

# Rheological Studies of Two-Component Inks for Pad Printing on Lenses

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Abstract: Two-component inks are used in the manufacture of coloured contact lens by pad printing. As the ink is reacting through out the print production run, the physical characteristics are continually changing. This has a significant impact on the ink transfer. This paper summarises the results of an extensive experimental investigation into the rheological behaviour of two-component inks and their main components such as binders and slurries. The viscosity of low and high viscosity binders as well as six coloured slurries falls as the shear rate increases, indicating shear thinning behaviour. The test results suggested that binders and slurries are strongly dependent on shear rate, frequency, and temperature. The results from thixotropic loop tests confirmed different degrees of thixotropy for binders and coloured slurries and highlighted a maximum for yellow slurry. At all times the high viscosity binder shows a more elastic behaviour than the low viscosity binder. The elastic component is smaller than the viscous component for both binders. The fact that the low viscosity binder is easier to print is reflected by the lower value of the loss modulus. The results from the flow curve tests confirmed the effect of solvent evaporation and polymerization on ink viscosity over period of four hours. The viscosity of the ink increased with time suggesting polymerisation occurred within the ink. The effects of these physical changes are discussed in relation to the printed properties of the lens and issues of quality assurance.

## Introduction

Pad printing is used for colour printing on lenses as it has the ability to print onto curved surfaces and characteristics that are ideally suited to high precision: thin ink films (typically limited to a dried film thickness of 4 microns), excellent dot reproduction, the ability to print fine line rulings, superior registration and no moiré [1,2]. The dimensions and the quality of the printed dot, hence the

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quality of the entire image, is determined by the ink characteristics, the pad surface characteristics, the engraving definitions, the lens surface characteristics and the pad press parameters. The technological status of the cliché plate and silicone pad development and pad printing machine parameters are not limiting factors. For an experienced pad press operator it is feasible to combine the different, and generally conflicting parameters and come to an acceptable printing result. The ink characteristics, however, are the least controlled, and yet they have an enormous impact on not only the printing behaviour, but also on the final dot definition and colour quality. A limiting factor is the availability of inks with appropriate printing characteristics. Up to now two-component inks for printing on lenses have been developed for their adhesion and hydro expansion behaviour, rather than to accommodate printing requirements.

An understanding of ink rheology and the ability to measure its rheological properties is necessary before its viscous behaviour can be controlled. In pad printing on lenses, rheology is crucial from the time that materials enter the ink manufacturing section to the time that the ink is applied onto the lens and dried. The inks used feature a polymerization process which is likely to affect the ink rheology during printing thus a key part of the study is to explore rheology and polymerization. The ability to measure rheological properties and polymerization is important to ensure product quality and consistency of printing. Standard tests have been developed for the characterisation of complex fluids such as polymer solutions, gels, colloidal suspensions, etc. some of the procedures may be adapted for pad inks. The adaptivity will be explored in the following sections together with results that have been derived from an extensive exploration of the different measurement methods.

### Materials

Ink is made of binder, slurries, solvents and catalyst. Initial ink viscosity is much lower than that of the binder and some slurries due to sufficient amount of low viscosity solvent and catalyst. Standard two-component red ink used in production of coloured lenses was tested along with low and high viscosity binders and six coloured slurries: black, blue, green, red, white and yellow.

### Experimental

The ARES rheometer was used to characterise low and high viscosity binders, six coloured slurries and red ink. Controlled strain for both steady and oscillatory shear measurements in a parallel plate geometry was employed. The set gap between plates was 1 mm for all tests.

### Results and discussion

## Rheological behaviour of binders

As a first step to explore the rheological behaviour of the low and high viscosity binders flow curves (shear stress vs. shear rate) were measured and the viscosity curves were then deduced. The results from flow curve tests showed that the viscosity of the samples falls as the shear rate increases for both high and low viscosity binders for four temperatures (10° C, 15° C, 20° C and 25° C), Figure 1.

