The production of ceramic parts by screen printing is a widely used industrial method due to its relative low cost and good reproducibility. Its use in the preparation of solder pastes and printed circuit boards (PCB's) in the electronics industry is well known. Recently, it has been applied to new applications in clean energy production such as Solid Oxide Fuel Cells (SOFC) and oxygen separation membranes.[1-3] In these applications, the requirements of the printed layers and the pastes for printing them are significantly different.

For example, in the preparation of fully dense ceramic layers, suspensions with the high solids loadings (>80 wt.%) must be used. This is to ensure that no voids or cracks are created during sintering. Achieving suspensions with such high solids loadings requires very good dispersion and de-agglomeration of the powders until a homogeneous paste is achieved.

After obtaining a suspension with a high solids loading, it is important that the paste composition is optimized through the addition of organic additives in order that it may be suitable for screen printing in terms of its rheological properties, amongst other characteristics. Binder may also be added to ensure that the printed layers retain green strength for handling after printing and drying. The viscosity requirements and shear rates experienced during the screen-printing process are summarised in Fig.1.

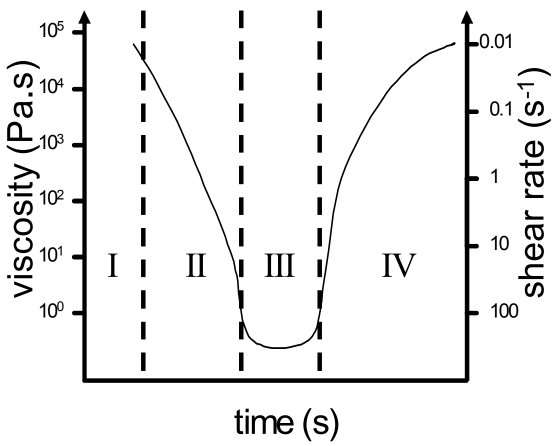


Figure 1.Viscosity and shear rate experienced during the four main stages (I-IV) paste screen printing as a function of time. Stages : I – Rest, II – Squegee, III – Mesh, IV – Recovery.[4]

According to Fig 1., the maximum shear rates experienced during the process are in the order of 1000 $s^{-1}$. Since we need a paste which can flow at such high shear rates, it is important for the paste to be shear thinning as well as thixotropic, for good levelling upon the cessation of shear.

Using rheology to characterize the properties of the inks enables the optimisation of highly concentrated slurries for screen printing applications. While a variety of rheological instruments are available for this purpose, the availability of highly accurate instruments for analyzing thick pastes with a high solids loading and viscosity is somewhat restricted. The use of cone & plate or parallel plate rheometry for this purpose is considered advantageous for its ability to assess both the static and dynamic rheological properties of the pastes. An outline of the parameters which may be obtained by cone & plate or parallel plate rheometry is provided in Fig. 2.

The present work provides a brief overview of the use of cone & plate and parallel plate rheometry for assessing the rheological properties of pastes used for screen printing. A discussion of the usefulness of the measurements and their corroboration with other experimental methods is provided. While initial results are promising, more work is still required to fully understand the capabilities of the rheometer for characterizing these pastes.

EXPERIMENTAL METHOD

Zirconia-based screen printings pastes were prepared as described previously.[1] The pastes consist of an ethyl cellulose-terpineol vehicle in addition to dispersion optimizers such as dispersants and plasticizers etc. Addition of the paste components was done stepwise followed by planetary milling. The pastes consisted of ~ 37 vol.% zirconia.

A Haake RheoStress 600 rheometer was used for all rheological measurements. The sensors used for the measurements were either serrated parallel plates (diameter = 35 mm, gap = 500 μm) for the pastes or a cone & plate for vehicle solutions (diameter = 60 mm, angle = $1^{o}$). The temperature during the experiments was maintained by a DC30 temperature control unit. No Weissenberg-Rabinowitsch correction was performed on the data.

