

REAL TIME MEASUREMENT OF CURE IN INKJET INKS

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Abstract

We report on the development of an ultrafast version of the Lambient LFT631 dielectric cure monitor. Data points may be obtained 10x faster than is achievable with earlier instruments, or indeed by the well-known FTIR, rheological and DSC approaches. The sensors are sufficiently small that they can be mounted on a laboratory transport system that mimics the action of the press. Results at realistic printing speed (50m/min) will be presented.

Introduction

Achieving satisfactory cure is a critical consideration for UV technology and yet formulators still depend heavily on subjective tests such as thumb twist, scratch and adhesion. There has long been a desire to find a more objective measure of cure, especially one that allows real time measurement as the polymerisation reactions progress under industrial conditions

One common approach for acrylate systems is to measure the consumption of carbon-carbon double bonds by infrared absorption. Uncured acrylate absorbs strongly at about 1408cm^{-1} and double bond conversion may be estimated by evaluating the extent to which this peak disappears during cure. The technique is particularly well suited when cure involves more than one type of functional group as the consumption of each may be independently evaluated – for example in systems where there is co-cure of acrylates and vinyl ethers¹. However, the rate of acquisition is relatively slow (typically 16 spectra per second if working with an MCT detector).

Another widely reported technique is to use DSC to monitor the heat that is released as a consequence of bond formation during polymerisation. There are however a number of limitations, notably that the film thickness is significantly greater than for some coating applications, and it can be problematic to achieve a constant thickness throughout the sample because of the meniscus effect on the edge of the pan². The consequence of that is that self screening by the photoinitiator can be a significant problem, ie the cure is not homogeneous within the sample because the UV light is significantly attenuated by the time it reaches the bottom of the film³. Further, the rate of data acquisition is quite slow, and clearly it is not possible to make use of the DSC method for in-line measurements on printing equipment. Nevertheless, the approach has been shown useful in laboratory studies^{4,5}.

There has also been considerable use of photo rheology as a means to follow the progress of curing reactions. In this case one plate of a parallel plate rheometer is replaced with quartz so that the

sample may be irradiated. The change in rheology is then monitored via an oscillation experiment so that G' and G'' are determined as a function of time⁶. This is actually a rather challenging experiment because to be rheologically valid the imposed strain must be maintained throughout the curing process; the stress required to achieve that is initially very small but rapidly becomes much larger. If one wishes to follow the curing reaction in real time it becomes necessary to slow down ink polymerisation by reducing the light intensity, and to use a very small diameter plate so that the rheometer still has sufficient torque to move it as the sample starts to cure. The point at which G' and G'' become equal is widely defined as the gel point and is considered important in determining when the system no longer has sufficient mobility for further curing reactions to occur⁷. In order that the data is rheologically reliable, it is necessary to set a gap of about 50 μ m or more, and this brings problems for light penetration in the same way as has been previously discussed for DSC. Realistically the approach is only useful for inks that are not pigmented.

Inkjet presses are now commonly used for label printing, typically operating at about 40-75m/min. It is common practice to partially cure the ink with LED immediately after printing (pinning) and then to finish off the curing process with an arc lamp at the end of the press. The time for the print to pass under each lamp is about 0.1s and the time delay between LED pinning and final cure with an arc lamp is typically between 1 and 2 seconds. It is a relatively simple matter to characterise the final cure state by infrared or by extracting unbound molecules into solvent and then quantifying by GC-MS or LC-MS. However, if one wishes to obtain real time data on the progression of the curing reactions under industrial conditions it becomes necessary to generate a succession of data points on a timescale of 50ms or less.

Dielectric analysis

At its simplest level, dielectric analysis requires the application of a sinusoidal voltage across a sample and detection of the resulting current. That current may be either totally in phase with the applied voltage (purely conductive behaviour) or its phase may lead the applied voltage by an amount that depends on the degree of capacitive behaviour (90° for an idealised capacitor). Application of a sinusoidal voltage therefore allows both the conductivity (loss part) and capacitance (storage part) of a sample to be accessed.

All samples have an inherent conductivity which depends on the movement of ions or other charge carriers in the formulation. As the material cures the ability of those species to move is restricted and therefore the conductivity decreases by at least one order of magnitude. Studies have shown that a good correlation exists between resistivity (the reciprocal of conductivity) and viscosity, resulting in the widespread use of the term ion viscosity as a surrogate for resistivity⁸. The data in this paper is presented as the log of that ion viscosity.

The technique is widely applied for the monitoring of thermoset formulations, although to date only a few papers have been published regarding application to radiation curable systems^{9,10,11}. Data acquisition times, where quoted, were in the 50-400ms range. The dielectric approach was attractive to Domino because data points could in principle be acquired faster than by infra-red or rheology, and because it is the only technique for which the sensor could be passed under industrial UV lamps on a laboratory transport system.