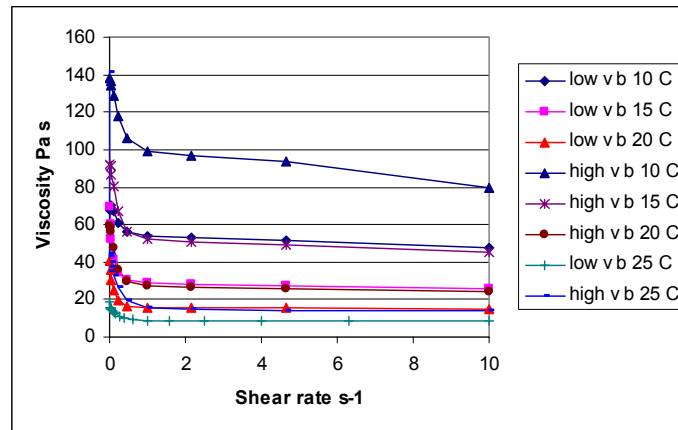


Figure 1. Typical flow curves for low and high viscosity binders for different temperatures

This is indicative of a shear thinning behaviour, particularly below a shear rate of 1 s<sup>-1</sup>. The viscosity is shear rate dependent, but the shear stress versus shear rate curve becomes nearly linear at high shear so permitting an extrapolation to the stress axis. This behaviour is very important for good printing, as the ink must flow easily into the small cells of the image area on the cliché plate. The high viscosity binder displays about 25 Pa s increase in viscosity in comparison to low viscosity binder at 10°C at the shear rate of 0.01 s<sup>-1</sup>. The difference in viscosity between low and high viscosity binders at higher shear rates decreases. The rheological behaviour is strongly dependent on shear rate, which means that during sample loading great care must be exercised to ensure that the sample is not sheared prior to testing.

A simple loop test was performed in order to investigate whether shear thinning of the binder is time dependent. Both the high and low viscosity binders exhibit thixotropic behaviour as the rheogram readings taken at increasing shearing stress differ from those where the shearing stress is being reduced, Figure 2.

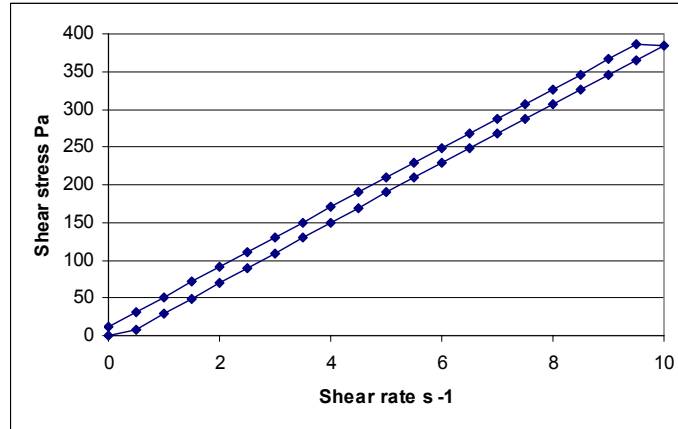


Figure 2. Typical thixotropic loop for low viscosity binder

In addition, oscillation measurements were performed to explore viscous and elastic behaviour. These were performed over a range of frequency and strain rate levels as well as duration.

The dynamic strain sweep test was used to determine the linear viscoelastic range. The ink sample was subjected to a sinusoidal oscillation at a fixed frequency of 1 Hz over a range of strain levels. The strain was gradually increased from a low value of  $0.0001 \text{ s}^{-1}$  to a high value of  $10 \text{ s}^{-1}$ . Storage modulus  $G'$  and loss modulus  $G''$  was calculated as a function of strain. The sequence of the dynamic strain sweep tests was run in order to determine the limits of linear viscoelasticity at four temperatures  $25^\circ \text{C}$ ,  $20^\circ \text{C}$ ,  $15^\circ \text{C}$  and  $10^\circ \text{C}$  for both low and high viscosity binders. Figure 3 illustrates the variation of storage modulus  $G'$ , loss modulus  $G''$  and phase angle for the low viscosity binder at  $25^\circ \text{C}$ .