Steady-state flow experiments consisted of a pre-shear of 0.1 $s^{-1}$ for 2 min followed by 2 min rest. Data were collected in logarithmic or linear step mode. Start-up shear experiments were also obtained using a pre-shear of 0.1 $s^{-1}$ for 2 min followed by 2 min rest with varying shear rates applied on new samples for 100 or 1000 s. Oscillatory frequency sweeps were measured at a stress amplitude of 1 Pa. The same pre-shear method was used for the oscillatory measurements.

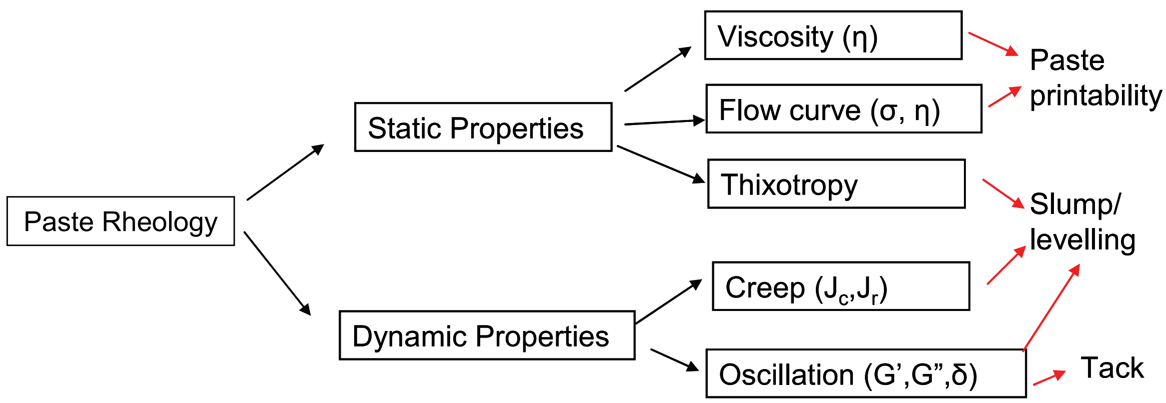


Figure 2. Rheological test protocol for assessing paste properties relevant to screen printing using a cone & plate and parallel plate rheometer.[5]

## RESULTS AND DISCUSSION

### Flowcurves

A typical flow curve for the characterization of the screen printing pastes of a high solids loading is presented in Fig. 3.

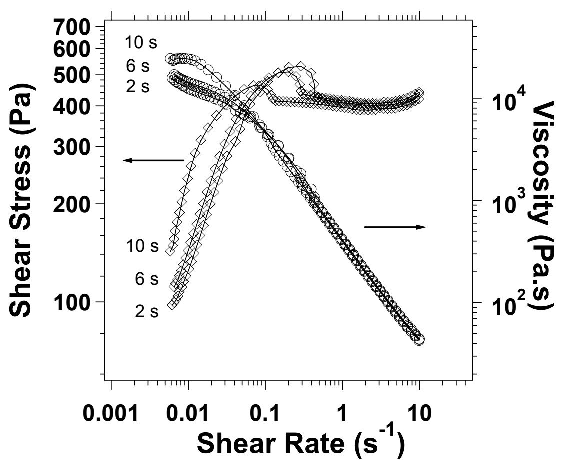


Figure 3. Effect of varying the data step (measuring) time for a shear rate sweep on a concentrated zirconia paste.[1]

The paste exhibits good shear thinning with a viscosity of around 40 Pa.s observed at 10 $s^{-1}$. Previously, commercial pastes suitable for screen printing have been reported to have a viscosity of between 10.6-309 Pa.s (at $\dot{\gamma} = 10\ s^{-1}$).[6] There seems to be no specific requirement for the viscosity however, its combination with other properties is extremely important. In addition, with an increase in the data step (measuring) time, it becomes clear that there is a reduction in the stress overshoot during the shear rate sweep.

Of interest is the fact that the shear sweep, particularly with increasing shear rate, is highly dependent on the data step time with a stress overshoot observed to be more prominent for shorter step times. Clearly, a certain period of time is required before the viscosity and shear stress equilibrate and can be determined with confidence.

Using parallel plate geometry, it was only possible to measure viscosity up to a shear rate of 10 $s^{-1}$ before considerable sample spillage began. The possibility of utilizing different rheometers for these measurements remains, but have not yet been investigated to date.