The experiments reported herein were undertaken with a Lambient High Speed Analyser (LTF631) with the electronics modified by the manufacturer to improve the data acquisition rate from approximately one data point every 70ms to one data point every 6ms (so called Ultrafast Option). Most tests were run at 100Hz as this gave smoother data and with less noise than at higher frequencies (it is not necessary to wait for a full cycle to extract a data point). The sensors were of the fringing field type, ie a comb type arrangement of the electrodes that is planar and therefore suitable for the application of a thin film followed by UV irradiation to cure. Mini-Varicon sensors have proved pragmatic and are just large enough to accommodate drawdown by Kbar. Tin plated copper electrode tracks are set at 100 μ m intervals on a Kapton (polyimide) support. The fringing field penetrates about 100 μ m into the sample which is more than adequate for thicknesses of interest for inkjet.

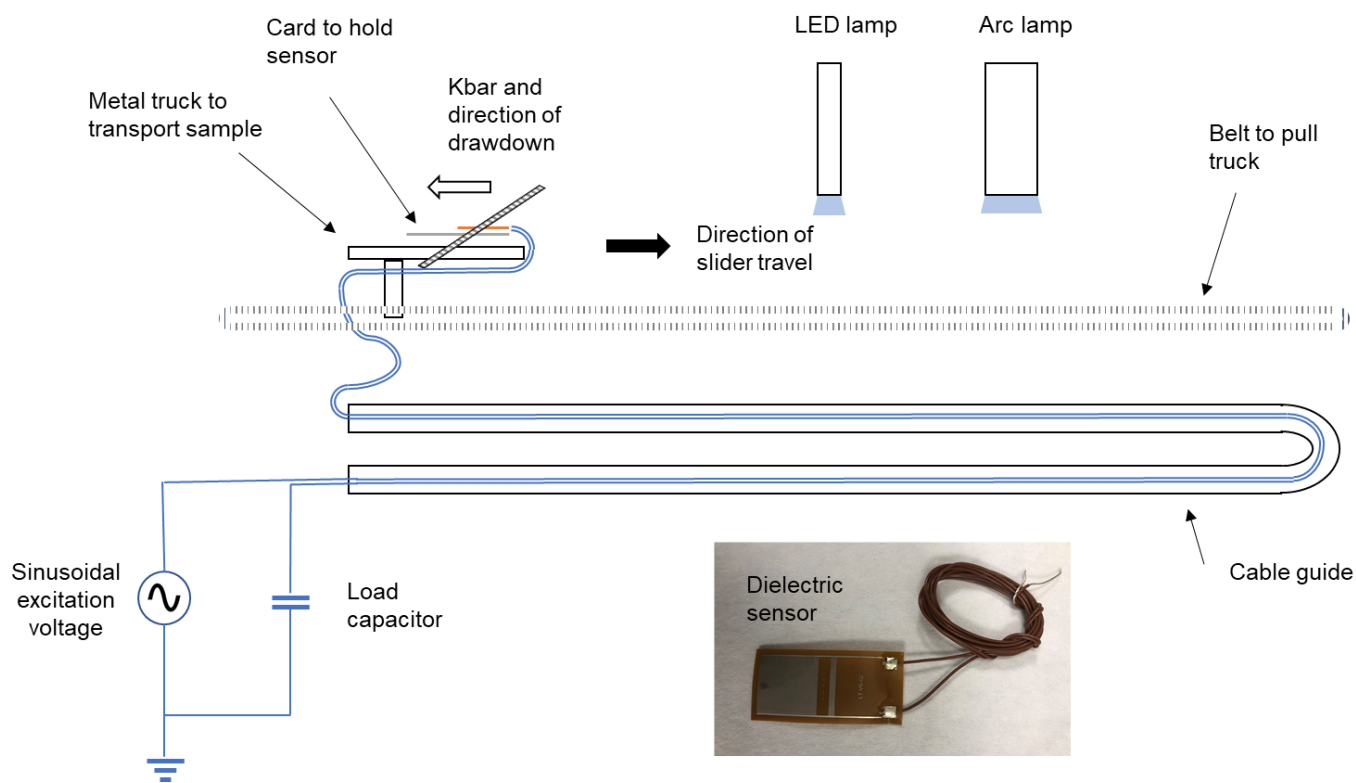


Figure 1. Schematic of the experimental set up. The dielectric sensor is shown in orange. The drawdown was prepared in-situ on the truck so as to minimise the delay before passage under the lamps. Dielectric measurement was made in a floating electrode configuration (here simplified for clarity) – the response measured is the voltage generated across the load capacitor which depends on the properties of the sample.

The sensor was taped to a non-absorbent card to help hold it in position such that an ink film could be cast with a Kbar. The top of the sensor was protected from short circuit due to excess ink by applying tape. It also turned out to be critical not to let any wet material (ink or solvent) accumulate underneath the sensor as this gives an alternative conduction path which can be important after curing. The card and sensor were mounted on a laboratory transport system (slider) which allowed the entire

assembly to be moved under LED and mercury arc lamps at a speed which can be made representative of commercial printing. The LED lamp was a Phoseon FP300 395nm rated at $20\text{W}/\text{cm}^2$; this delivers a dose of about $240\text{mJ}/\text{cm}^2$ when the slider operates at $50\text{m}/\text{min}$ and with the lamp at full power. The arc lamp was a Baldwin CoolArc operating with an iron doped bulb and delivering about $210\text{mJ}/\text{cm}^2$ of UVA at $50\text{m}/\text{min}$ and at full power. The experimental set up on the slider is shown schematically in Figure 1.