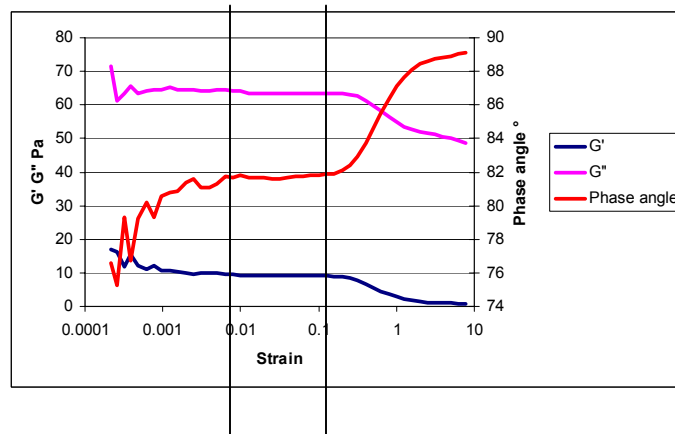


Figure 3. Typical linear viscoelastic range for low viscosity binder at 25° C

At low levels of strain the relationship between strain and storage modulus  $G'$  and loss modulus  $G''$  was erratic and fluctuating. As the strain was increased a range of points was observed where  $G'$  and  $G''$  did not vary significantly indicating linear viscoelastic behaviour. Beyond this range (denoted by two parallel lines in Figure 3) both  $G'$  and  $G''$  fell and the phase angle was increased due to shear thinning of the binder. The phase angle increases at high levels of shear strain. The binder behavior is changing from semi-solid-like to fluid-like as the shear strain is increased.

A similar trend was observed for both binders for all temperatures. The overall result from these tests shows that despite significant variation in storage modulus  $G'$  and loss modulus  $G''$  due to initial viscosity and temperature both binders exhibit linear viscoelastic behaviour within the same shear rate region  $0.01 - 0.1 \text{ s}^{-1}$ .

Figure 4 illustrate typical results from dynamic frequency sweep for low viscosity binder. The rate of shear was sufficiently low to not allow the samples to exceed the linear visco-elastic range. The return sweeps did not deviate from the initial sweeps, as there was no significant physical change in the samples. The tests showed that  $G'$  and  $G''$  increased as frequency of oscillation was increased. The elastic component  $G'$  tends to increase linearly with frequency while the response of the viscous component  $G''$  was more linear as frequency was increased. The sensitivity of  $G'$  and  $G''$  to frequency means that frequency settings used in successive time sweeps need to be consistent if their results are to be compared.

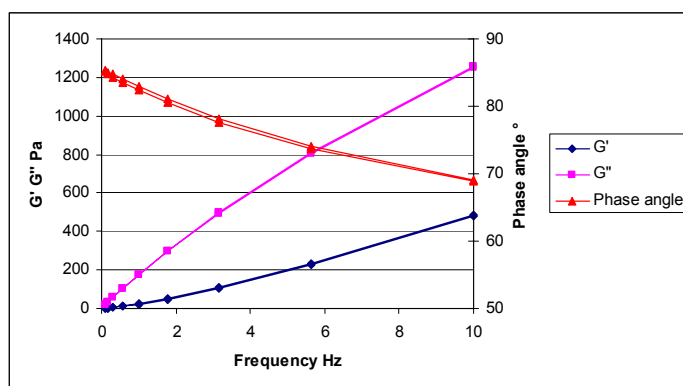


Figure 4. Typical storage modulus  $G'$ , loss modulus  $G''$  and phase angle and their variations for low viscosity binder at 15° C at a fixed level of strain about  $0.01 \text{ s}^{-1}$

Eight dynamic time sweep tests were carried out in order to monitor the buildup or breakdown of a given binder structure at different temperatures. A sinusoidal strain at constant frequency of 1 Hz was applied to the sample. The peak amplitude of strain was equal to  $0.1 \text{ s}^{-1}$  to ensure linear viscoelastic behaviour. Successive measurements were taken every 8 seconds during the entire time interval of the test. Storage modulus  $G'$  and loss modulus  $G''$  were measured, representing the elastic and viscous behaviour of the binders respectively. An example of the results is presented in Figures 5 and 6, where the low viscosity binder is compared to the high viscosity binder.