### Start-up shear

The utilisation of shear start-up experiments for characterizing screen pastes has been sought to further clarify the issue of the shear stress overshoot observed during the flow curves. Fig. 4 illustrates the effect of changing the shear rate during the start-up of shear as a function of time for a concentrated zirconia paste. At this stage there appears to be a discrepancy between whether the observed overshoot is wholly attributable to the paste system or whether it is an instrument artefact. Further experiments are required on higher resolution instrumentation in order to resolve this issue. It appears that there are real and significant trends in the characteristics of the stress overshoot with changing composition of the paste and ink vehicles.[1]

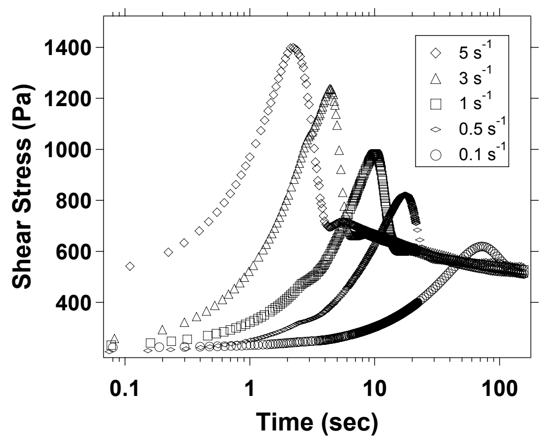


Figure 4. Effect of varying the shear rate on a shear rate start-up experiment on a concentrated zirconia paste.[1]

### Oscillatory Rheometry

While viscosity provides useful paste information for screen-printing, further information regarding the surface properties of the pastes is also required. This is because screen-printing is very much dependent on the (surface) interactions between the paste and the printing mesh, squeegee and printing substrate. Oscillatory rheometry provides the possibility of quantifying the effect of the surface interactions based on an analysis of the viscous and elastic components of the paste as a function of composition over a specified frequency range.

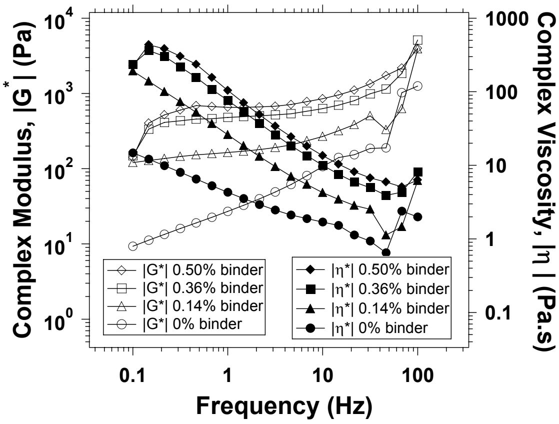


Figure 5. Complex modulus and complex viscosity of concentrated zirconia pastes with different binder content as a function of frequency.

Typical frequency sweeps for concentrated zirconia pastes are provided in Fig. 5 in terms of both the complex modulus and the complex viscosity. The complex modulus represents the vector sum of *G'* and *G"* that characterizes the complete viscoelastic behaviour while the complex viscosity represents the vector sum of the real ($\eta'$) and imaginary ($\eta''$) viscosity. In Fig. 5, *G'* is larger than *G*" and increases upon the addition of binder. This is reflected by the trend in the complex modulus with frequency. Recent literature has suggested that the relative magnitude of the loss tangent ($\tan\delta = G''/G'$) can provide a relative measure of the apparent stickiness or tack of a polymeric or resin pressure sensitive adhesive.[7] If $\tan\delta$ is an intermediate range relative to 0 and 1 (i.e. ~0.5), then it has been correlated to observed sticky properties.[8] While this may be useful for describing the surface properties of polymeric adhesives in terms of fundamental viscoelastic parameters, they have the advantage of being a relatively well-defined system with established characteristics.