The irradiance profile of the lamps was measured with an EIT PowerMAP and is shown in Figure 2. It is seen that the duration of exposure in each case is about 0.1s.

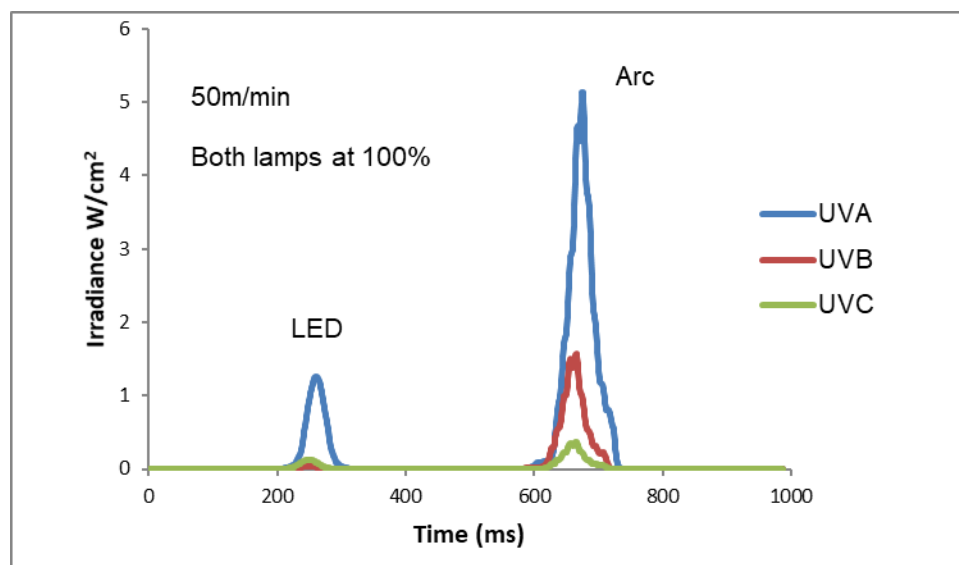


Figure 2. Irradiance profile of 395nm LED and Fe doped arc lamp as experienced at $50\text{m}/\text{min}$

Results

Figure 3 shows the cure response as a function of film thickness for a simplified yellow ink. The first point to note is that, prior to cure, the log ion viscosity decreases with increasing film thickness. This is not surprising because we might expect a thicker film to conduct better (ion viscosity is the same as resistivity), although the relationship with ion viscosity is not linear (Figure 4). The ion viscosity in the wet state offers a way to check whether the film has been successfully and evenly applied with the Kbar (although the numerical value is expected to depend on the nature of the formulation).

The second point to note from Figure 3 is that there is a decrease in log ion viscosity when the sample is first exposed to the lamp and this effect increases for greater film thicknesses. This is attributed to the heating effect of the lamp which causes a decrease in viscosity and therefore an increase in conductivity - until the point at which the curing reactions start to dominate. At 24 and $40\mu\text{m}$ the full depth of the ink is not cured and a skin sits upon the bulk of the ink which is heated by the lamp; these results are included to illustrate the thermal effect. Of course, the final (average) cure state of the ink as evidenced by the log ion viscosity at 12 seconds is highly dependent upon the film thickness.