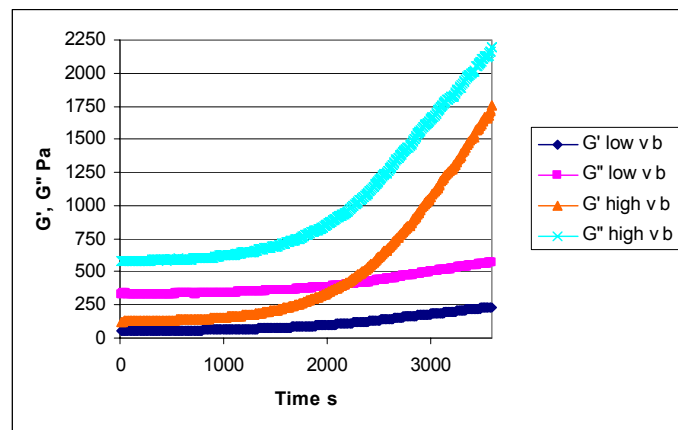


Figure 5. Storage modulus  $G'$  and loss modulus  $G''$  and their variations at constant frequency of 1 Hz over one hour for low and high viscosity binders at  $10^\circ \text{C}$

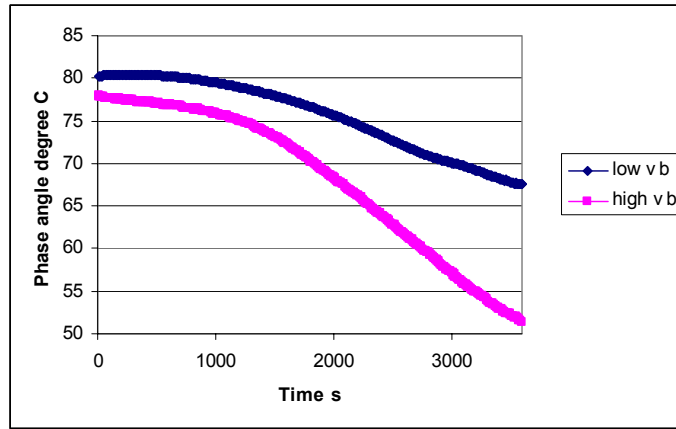


Figure 6. Phase angle and its variation at constant frequency of 1 Hz over one hour for low and high viscosity binders at 10° C

At all times the high viscosity binder shows a more elastic (meaning solid) behaviour than the low viscosity binder. The elastic component is smaller than the viscous component for both binders. The fact that the low viscosity binder is easier to print is reflected by the lower value of the loss modulus.

It should be noted that rheological behaviour of binders is strongly dependent on temperature, which means that during measurements great care must be exercised to ensure that temperature is kept constant. Viscosity is always reduced by increasing the temperature.

#### Rheological behaviour of six coloured slurries

In preparing the slurries for rheometric measurements it was observed that all slurries lacked stability and the uniformity of the slurries varied depending on the colour. In order to get consistent rheometric data and to understand the rheology of the slurries it was vital that the solid and liquid components of the sample to be measured were evenly distributed. This was achieved by sufficient stirring prior testing.

Figures 7 and 8 represent typical flow curves for six slurries at the two most important temperature values of 10°C (close to storage temperature) and 25°C (close to production temperature). The viscosity of the samples falls as the shear rate increases for all slurries for both temperatures, confirming a shear thinning behaviour. The blue slurry displays the highest viscosity followed by yellow, white, red, black and green slurries. The high viscosity blue slurry displays

about 1289 Pa s increase in viscosity at the shear rate of  $0.01 \text{ s}^{-1}$  in comparison with the low viscosity green slurry. The difference in viscosity between low and high viscosity slurries at higher shear rates decreases.

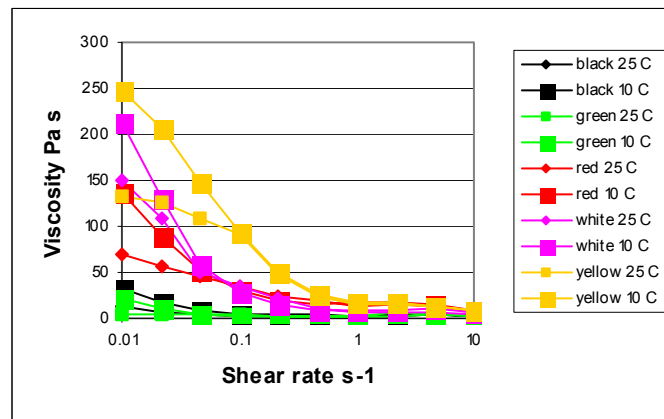


Figure 7. Typical flow curves for five coloured slurries (see legend) at 10°C and 25°C

