Localised Broadband Curing of Directly Written Inks for the Production of Electrical Devices for Aerospace Applications

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Abstract: Direct Write (DW) technologies afford the possibility of printing electronics and sensors directly onto structural components. This allows advantageous weight saving by making good use of available space through conformal printing whilst adding functionality. To enable DW fabrication of devices onto large aerospace structures a localised processing method is required. This paper investigates the feasibility of using a broadband thermal spot curing system for processing DW Inkjet and Polymer Thick Film (PTF) materials onto composite structures. The characteristics of spot cured tracks were compared to conventional oven cured tracks and were shown to exhibit equivalent resistances.

Keywords: Direct Write, Additive Manufacturing, Polymer Thick Film Inks, Inkjet Inks, Curing Kinetics

1. Introduction

Direct Write is a term describing processes that allow the addition of functional materials onto an existing surface. These materials are deposited in computer-generated patterns to enable the additive manufacturing of components. Fabrication of electrical devices using Direct Write (DW) printing processes, have particular advantages where the key drivers are low weight and low volume production. Given the high durability of DW materials and development of DW conformal printing capabilities[1] there are a number of applications in the aerospace industry where this technology can be utilised. These include low power interconnects, passive devices for structural health monitoring, and micro-strip antennas[2,3,4].

DW materials come in a number of different variants specific to the DW technique employed. The most common DW materials include thermosetting and thermoplastic Polymer Thick Film (PTF) inks and inkjet solutions. These compositions are usually loaded with some form of functional element such as conductive or dielectric particles. Once deposited these materials require thermal processing in order to solidify them, conventionally achieved by using an oven. This requirement can present a challenge when fabricating DW elements onto large aerospace structures which are increasingly constructed out of composite materials such as carbon fibre. Composite materials such as carbon fibre are sensitive to the relatively high temperatures needed to cure or sinter DW ink compositions (typically above 120^{o}C). One solution to this problem is to employ a localised heat treatment approach.

A number of investigations have explored localised curing using a laser source to process DW materials such as PTF and Inkjet inks[5,6,7]. One of the biggest advantages of laser processing is that heat is restricted to a small area thereby minimising thermal penetration into the substrate surface[8]. Furthermore, if the source can be integrated within the DW system then heat treatment can take place *in situ* with printing. This enables DW processing onto large structures and removes re-registration problems that could occur when printing devices with multiple material layers.

Optimal localised processing is dependant on generating a sufficient heat rise within the material which is distributed evenly throughout the material layer. The heat rise will be dependant on the heat capacity of the composition and the coupling efficiency of the laser power to the ink sample. According to Beers law, the amount of energy that can be coupled into a material is dependant the absorption coefficient of the material which can change as a function of wavelength and material composition. The distribution of heat is a function of the penetration depth of the EM radiation and thermal conductivity of the material. The substrate can also play a part in curing the inks and can act as either a heat sink or insulator[5]. One disadvantage of laser heating is that radiation is only generated at a single wavelength. For materials which have absorption bands at different of even multiple wavelengths the majority of the energy may be lost.

This paper focuses on investigating the suitability of PTF ink compositions for localised broadband curing as an alternative to laser processes. By implementing a broadband spot curing system[9] the curing performance of deposited silver based thermosetting PTF inks were compared to oven cured samples. In addition both inkjet and thermoplastic PTF silver inks were also tested for broadband curing.

2. Methodology

For this investigation two conductive thermosetting PTF inks, a silver ink and a hybrid ink[10] were studied for their suitability for localised broadband curing. Both conductive inks contain silver flakes (30μm diameter 2μm thickness) dispersed (approximately 60% in volume) in the same thermosetting epoxy resin binder which is designed to cure/crosslink at temperatures as low as 90^{o}C. The recommended oven curing temperature for this resin as stated by the manufacturer is 130^{o}C for 30mins; this allows the composition to achieve high flexibility, good adhesion and electrical conductivity. The hybrid ink contains an additional organo-metallic component. At high temperatures (>160^{o}C) the organo-metallic component in this 'hybrid ink' decomposes into silver nano-particles which fuse, thereby increasing the electrical conductivity of the composition.

To determine if PTF inks are suitable for localised curing (i.e. high thermal energy for short exposure times) it is necessary to characterise how temperature and time affect the curing kinetics of PTF inks. The degree of curing for thermosetting resin system can be characterised by the glass transition temperature, Tg, which can be measured using Dynamic Mechanical Analysis (DMA). As the silver and hybrid inks are based on the same resin system it was only necessary to conduct DMA on samples of the resin binder which was cured at different temperatures and times.