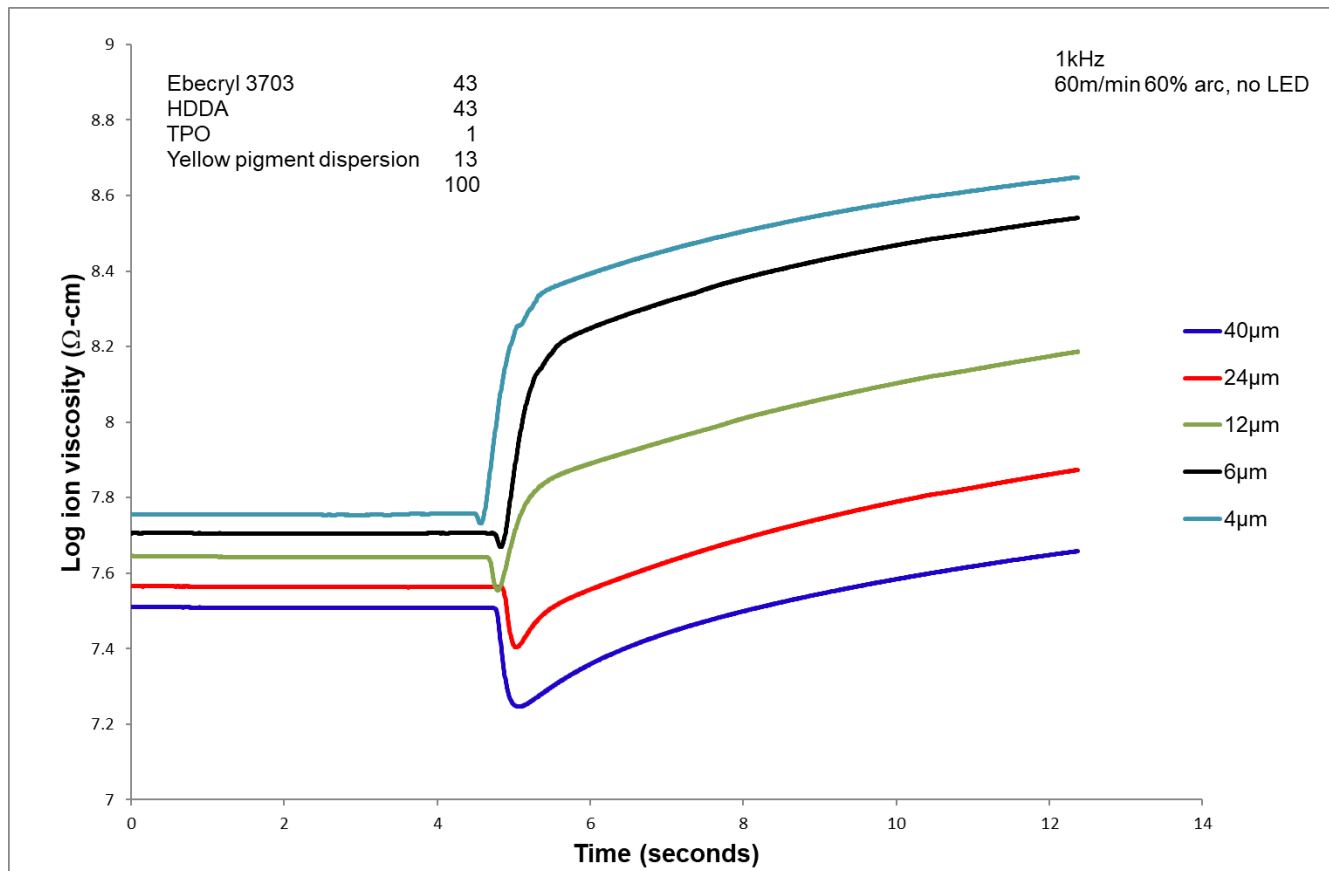


Figure 3. Dielectric response as a function of film thickness (Kbar)