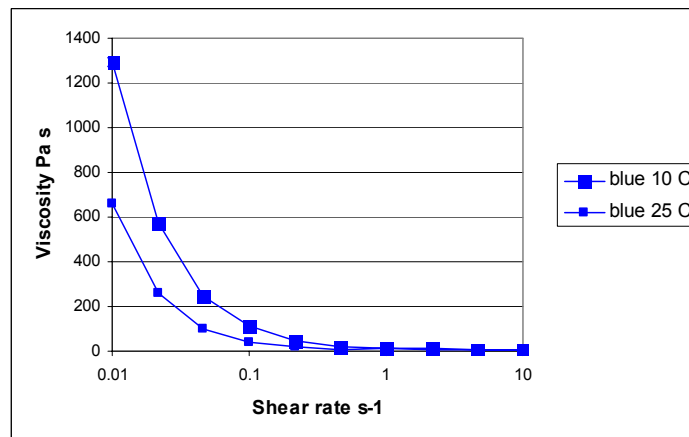


Figure 8. Typical flow curves for blue slurry at 10°C and 25°C

All slurries display thixotropic behaviour (see Figure 9).



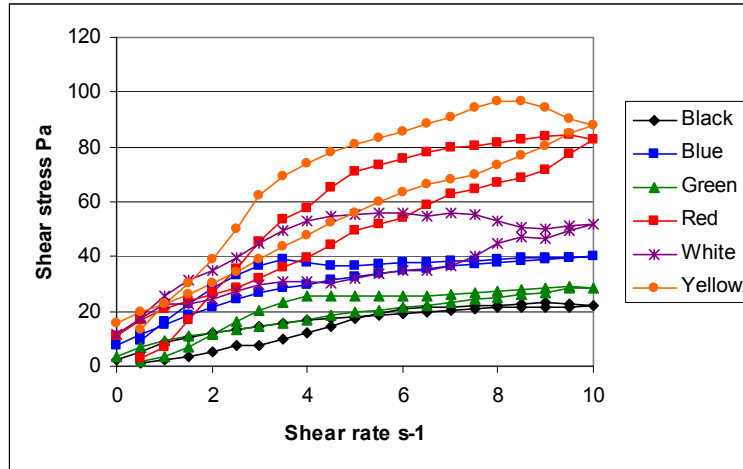


Figure 9. Thixotropic loop for six coloured slurries at 10°C

The results show that the yellow slurry has the highest degree of thixotropy followed by red, white, blue, green and black slurries.

The sequence of the dynamic strain sweep tests was run in order to determine the limits of linear viscoelasticity at two temperatures 25° C and 10° C for the six slurries. The overall result from these tests shows that despite significant variation in storage modulus  $G'$  and loss modulus  $G''$  due to initial viscosity four slurries (red, yellow, white and black) exhibit linear viscoelastic behaviour at the same shear rate of  $0.16 \text{ s}^{-1}$ . The green slurry exhibits linear viscoelastic behaviour at the shear rate of about  $0.13 \text{ s}^{-1}$ . The blue slurry has a narrow range around  $0.6 \text{ s}^{-1}$  where it exhibits linear viscoelastic behaviour.

A series of dynamic time sweep tests were carried out in order to monitor the buildup or breakdown of given slurry structure at different temperatures. An example of the results is presented in Figures 10 and 11, where three slurries (blue, green and yellow) are compared.