To determine the benefits of broadband curing for PTF inks spectral analysis was conducted for the silver, hybrid and resin binder compositions using a UV/Vis spectrometer from 300nm to 3500nm. In addition, a dielectric thermoplastic PTF ink was also investigated for its spectral properties[10]. Transmission spectra were obtained by coating glass slides with a thickness of approximately 40μm of ink. Reflection measurements were made by placing ink samples into an integrating sphere to capture all the reflected radiation. The corresponding absorption percentage was then plotted as a function of wavelength for all inks. The absorption coefficient, α, can also be calculated from this data using the Beer-Lambert law given in Equation 1. From this the penetration depth, δ, can be calculated (Equation 2) and plotted against wavelength.

$$I(z) = I_0 e^{-\alpha z} \qquad \text{Equation 1}$$

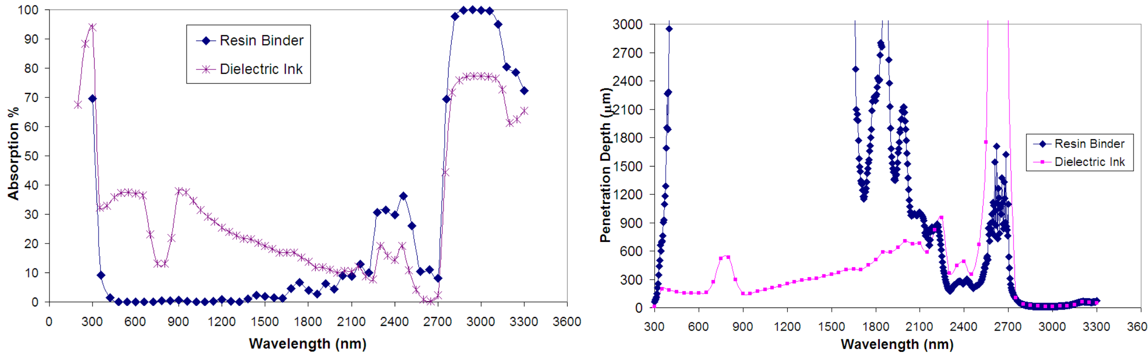
$$\delta = \frac{1}{\alpha} \qquad \text{Equation 2}$$

Where, I(z) is the incident radiation (100%) minus the reflected radiation, I_o is the transmitted radiation, α is the absorption coefficient, z is the film thickness and δ is the penetration depth.

Only conductive ink samples were tested for broadband localised curing. To prepare the samples the inks were screen printed with consistent dimensions (100mm x 1.5mm x 0.04mm) onto composite FR4 substrates. FR4 was chosen as it is a non-conductive composite structure. The IR Photonics AS200 iCure^{tm} system uses an optical fibre to deliver broadband (300nm to 3500nm) thermal energy from a 200W mercury vapour lamp[9]. The Full Width Half Maximum (FWHM) spot diameter from the fibre is 2.4mm with a standoff height of 9mm from the surface of the ink track. Track resistance measurements were made after successive passes with the iCure^{tm} system and then compared to equivalent oven cured samples. Measurements were made for the silver and hybrid conductive PTF inks as well as silver inkjet[13] and thermoplastic inks [14].

3. Spectral Analysis of Polymer Thick Film Inks

A Varian Cary 5000 UV/Vis spectrometer was used to analyse the spectral properties of air dried thermoset PTF silver and hybrid inks as well as the unfilled resin binder and thermoplastic dielectric ink. For all measurements, background spectra were removed from the results beforehand.

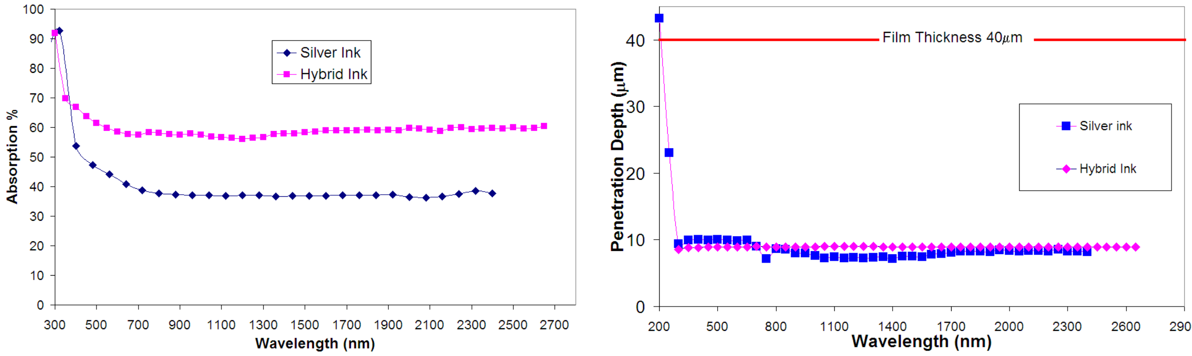


(A) (B)