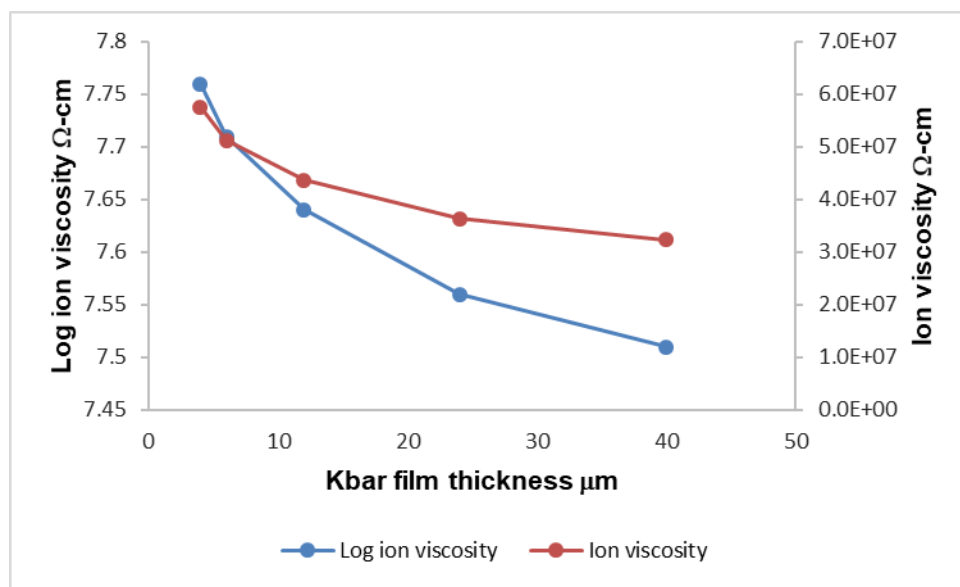


Figure 4. Relationship between ion viscosity and film thickness

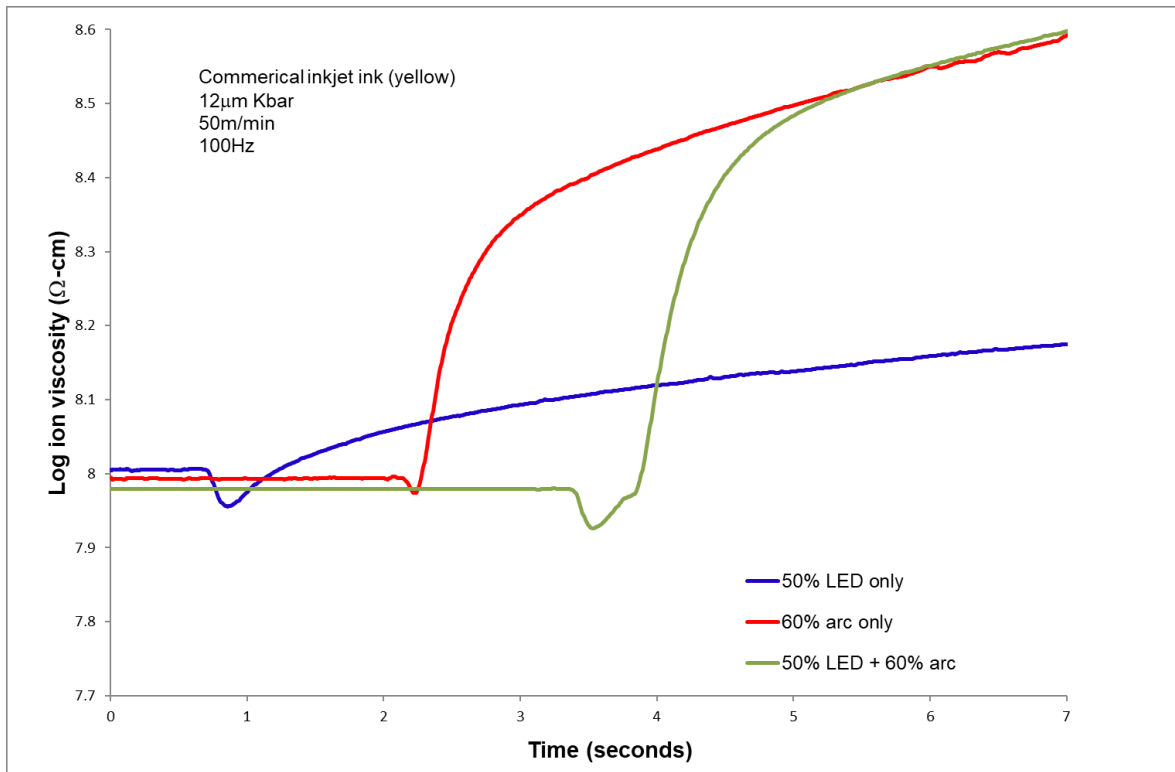


Figure 5. Time resolution of cure by LED and arc lamps

Figure 5 shows the cure response of a yellow inkjet ink that is supplied commercially for drop on demand application on self-adhesive labels. The ink film was prepared at 12μm and the data shows the effect of curing with LED (395nm) and arc lamps separately and together. The arc lamp shows a smaller decrease due to the initial heating effect because it initiates the curing reaction much more effectively. When the two lamps are used in quick succession the arc cure is seen to superpose on the LED response before thermal equilibration and post-cure have run to their full extent.

The data of Figure 6 offer several insights into the parameters influencing the test results. The blue graph shows the (partial) cure response of a yellow inkjet ink exposed to a modest dose of 395nm LED (pinning conditions). The dielectric measurement was restarted a few seconds later (as a second test; red graph), and the log ion viscosity is seen to be higher than it was prior to pinning. Instead of moving the test sample under the lamps, hot air was applied to the sensor for about 2 seconds and the log ion viscosity was seen to decrease – as expected because the charge carriers are more able to move through the sample. The subsequent recovery of the log ion viscosity happens with the same trajectory as when the sample was originally cured – suggesting that the apparent curing that takes place between about 1 and 10 seconds after exposure is predominantly a thermal effect (the sample cools and the charge carriers become less mobile on account of the increasing viscosity).

