



HAL
open science

Ohmic Curing of Silver Micro-Particle Inks Printed on Thermoplastics

F. Tricot, C. Venet, D. Beneventi, D. Curtil, D. Chaussy, T. P Vuong, J. E Broquin, N. Reverdy-Bruas

► **To cite this version:**

F. Tricot, C. Venet, D. Beneventi, D. Curtil, D. Chaussy, et al.. Ohmic Curing of Silver Micro-Particle Inks Printed on Thermoplastics. *Journal of Electronic Materials*, 2021, 50 (11), pp.6183-6195. 10.1007/s11664-021-09145-7 . hal-03440237

HAL Id: hal-03440237

<https://hal.science/hal-03440237>

Submitted on 9 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ohmic curing of silver micro particle inks printed on thermoplastics

F. Tricot,^a C. Venet,^b D. Beneventi,^a D. Curtil,^a D. Chaussy,^a T.P. Vuong,^c J.E Broquin,^c
N. Reverdy-Bruas^a

^a Univ. Grenoble Alpes, CNRS, Grenoble INP*, LGP2, F-38000 Grenoble, France

^b Schneider Electric.

^c Univ. Grenoble Alpes, CNRS, Grenoble INP*,IMEP LAHC, F-38000 Grenoble, France.

* Institute of Engineering Univ. Grenoble Alpes

Introduction

Printed electronics deals with the manufacturing of electronic circuits by printing functional inks on a substrate to create an electrical circuitry. Conventional microelectronic components could be added to access more functions. In the flexible hybrid electronic area as in the in-mold electronics field, the IDTechEx report forecasts a huge demand at 2030 horizon. The market value is estimated at 3 billion \$ in 2030 for the first one [1] and at 750 million \$ in 2028 for the second [2]. Printed electronics opens the way to produce new devices such as energy conversion and storage devices, flexible displays, sensors, printed field effect transistors, intelligent and interactive packaging [3]. As an additive manufacturing process, this technology allows using only the necessary material quantity to create circuits [3] [4] [5] [6]. The latter can be made on a considerable variety of substrates: flexible or rigid, thermal sensitive, plastics, paper... Besides, by using conventional printing processes, it permits to envisage low cost and high volume devices production [6] [7], in particular thanks to roll to roll processes [8]. Most of the commercially available inks are composed of metal micro or nano particles embedded in an organic material. To reach good electrical performances, the amount of organic material has to decrease to permit the direct physical contact between metal particles. To do that, printed inks need to be cured without damaging the substrate. Consequently, to tend toward high productivity, the ink curing process has to combine a high speed with a temperature limitation in order to preserve polymeric substrates. This paper is focused on this topic and considers thermoplastic substrates.

Most of the research is done on nanoparticles inks printed by inkjet. Patterns thickness is inferior to 5 μm [3–6,9–15]. Those inks are composed of metal nano-particles coated by a stabilizing agent in an organic medium. The role of the stabilizing agent is to prevent particles agglomeration [8]. Most of the time, silver is used because it presents the best compromise between electrical conductivity and chemical stability [8]. Thanks to their small size, metal nanoparticles own specific thermal properties. In particular, it has been demonstrated that the melting temperature of a metal particle decreases with the decrease of its size [16] [17]. While the melting temperature of the silver bulk is about 960°C, silver nano-particles of 11 nm diameter are characterized by a melting temperature of 200 °C [8]. For the curing of metal nanoparticles inks, the word “sintering” is usually employed since particles stick together during the process [18]. The first step of this process is the removal of the stabilizing agent. Particles enter into contact and neck structures are formed at their interface [8,19]. According to the applied temperature, the structure becomes denser and the porosity decreases until remaining only isolated pores [8] [10]. Generally, the final resistivity of silver nanoparticle inks ranges between 2.5 and 40 $\mu\Omega\cdot\text{cm}$ [8]. This large

interval could be explained by the size of nanoparticles and the thermal sensitivity of considered substrates. The most common sintering process is a thermal treatment by means of an oven. Mainly, it permits to reach electrical resistivity values in the range of 11 – 40 $\mu\Omega\cdot\text{cm}$ [8], that is 6 to 25 times superior to the silver bulk resistivity. This technique causes an increase of temperature of the entire sample, i.e the printed ink plus the substrate. In case of thermoplastic substrates, the applied temperature is limited below the glass transition of the support to prevent its deformation. That is why, this process is time consuming.