Figure 1: A) Absorption spectra unloaded resin binder and dielectric ink. B) Penetration depth as a function of wavelength in the resin binder and dielectric inks

The resin binder with no silver present has a number of absorption bands primarily at UV and the mid to high infra-red (above 2700nm) wavelengths. Between these wavelengths most of the radiation will penetrate straight through the resin (Figure 1B) however, at certain wavelengths it can be seen that the resin could be heated uniformly depending on the film thickness. The dielectric system also contains a number of absorption bands almost identical to the resin system. A broadband system such as the iCure^{tm} would be able to take advantage of all these absorption bands. This could be particularly useful for thick dielectric layers which would rely on the penetration depth as opposed to its thermal conductivity.

A downside to broadband curing could be the issue of unwanted radiation i.e. radiation that could penetrate through the ink sample into the substrate material. Whilst this could aid the curing process by transferring heat to the ink via heat conduction, it may be undesirable for temperature sensitive substrates.



(A) (B)

Figure 2: A) Absorption spectra unloaded resin binder and dielectric ink. B) Penetration depth as a function of wavelength in silver and hybrid inks.

The results in Figure 2 A show that the silver inks and hybrid inks only absorb approximately 40% and 60% of radiation above 400nm respectively. Comparison of this with the calculated penetration depth in Figure 2 B shows that the majority of this radiation only penetrates 10µm into the ink layer (approx 25% of the film thickness), the rest of the radiation is reflected away. As the ink layer is composed from silver, the high thermal conductivity of the sample should compensate for low penetration depth. This could pose a problem for thicker films where the heat energy might not be distributed so evenly. There is however, strong absorption in the UV wavelengths which is capable of penetrating further into the ink layer.

The normalised intensity output from the iCure^tm system is plotted as a function of wavelength in Figure 3. This shows that the system compliments the absorption bands in the PTF inks by delivering power in both the UV and mid IR regions.

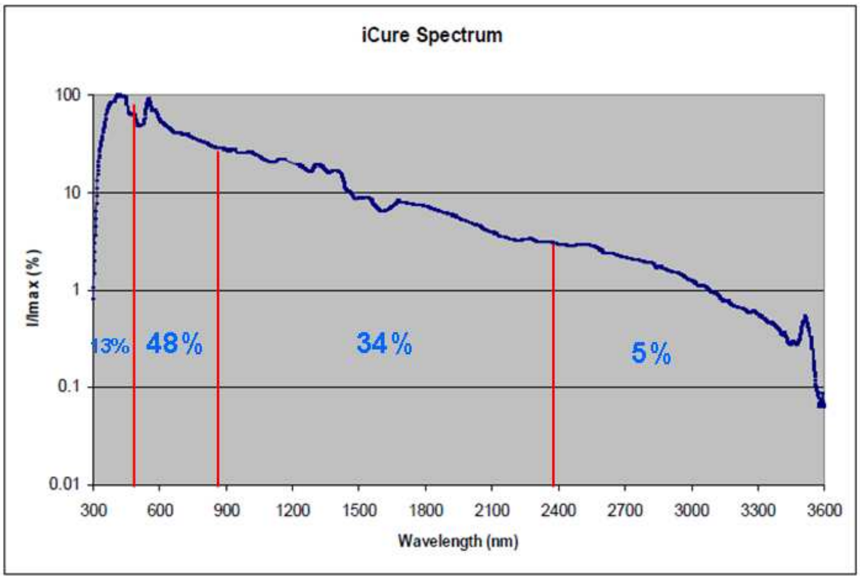


Figure 3: Output spectrum from iCure^tm system normalised to the maximum intensity of the system (I/Imax) the distributed power from the iCure^tm is also indicated as a percentage of the total power[9]