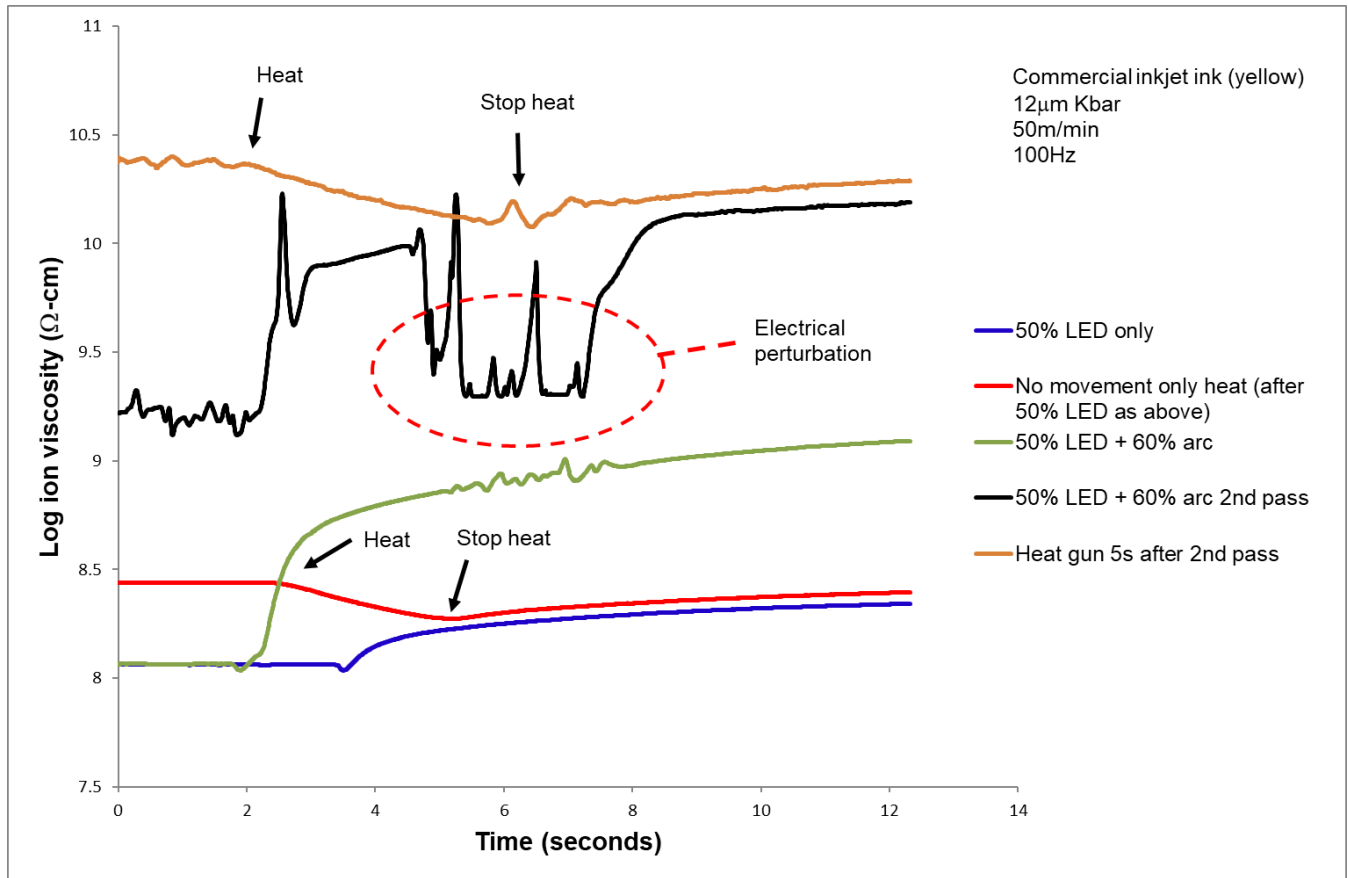


Figure 6. Thermal and electrical effects

A fresh sample was tested with sequential LED and arc curing (green graph). The perturbations between about 5 and about 8 seconds are caused by the movement of the slider as it returned to the starting position. The slide and cure cycle was repeated on the cured ink (black graph). It is seen that the starting log ion viscosity is similar to the final value of the previous test, but that the second passage under the lamps causes a further increase in ion viscosity by an order of magnitude (ie the conductivity was already small but some further crosslinking has caused it to further decrease by a factor of 10). This time there was a much larger perturbation caused by the returning slider; The movement induces tiny currents in the sensor wiring which are not sufficient to affect the result when the conductivity is high (wet ink), but which become dominant when the response from the (now cured) sample to the applied voltage is very small. Finally (brown graph) it is shown that applying heat to the double cured ink causes a similar change in ion viscosity as occurred with the ink which had only been pinned – although now with a less smooth response as we are on the limit of the ability of the sensor to detect conductivity.

Figure 7 shows the effect of curing with different lamp powers. As expected, curing is both faster and more complete as the lamp power is increased. The data are sufficiently good to allow calculation of the differential as a measure of reaction rate (inset).