However, some studies [4–7,9,11–15,19–22] experimented local sintering processes. The use of microwave radiation has been explored. It exploits the selective absorption of materials. In that case, metal nanoparticles absorb microwave whereas the substrate, polyethylene naphthalate in the study [15], not. The microwave sintering was performed with a power of 1 W during 1 to 60 seconds. The final sample was characterized by nanoparticles agglomerated in layers. The ink owned a resistivity 3 times superior to that of the bulk silver [15]. The technique is more efficient than thermal process since it allows time and performance saving.

Some authors experimented a process under low pressure argon plasma. Studies were made on thermoplastic substrates. The plasma breaks down the stabilizing agent and permits the sintering of nanoparticles. Final samples exhibit undamaged substrates and an electrical resistivity compatible with some printed electronic applications. However, some limitations were highlighted: (i) higher electrical conductivities can be reached with others processes, (ii) the process weakens the adhesion of the ink on the substrate, (iii) plasma sintering takes from 1 to 4 hours to be effective [4] [20].

Laser radiations are also reported in the literature to sinter printed metal nanoparticles inks. Studies focused on UV [5] [13] [21] or visible radiations [6]. The sintering of printed inks is made possible thanks to the radiation absorption of the metal nanoparticles on top of the printed pattern and the heat diffusion toward the deeper nanoparticles. Thermoplastic substrates are not sensitive to the specific radiation wave length used in the studies and the laser exposure is localized on the printed patterns. Consequently, this technique does not damage substrates and leads to electrical resistivity of the sintered inks similar to values obtained with thermal sintering. However, laser radiations permit a considerable time saving since sample were sintered with a laser speed running superior or equal to 3 mm/s.

Others studies [7,20] deal with photonic sintering. Samples are subjected to an intense light pulse with a broad spectrum, ranging from UV to IR, generated by a Xenon strobe. On one hand, the sintering is based on the high absorption of nanoparticles causing their heating and sintering. On the other hand, a very short process time, inferior to 1 millisecond, avoid reaching the thermal equilibrium and so the degradation of the substrate. The limitation of this technique is the efficiency only on thin films with a thickness inferior to 5 μm . However, it permits a huge time saving and a process time compatible with industrial roll to roll printing systems. The final electrical performance of sample is similar to that obtained with thermal treatment [7] [20].

The last technique reported in literature is electric sintering. The principle starts from a highly resistive sample where an intense Ohmic effect can be induced by a low electrical current flow. A resistive pattern can be obtained thanks to a mild pre-curing in an oven. A voltage difference is then imposed between two electrodes in contact with the printed ink pattern. Because of the difficulty of the current to flow, the Joule effect causes a local increase of temperature leading to the sintering of nanoparticles.

An electrical path is therefore built. A virtuous loop is generated. The current flow favors the connection between nanoparticles and that favors the flow of the current. Authors [10–12,14,19] experimented several kinds of imposed signals. Parameters have to be monitored relative to the used ink and substrates. The latter could be affected by the thermal diffusion if the process is not controlled. Best results are a final resistivity equals to 2 times that of the bulk silver with a process time in the range of 0.15 to 60 seconds. Electrical sintering is more efficient than thermal sintering [10] [23] [14] [12] [11]. However some limitations remain. This technique forms localized conductive channels in the printed material, meaning that the electrical performances in the path cross section can be heterogeneous. It requires a contact with the printed ink.

To overcome these limits, some authors [9,22] developed a contactless electrical sintering. They set up an alternative current source supplying a coaxial cable ended by two electrodes or an inductive coil. The electromagnetic field generated by the head induced current in the printed ink causing an increase of temperature and the sintering of nanoparticles due to the Joule effect. Several plans are reported. Some move the sintering head at a speed of 22 mm/s above the printed pattern to sinter it homogeneously [9]. Another work advises to place the printed pattern over an induction coil supplied by an induction heater. The latter is powered by 3s electric pulse in order to lead to the sintering of the metal ink without overheating the substrate [22]. Sample electrical resistivity equals to 1.5 times the one of the silver bulk is mentioned [22].

Micro-particle inks were less studied. In that case, the sintering is not possible because it involves too high temperature to be withstood by most of substrates such as thermoplastics. The curing leads to decrease the quantity of organic material causing a physical contact between metal particles thanks to the percolation process [19]. Generally, the obtained resistivity of silver micro-particle inks is comprised between 30 and 50 $\mu\Omega\cdot\text{cm}$ [8]. However, the use of micro-particles inks is preferred for industrial applications because of health consideration. Indeed, the action on nanoparticles on living organisms is still little known and it is potentially dangerous for the human health [8]. Because of the larger size of particles and implemented printing processes, the thickness of printed patterns is generally superior or equal to 5 μm .