4. Thermal Analysis of DW Polymer Thick Film inks

For DMA analysis, steel coupons were coated with approximately 40µm of the unfilled resin binder and heated at a rate of 10°C/min from 25°C to 170°C at an oscillating frequency of 5Hz. Steel coupons were used as they are unaffected by DMA and therefore isolate the ink layer for testing. DMA measures the glass transition temperature (Tg) as a peak maxima in the tanδ curve[11]. Figure 4 shows that for a constant oven curing time, the tanδ curve shifts to the right (indicating an increase in Tg) and becomes narrower and better defined (indicating an increasing degree of cure) as the curing temperature increases. No further increase could be achieved after a Tg of 137°C is obtained. In this state the ink is said to be fully cured and will achieve its greatest physical and electrical properties. Table 1 compares the peak maximum in the tanδ curves as a function of curing time for cure temperatures of 120°C and 220°C respectively. A glass transition temperature of approximately 90°C can be achieved by curing the resin at 220°C for 5mins, compared to curing at 120°C for an hour. This suggests that localised processing times can be greatly reduced if the inks are heated to high temperatures.

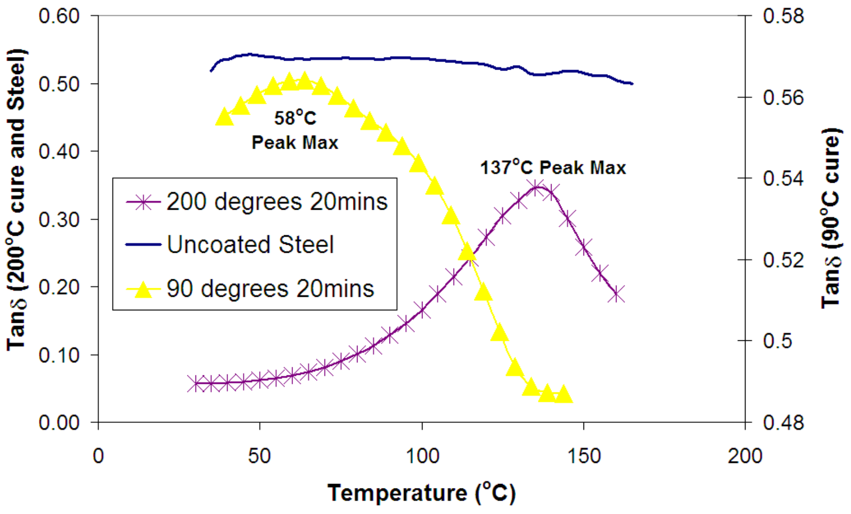


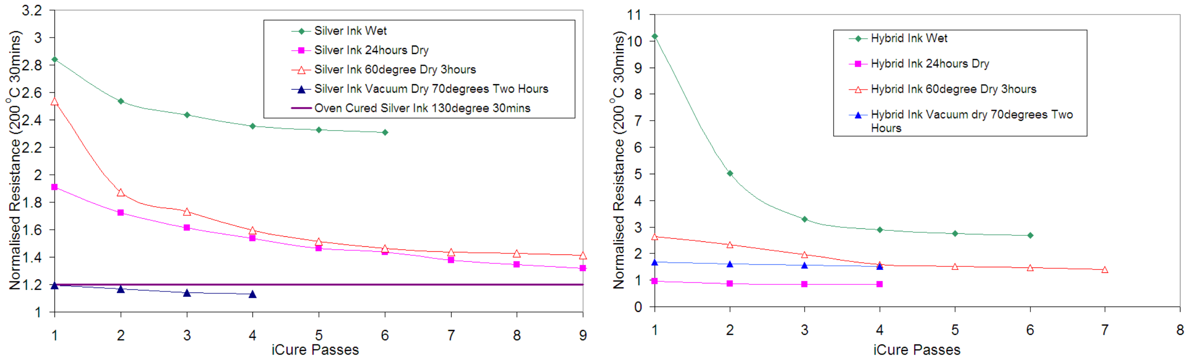
Figure 4: Characteristic tanδ curve for unloaded resin system cured for 20mins at 90°C and 200°C

Cure Temperature (°C)	Cure Time (mins)	Tanδ Peak Maximum (°C)
120	5	Insufficiant Curing
120	20	73
120	60	93.2
220	1	68
220	5	98
220	20	136