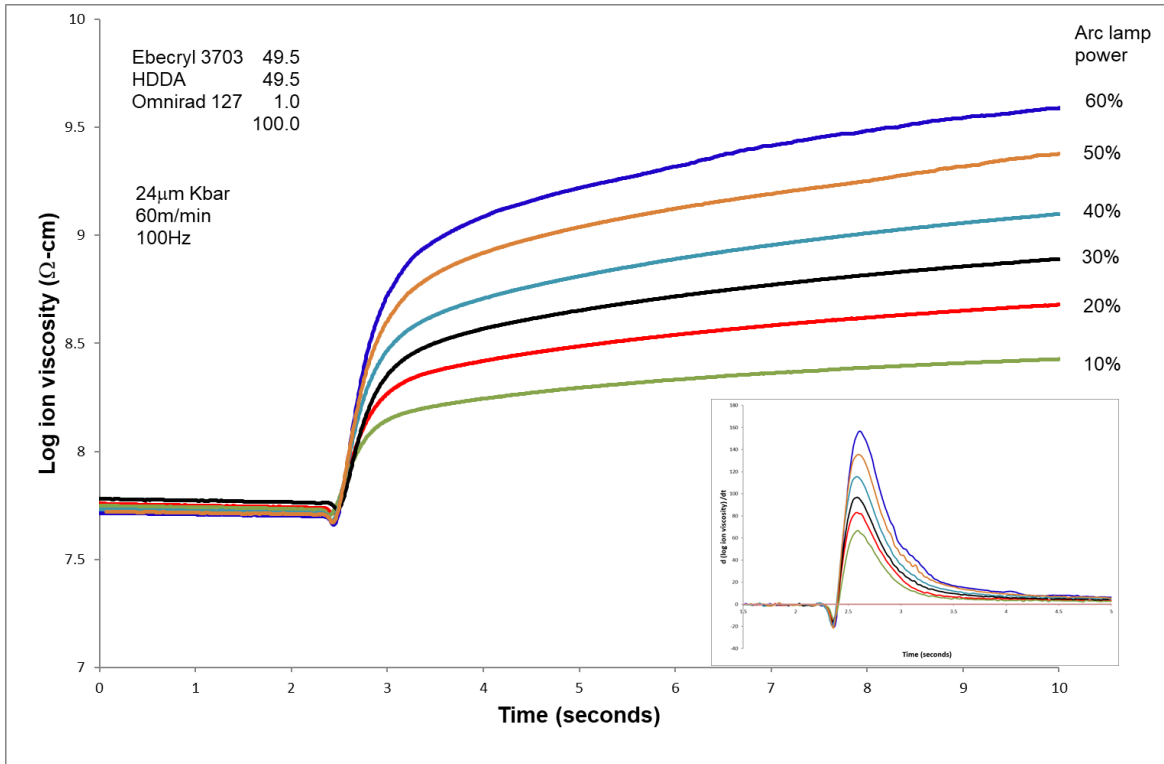


Fig 7. The effect of lamp power. The data has been shifted on the time axis so that the start of cure is coincident. The inset shows the rate of change of log ion viscosity.

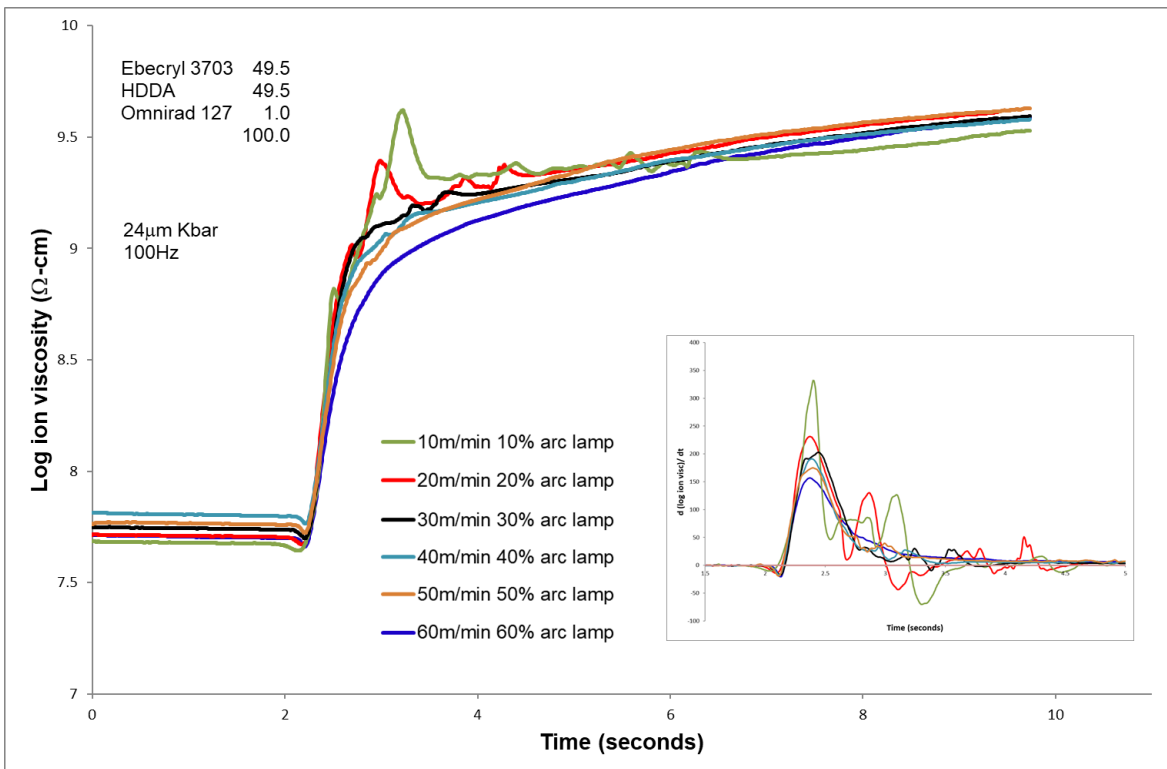


Fig 8. Cure response at constant UV dose.

In Figure 8, the power of the arc lamp has been adjusted to match the speed of the slider so that the same dose was delivered over different timeframes. In all other respects the data are equivalent to those in Figure 7. The results are seen to be quite consistent, both in terms of the final response after 10s and the rate of cure. This is a little surprising given that at 10m/min the slider will take about 0.6 seconds to pass the lamp; the fact that the response is apparently not slowed according to time necessary to deliver the full dose may reflect uncertainty about when the slider first passed the lamp as judged by the initial thermal decrease (the magnitude of which should also be dependent on dose delivered rather than slider position). It is also noted that the electrical perturbations became worse (and lasted longer) as the slider speed decreased.