However, the validity of making such an analysis for more complicated suspensions of ceramic powders has not been well established. Based on observations for polymeric adhesives, by altering the paste composition to either a high (~1) or low (~0) value of $\tan\delta$, it may be possible to minimize the stickiness. According to Table 1, which provides an illustration of the effect of the composition of zirconia pastes on rheological and screen printing parameters, both $\tan\delta$ and the viscosity were correlated to the tackiness/stickiness observed during screen printing. While $\tan\delta$ tends towards intermediate values (~0.4) with increasing

Table 1. Effect of composition of zirconia pastes on rheological and screen printing parameters.[2]

| *Binder wt.%* | $\eta_0$ (Pa.s) | $\tan\delta$ (at 10 Hz) | $\lvert G^*\rvert$ (Pa) (at 10 Hz) | Stencil clogging | Ink Rolling | Missing | Slumping |
|---|---|---|---|---|---|---|---|
| 0 | 53 | 1.28 | 106.5 | ✓ | ✓ | ✓ | × |
| 0.14 | $1.4 \times 10^4$ | 0.57 | 267.9 | ✓ | ✓ | ✓ | ✓ |
| 0.36 | $8.0 \times 10^4$ | 0.40 | 628.3 | ✓ | × | ✓ | ✓ |
| 0.50 | $1.2 \times 10^5$ | 0.40 | 849.6 | × | × | × | ✓ |

N.B. ✓ or × = good or bad performance

binder content, the complex modulus ($|G^*|$) and the viscosity ($\eta_0$) increase in an almost linear fashion. When the viscosity almost doubles from a binder increase of 0.36 to 0.50 wt.%, the paste stickiness becomes unsuitable for screen printing.

Cleary, there is a complex inter-relationship between the viscosity, tangent loss, complex modulus and the observed stickiness/tack of the paste defining its usefulness for screen printing.

## CONCLUDING REMARKS

A better understanding of the rheological properties of pastes is required in order to optimize the layers formed by screen-printing. While cone & plate and parallel plate rheometry appear to be useful for determining the viscosity of pastes, accurate measurements are limited to shear rates of around 10 $s^{-1}$, and a large step time between measuring data points in order to negate any possible transient effects. Shear start-up experiments have shown that the stress-overshoot is related in part at least, to the composition of the paste. The extent to which the overshoot may be attributed to the instrument requires further experimentation and trials on instruments with higher resolution, particular at short transient times.

Oscillatory data provides a useful method for non-destructively determining the viscoelastic properties of the pastes. However, further work is required to establish if any other physical properties of the paste such as their tack, stickiness or adhesion may be correlated to the oscillatory data. This may include the commission of a study utilizing tack testers or surface tension analysis, in order to quantify the observed properties more scientifically. Such data will greatly enable the development of more rigorous rheological protocols for the characterization and optimization of pastes for screen printing in the future.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Phair, J. W. (2008), “Rheological analysis of concentrated zirconia pastes with ethyl cellulose for screen printing SOFC electrolyte films”, *J. Am. Ceram. Soc.*, **91,** 2130-2137.

2. Phair, J.W., Lundberg, M. and Kaiser, A. (2009), “Levelling and screen printing characteristics of concentrated zirconia pastes”, *Rheol. Acta*, **48**, 121-133.

3. Phair, J.W. Lönnroth, N., Lundberg, M. and Kaiser, A. (2009), “Characteristics of cerium-gadolinium oxide (CGO) suspensions as a function of dispersant and powder properties”, *Coll. Surfaces A.*, **341**, 103-109.

4. Trease, R.E and Dietz, R. L. (1972), “Rheology of pastes in thick-film printing”, *Solid State Technology*, 15, 39-43.

5. Dušek, M., Zou, L. and Hunt C. (2002), “Rheology testing of solder pastes and conductive adhesives – a guide” NPL MATC(A) Report 109, 1-8.

6. Lin H.W., Chang C.P., Hwu W.H., Ger M.D. (2008), “The rheological behaviors of screen-printing pastes” *J. Mater. Process. Technol.,* **197**, 284-291.

7. Mazzeo, F.A. (2002), “Characterization of pressure sensitive adhesives by rheology”, TA Instruments report RH082, 1-8.

8. Mezger, T.G. (2006), "The Rheology Handbook", 1-299.