Table 1: Comparison of peak tanδ against cure time for 120°C and 220°C

5. Broadband Spot Curing of Thermosetting Silver PTF Inks

For consistency the traverse speed of the iCure^{tm} system was kept constant at 4mms^{-1} and the energy density of the spot was altered by changing the output power only. For comparison, a sample of each ink was cured in an oven at 220°C for 20mins to achieve maximum crosslink density. According to the manufacturer this temperature will also be sufficient enough to cause nano-particles in the hybrid ink, to sinter[10]. Oven cured measurements were conducted on ceramic substrates since FR4 has a maximum operating temperature of 130°C. Oven cured hybrid inks exhibit lower track resistances (0.77Ω) than silver loaded inks (1.01Ω) when printed with the same film thickness (40µm). Average resistance measurements for iCure^{tm} silver and hybrid ink tracks were normalised against their respective oven cured values and plotted as a function of the number of iCure^{tm} passes over the track (Figure 5 A, B). At first all ink tracks were processed with the iCure^{tm} system whilst wet. When the power was kept constant the resistance of these tracks decreased asymptotically with the number of passes until only a small reduction in resistance was observed. Upon inspection of these tracks it was found that the surface roughness of these tracks was significantly higher than their oven cured counterparts (Table 2). High surface roughness can be problematic for high frequency application such as transmission lines and antennas[12]. It was hypothesised that the main reason for the high surface roughness was the fast evaporation of the volatile solvents within the ink. In order to remove these solvents without curing the ink a number of processes were employed. These included air drying the sample for 24 hours, pre-treating samples in an oven at 60°C for 3 hours and finally vacuum oven drying under 1000mbar at 70°C for 2 hours. The resulting performance of these samples after iCure^{tm} processing is also shown in Figures 5 A, B and Table 2 for the silver and hybrid inks.



(A) (B)

Figure 5: A. Normalised resistance (against 200°C 30min oven cured silver inks) for successive iCure^{tm} passes at 4mms^{-1} traverse speed, 5W power for Silver inks using different pre-treatment methods, B. Normalised resistance (against 200°C 30min oven cured hybrid inks) for successive iCure^{tm} passes at 4mms^{-1} traverse speed, 5W power for Hybrid inks using different pre-treatment methods

	Silver Ink		**Hybrid Ink**	
Process	Ra (µm)	Feature Size (µm)	Ra (µm)	Feature Size (µm)
Oven Cured 200°C 30mins	2.565	N/A	1.53	N/A
iCured 5W Wet	26.47	N/A	15.11	N/A
iCured 5W 24hour Dry	12.6	30	5.11	N/A
iCured 60°C 3hr Oven Dry	43.55	120	22.3	40
iCured 5W 70°C 2hr vacuum oven dry	2.835	N/A	1.65	N/A

Table 2: Comparison of silver and hybrid track surface roughness, Ra, after iCure^{tm} treatment for different pre-treatment methods. If blistering is present then average height of blisters is also included.

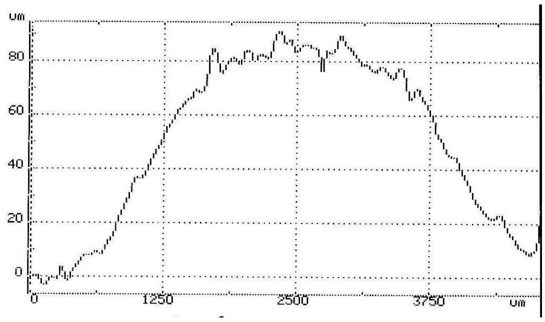


Figure 6: Alpha-step image of surface defect present on an iCure^{tm} silver track which is pre-treated in an oven at 60^{o}C for 3hours

Figure 5 A and B show that when wet, the resistance of the silver and hybrid inks is the highest when iCure^{tm} processing. The surface roughness of ink samples were measured using a Tencor Alpha-step 200 (Table 2, Figure 6). Oven cured hybrid tracks exhibit the lowest surface roughness as a consequence of nano-particle sintering within the inks. When processed in a wet condition the surface roughness of the hybrid and silver inks increases by almost 10 times the oven cured value (Table 2).

If dried for 24 hours the surface roughness of the silver and hybrid inks reduces, however, the silver inks start to blister after iCure^{tm} processing. The resistance of these tracks after iCure^{tm} processing was also improved. Although silver tracks exhibited resistances 40% higher than 200^{o}C oven cured resistances and 20% higher than 130^{o}C oven cured resistances after 9 passes. The hybrid ink on the other hand was able to achieve resistances equivalent to 200^{o}C curing after a single pass. This could be a combination of the lower reflection of the hybrid ink (Figure 2 D) when compared to a silver ink and the ability of the nano-particles to sinter when subjected to high temperatures.