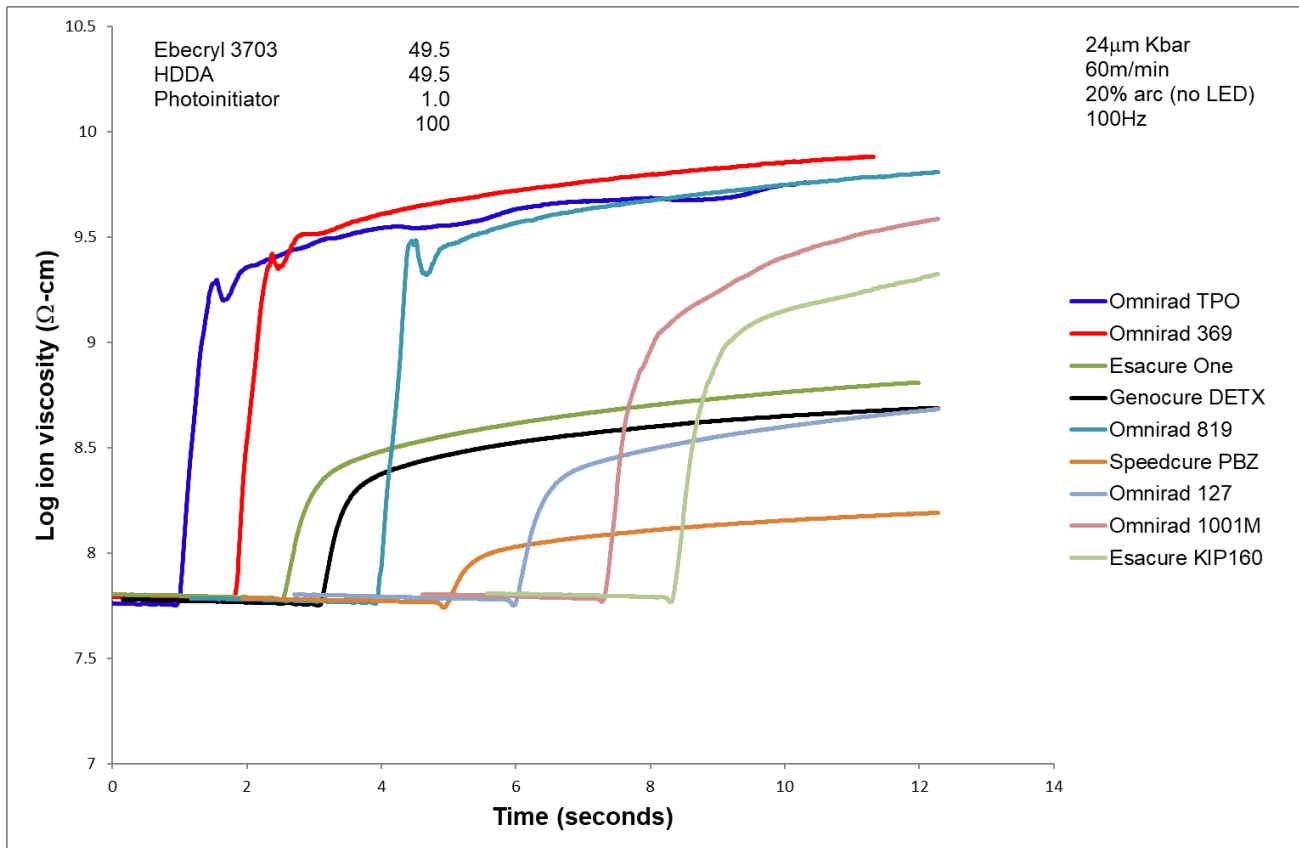


Figure 9. Comparison of photoinitiators in a varnish. Ebecryl 3703 is an amine modified epoxy acrylate.

Finally, in Figure 9 a selection of photoinitiators were tested at 1% content in a simple varnish. The dielectric responses were broadly in line with expectations of cure performance, with Omnirad 369 and the phosphine oxides (Omnirad TPO and Omnirad 819) performing well - here on a relatively thick film.

Conclusions and comments

Dielectric measurements have been used to monitor UV curing with a data point logged every 6ms. That is sufficiently fast to monitor curing processes occurring on a sub-second timescale. It has been shown that it is feasible to mount the sensors on a laboratory transport system operating at the same speed as a commercial inkjet press. The technique works well during the early stages of cure when the conductivity of the sample is high and the electrical response from the sensor is large. However, when the sample is well cured, the sample response becomes very small and may be insignificant compared with currents induced in the wiring when in motion. It has not so far been possible to fully eliminate that effect either by screening the wires or by placing the interface board on the moving slider so that the connections are kept as short as reasonably practicable. It is also important that the ink film applied wets the sensor well so that a film of uniform thickness is obtained; an unexpected value for the pre-cure resistivity can be an indicator of inconsistent drawdown preparation. Our experience has been that it is easier to achieve consistent drawdowns on the sensor with inks of artificially high viscosity (100-200mPas) although this does also have implications for oxygen inhibition.

Interpretation of the results is not straightforward. The profiles obtained are a superposition of cure and thermal effects, the latter continuing for at least several seconds after cure. It is however clear that the process associated with LED pinning is not complete by the time the print reaches an end of press arc lamp.

The parameter measured is resistivity (aka ion viscosity) and this gives different information about the curing process than would be afforded by infrared analysis or DSC. As such the dielectric technique should be regarded as complimentary to other techniques for monitoring cure rather than as a replacement for them.

Acknowledgement

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