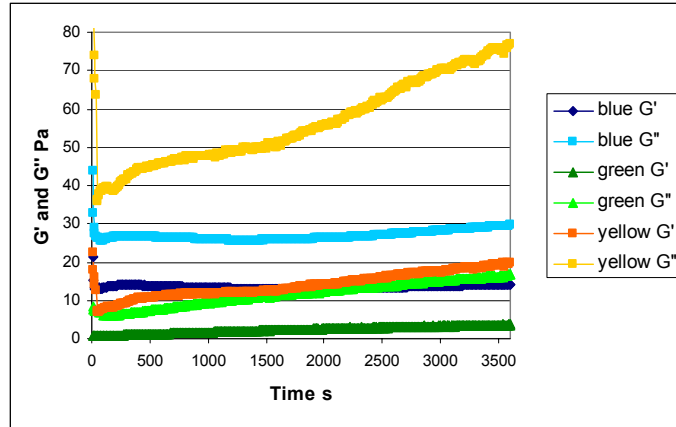


Figure 10. Typical storage modulus  $G'$  and loss modulus  $G''$  and their variations over test time for blue, green and yellow slurries at  $10^\circ\text{C}$

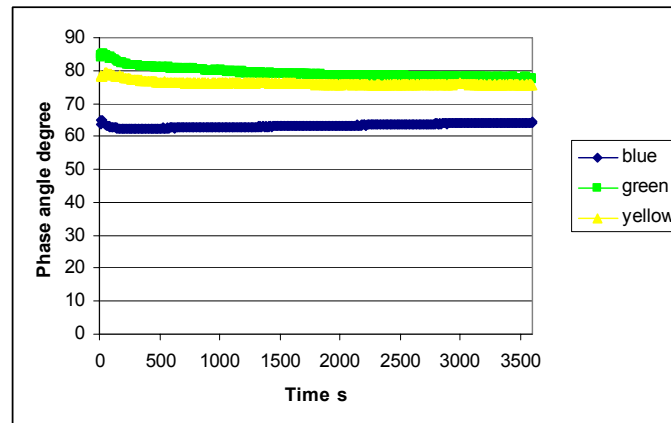


Figure 11. Typical phase angle and its variations over test time for blue, green and yellow slurries at  $10^\circ\text{C}$

At all times the high viscosity yellow slurries show a more elastic behaviour than the low viscosity green slurry. The elastic component is smaller than the viscous component for all slurries. During the test interval both the elastic and viscous components increased dramatically for the high viscosity yellow slurry. Levels of  $G'$  and  $G''$  increased with time while phase angle fell indicating an increasing proportion of the elastic component to the viscous component. At all times the medium viscosity blue slurry shows a more elastic (meaning solid) behaviour than the low viscosity green slurry and a less elastic than the high

viscosity yellow slurry. During the test interval both the elastic and viscous components as well as phase angle remain almost constant indicating that there was no physical change in the sample.

In dynamic frequency sweep, the return sweeps deviate from the initial sweeps for all slurries indicating physical change in the samples. Figure 12 illustrates typical results from dynamic frequency sweep for white slurry.

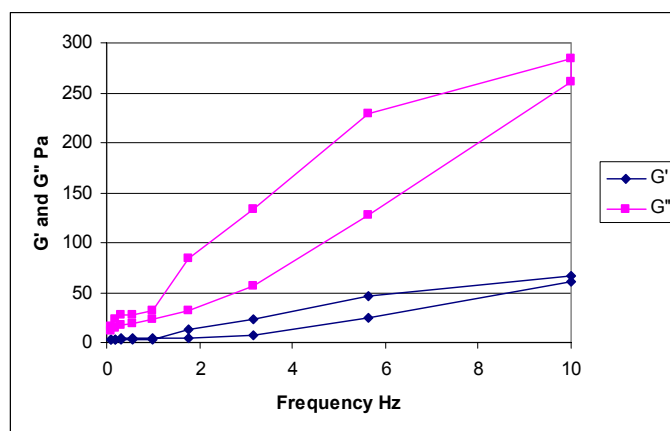


Figure 12. Typical storage modulus  $G'$  and loss modulus  $G''$  and their variations for white slurry at  $10^{\circ}\text{C}$

The test results showed that  $G'$  and  $G''$  increased as frequency of oscillation was increased. The elastic component  $G'$  tends to increase almost linearly with frequency while the response of the viscous component  $G''$  was non-linear and very different for different slurries. This is most likely to be associated with the time dependent processes of breakdown, and the consequent thixotropy. The degree of deviation between upward and downward curves in Figures 12 indicates the degree of thixotropy existing in the white slurry. The sensitivity of  $G'$  and  $G''$  to frequency means that frequency settings used in successive time sweeps need to be consistent if their results are to be compared.