When pre-treated in an oven for 60^{o}C for three hours the average surface roughness of the silver and hybrid inks increases dramatically due to blistering of the tracks. The silver ink tracks for example can contain blisters typically 80-120µm in height (Figure 6). Although the pre-treatment temperature is not high enough to significantly cure the ink it seems that this causes solvent to be trapped within the ink layer. This blistering also appears to affect the resistance of the ink which is higher when compared to air dried ink tracks. Another significant consequence of blistering is that the adhesion of the inks tracks could be reduced.

By vacuum drying the ink tracks at elevated temperatures the surface roughness can be reduced dramatically with values only 10% higher than oven cured samples. For silver tracks this also seems to assist its ability to cure under the iCure^{tm} system with resistances lower than 130^{o}C oven cured tracks obtained after a single pass. This resistance is still approximately 15% higher than 200^{o}C oven cured samples. The Hybrid ink tracks do not follow the same trend with resistances almost 50% higher than those obtained when ink is air dried. One explanation for this could be due to the formation of large air gaps between the nano-particles as solvent is removed via the vacuum thereby hindering their ability to sinter efficiently.

Figure 7 shows ink tracks that were pre-treated in a vacuum oven and processed with the iCure^{tm} for different powers. As mentioned previously increasing the number of passes is not sufficient as the resistance reaches an asymptotic value. However, as shown in section 4 temperature can be more predominant than exposure time when curing PTF inks. This is reflected in the results in Figure 7 which shows how effective temperature or incident iCure^{tm} power is more successful at reducing resistance than increasing the number of iCure^{tm} passes. When vacuum dried, the silver inks are able to achieve oven cured ink resistances after four passes at 6.5W. The hybrid ink has nominally higher resistance than oven cured tracks (approximately 4%) however, this value was achieved at a lower power of 6W. Significantly, at theses powers there was no visual damage to the surface or cross-section of the FR4 substrate.

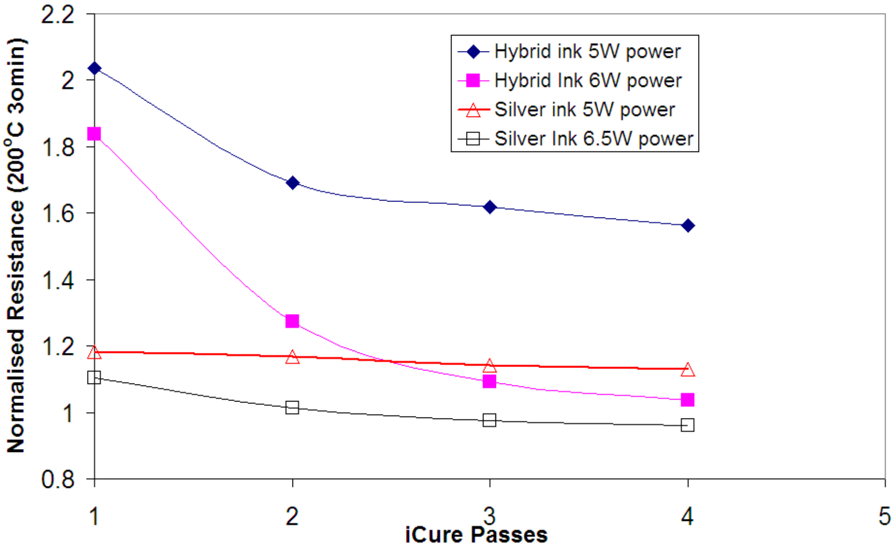


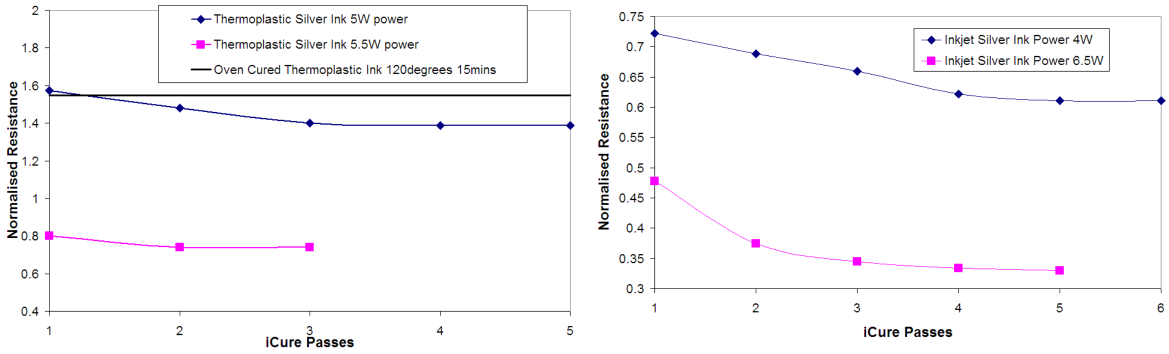
Figure 7: Normalised resistance (200°C 30min oven cured) vacuum dried silver and hybrid ink tracks cured at different iCure^{tm} powers

6. Broadband Spot Curing of Silver Inkjet and Silver Thermosetting Silver PTF Inks

As before silver ink-jet[13] and silver thermoplastic[14] inks were printed onto FR4 substrates with track dimensions of 100mm by 1.5mm. Inkjet samples required printing via a Microfab MJ-ATP 80µm head attached to an X/Y motion stage. The droplet size was approximately 150µm in diameter when printed at 1000 Hz at 80mm/s. To build a track width of 1.5mm an overlap of 120µm was used between each inkjet track. Thermoplastic inks were screen printed in the same manor as the thermosetting inks.

The recommended cure for the thermoplastic silver ink is 120°C for 15mins. These parameters result in a resistance of 1.16Ω when printed with a track thickness of 40µm onto a ceramic substrate. When cured at 200°C for 30mins the track resistance reduces further to 0.75Ω. The inkjet ink is composed of silver nano-particles in a solvent based solution. Nano-particle sintering takes place at temperatures above 150°C. Oven cured resistances for inkjet tracks with a thickness of 2µm on polyamide substrates were 2.7Ω and 8Ω when cured at 330°C and 180°C for 30mins respectively.

The surface roughness of both inks was significantly higher when processed whilst wet with both inks containing blisters. The inkjet ink also exhibits poor adhesion and delaminates from the substrate very easily. High surface roughness in the thermoplastic ink could be easily reduced by air drying the sample for a few hours or heating at 60°C for 60mins resulting in a surface roughness of 1.45µm. The inkjet silver ink on the other hand required temperatures above 100°C for 120mins before the solvent could be removed. The inkjet track however had the lowest surface roughness with a value of 630µm. Resistance results for both oven dried inkjet and thermoplastic silver inks are given in Figure 8 A, B.



(A) (B)

Figure 8: A. Normalised Resistance (against oven cured tracks, 200°C 30min tracks) of pre-treated (oven, 60°C 1hour) silver thermoplastic ink tracks against successive iCure^{tm} passes for different powers B. Normalised Resistance (against oven cured track 330°C 30min tracks) of pre-treated (oven, 60°C 1hour) silver inkjet ink tracks against successive iCure^{tm} passes for different powers

The thermoplastic ink requires the least amount of pre-treatment to remove solvent content and at 5.5W is able to achieve resistances 20% lower than those obtained at 200°C oven curing. These track resistances were obtained by using less power than the thermosetting silver inks described in section 5. Similarly the resistance of the inkjet inks are far superior than their oven cured counterparts when pre-dried in an oven. At 4W only one pass was needed to obtain a track resistance nearly 25% below a sample cured in an oven at 330°C for 30mins. Even better resistances could be obtained at 6.5W resulting in a resistance almost 75% better than an oven cured sample after 3 passes. Again no visual damage was observed on the surface or cross-section of the FR4 at these powers. One of the reasons that such low resistances might be obtained in inkjet tracks when compared to other compositions is that a greater density of silver is able to be obtained without hindrance from a resin binder.

7. Conclusions

Optimum localised processing of DW inks requires generating a high heat rise at relatively short exposure times whilst heating the ink layer uniformly. Track resistances must be equivalent to oven cured samples and if possible surface roughness should be reduced for high frequency applications.

Spectral analysis of different thermosetting PTF inks has shown that there are number of different absorption bands present across a wide range of wavelengths. Silver inks for example show particular large absorption in UV wavelengths whilst dielectrics and resin systems have absorption bands at mid to high IR as well as UV wavelengths. For inks with particularly low thermal conductivity such as dielectric compositions the penetration depth of the radiation is important as this will be predominant when heating the ink layer uniformly. A dielectrics material measured here was shown to have a larger penetration depth at higher wavelengths, of particular consequence for thick film curing. Investigation of the curing kinetics of DW thermosetting PTF inks has also shown that if the temperature of cure is high enough, curing times can be greatly reduced. These results indicate that these inks lend themselves well to high power, localised, broadband curing.