The results from the rheology study for binders and slurries showed significant difference in their rheological behaviour. As the inks are made by mixing of binders and slurries the range of rheological properties will lead to inks having different rheological properties and the need to tune the process for each ink type.

Effect of solvent evaporation and polymerisation on red ink viscosity over time

The aim of this part of the test programme was to establish the affect of solvent evaporation and polymerisation on the apparent viscosity of the red ink during the usual production time interval (four hours).

Rotation rheometry was used to perform simple shear tests. As explained previously, this type of test leads to a simple apparent viscosity. Although these tests were not sufficient to completely characterise the ink, oscillation based measurement could not be performed due to a need for a short test duration while the polymerisation process is active. There was only enough time for the flow curves measurements from which the viscosity curves were then deduced.

The ink comprises slurry, binder, solvent and a catalyst designed to initiate polymerisation. Polymerisation is unwanted before printing as it is thought to affect the rheology of the ink and hence the consistency of the print quality over time. For this reason the ink was made up and tests were performed to establish the changes in rheological behaviour of ink that occur over that four hour time period. The red ink was made up and then divided into two halves, the first was sealed for the duration of the tests and the second was exposed to atmosphere for the duration of the tests. It was impossible to completely prevent evaporation of the solvent from the sealed jar. The solvent loss from the sealed jar occurred only during sample loading. The viscosity of the ink samples was measured at 30 minute intervals over a four hour time period.

The change in viscosity with time of the sealed and open ink samples, over the range of shear rates, is given in Figure 13.

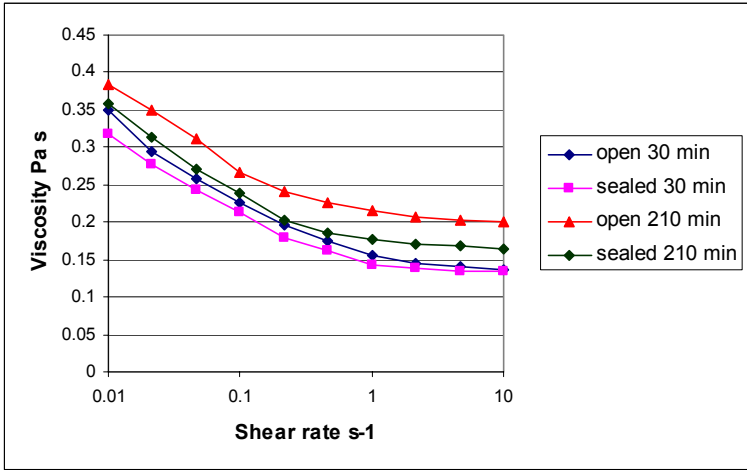


Figure 13. Change in viscosity over time for open and sealed ink samples

At all shear rates the viscosity of the ink from the open jar is slightly higher than that from the sealed jar indicating a higher rate of solvent evaporation in the open jar. The viscosity of both sealed and open ink samples increased with time suggesting polymerisation occurred within the ink. The open ink sample had a higher viscosity, as a greater proportion of its solvent content was lost to evaporation.

### Conclusions

The laboratory rheological tests suggested that both main components of ink binder and slurry are strongly dependent on shear rate, frequency and temperature. This confirmed the shear thinning characteristics of binders and slurries. This means that during QC measurements great care must be exercised to ensure that a sample is not sheared during loading or stirring and its temperature is kept constant. The results from thixotropic loop tests confirmed a different degree of thixotropy for different binders and coloured slurries and highlighted a maximum for a yellow slurry.

The main result from rheological study showed that both the binders and slurries possess viscoelasticity and can be characterised most fully using a mixture of steady and dynamic (oscillation) tests. The viscous response to deformation predominates over the elastic response even at the lowest tested frequency. The  $G'$  and  $G''$  values showed a large frequency dependence especially at higher frequencies.

A simple flow curve test was used to explore the effect of solvent evaporation and polymerization on red ink viscosity over ink lifetime. The viscosity of both sealed and open ink samples increased with time suggesting polymerisation occurred within the ink. The open ink sample had a higher viscosity, as a greater proportion of its solvent content was lost to evaporation.

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