Silver and Hybrid silver/organo-metallic inks were successfully cured onto composite FR4 using IR photonics iCure^{tm} system. Although low resistances could be achieved the surface roughnesses of the cured inks was shown to be higher than their oven cured counterparts. To minimise high surface roughness, inks were pre-dried in a vacuum oven (70°C for 2 hours at 1000mbar) to remove volatile solvent content before processing. By optimising localised processing power, it was shown that resistances equivalent to that of oven cured tracks could be achieved whilst obtaining low surface roughnesses.

Silver Inkjet and thermoplastic PTF inks were also tested for iCure^{tm} processing. Again solvent content was a factor in causing high surface roughness effects. The inkjet inks also showed a visible reduction in adhesion. Solvents were easily removed from the thermoplastic ink by air drying or oven drying at 60^{o}C, however, inkjet inks required temperatures greater than 100^{o}C to remove solvents. As this process did not require a vacuum it suggests that iCure^{tm} system itself could be used to dry the inks if low powers are used. For these inks it was shown that localised processing was able to achieve much lower resistances than oven cured tracks.

Although the thermoplastic ink required the least amount of pre-treatment before processing via the iCure^{tm} system, thermoplastics are not as resistant to harsh environments when compared to thermosetting inks and therefore might not be as suitable for aerospace applications[1]. In terms of track resistances and surface roughness inkjet inks produce the best results. However, these inks require high temperature pre-treatment and the adhesion of inkjet tracks can be lower than PTF inks. One suggestion to improve the ability of PTF inks for localised curing could be to reducing the solvent content within the inks or to implement lower boiling point solvents.

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REFERENCES

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[1] Unpublished work in the Direct Write Elements and Sensors (DW EASY) project, 2009, http://www.dweasy.co.uk/project_7.asp

[2] Wilhelm, M. J., Weme, D. H., Wemer, P. L., Church, K., Taylor, R., 2002, Direct Write Processes as Enabling Tools for Novel Antenna Development, Antennas and Propagation Society International Symposium, IEEE

[3] Piqué, A., and Chrisey, D.B., 2002, Direct-Write Technologies for Rapid Prototyping Applications, Academic Press, San Diego

[4] Panitz, M, Hope, D. C., Sato, T., Harley, C. D., 2009, The Opportunities and Challenges for Wireless Interconnects in Aircraft, Proc. IMechE. Part G: Journal of Aerospace Engineering, Prof Eng Publishing

[5] Sato, T., Fearson, E., Curran, C., Watkins, K. G., Dearden, G., Eckford, D., 2009, Laser-assisted Direct Write for Aerospace Applications, Proc. IMechE. Part G: Journal of Aerospace Engineering, Prof Eng Publishing

[6] Ko, S. H., Pan, H., Grigoropoulos, C. P., Luscombe, C. K., Fr' eschet, J. M. J., Poulikakos, D., 2007, All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles, Nanotechnology, IOP Publishing, 18, 345202

[7] Marinov, V. R., 2004, Electrical Resistance of Laser Sintered Direct-Write Deposited Materials for Microelectronic Applications, Journal of Microelectronics and Electronics Packaging, Vol 1, pp261-268

[8] Kinzel, E., 2005, Laser Micro Fabrication of Thick-Film Microelectronics Thesis, Purdue University

[9] iCure^{tm}, http://www.icure-irphotonics.com/, last accessed on 05/08/09

[10] Gwent Electronic Materials Ltd Silver ink (C2050712D58), hybrid ink (C2080929D6), dielectric ink (D2091022D2), Available from www.g-e-m.com

[11] Fried, J. R., 2003, Polymer Science & technology, Second Edition, Prentice Hall, ISBN 0130181684, pp208-214

[12] Marinoc, V., Atanasov, Y., 2006, Improved Direct Write Technology for High Frequency Interconnects on Flexible Substrates, Proceedings of IMAPS 2006, 39th International Symposium on Microelectronics, San Diego, California, 8-12

[13] Suntronic Jettable Silver U5714, datasheet available from SunChemical, www.sunchemical.com

[14] Acheson Electrodag 725A silver ink, http://tds.loctite.com/tds5/docs/ELECRODAG%20725A%20(6S-54)-EN.PDF, last accesses on 09/07/2010