Few studies dealt with selective curing of micro-particle inks. In the literature, continuous [21] or pulsed [24] UV laser curing has been reported. The principle is the same that mentioned for nanoparticle inks. Particles are not sintered but coalesce. A final electrical resistivity inferior or equal to 30 $\mu\Omega\cdot\text{cm}$ is reported [21]. Such resistivity value is similar to the one obtained by thermal curing of micro-particle inks.

Finally, only one article was found dealing with the electrical curing of micro-particle inks [23]. The study was done on two micro-particle inks printed on polyimide substrate by a micro-dispensing method. The printed patterns were lines with a thickness of about 5.5 μm . Results highlighted the efficiency of the ohmic curing since the obtained resistivity was 36% less than the one reached with thermal curing. Microstructural behavior was different according to the considered ink. For one of them, the ohmic curing caused no visible signs of a microstructural modification whereas, for the second ink, an inhomogeneous change was observed. It was due to local melting of particles. This article brings very promising results about an efficient curing thanks to ohmic technique. However, there is no information about the kinetic of the curing and the influence on thermoplastic materials more sensitive to the temperature than polyimide. That is the topic of the present publication.

The ohmic curing of two micro-particle inks printed on two different thermoplastics was studied. Firstly, the temperature variation due to the curing process and its impact on the substrate was analyzed. Secondly, the resistivity evolution during the curing and the final electrical performances were discussed. Finally, some elements were given about the microstructure modification of the inks caused by the ohmic curing.

Experimental

Materials. Two inks containing silver micro particles dispersed in an organic solvent were studied. The first one (Electrodag 418 SS, Henkel) was characterized by a silver content superior to 50% and a D50 particle diameter of 8 μm . The advised curing treatment was 90°C / 20 minutes or 120°C / 15 minutes.

The second ink (CM 125-13, Creative Material) had an estimated silver solid content lower than 70% and a D50 particle diameter of 2 μm . The supplier advised curing treatment was 170°C for few minutes.

Two thermoplastic plates with different composition were provided by Schneider Electric and used as substrate: a) a mixture of PC+ABS and (b) a PA6 MD25 FR(30) thermoplastic. Preliminary TGA and DSC measurements showed that: the PC+ABS substrate was characterized by a phase transition temperature of 110°C and a damaging temperature of 370°C and the PA6 MD25 FR(30) substrate by a phase transition temperature of 225°C and a damaging temperature of 280°C.

Printing. The printing process used in this study was a home-made system described in a previous work [25]. A volumetric dosing dispenser (Preeflow® eco-PEN300 from Viscotec) was fixed on the X axis of a Cartesian 3D printer Prusa i3 rework 1.5 (EmotionTech). The 3D printer permitted to move the dispenser and to print on 2D and 3D objects. To be deposited, the ink stored in a pressurized syringe is pneumatically fed into the volumetric dosing system. An eccentric endless screw brings the ink to the extremity of the dispenser, where a needle is fixed. The ink is finally extruded through the needle and laid-down on the substrate.

The printed pattern, a “dog bone” form, and the printing parameters are presented in Figure 1.

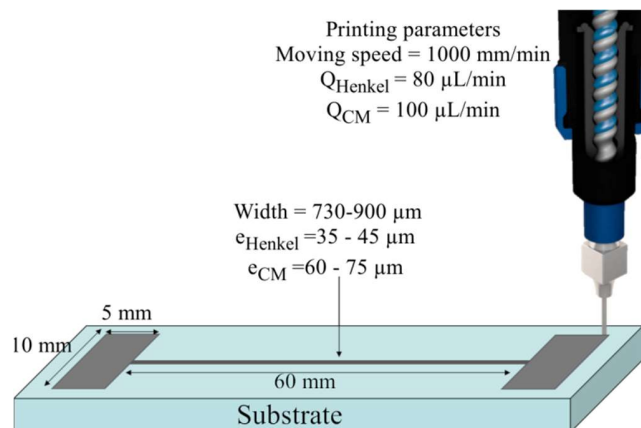


Figure 1: Schematic of the printed pattern dimensions and printing parameters.

e refers to the thickness of the printed lines, Q refers to the flow rate in the dispenser according to the used ink.

Curing. After printing, the samples were stabilized 48 hours under a fume hood and ambient conditions before curing. For each pair ink/thermoplastic, a control sample was made by curing it at 110°C for 90 min in an oven. All other samples were cured by applying a current through the dog bone pattern. A homemade electrical assembly was set up. It is composed of a power generator, an oscilloscope and a device to apply with constant pressure an electrode tip at each extremity of the printed pattern. The assembly is shown on Figure 2.

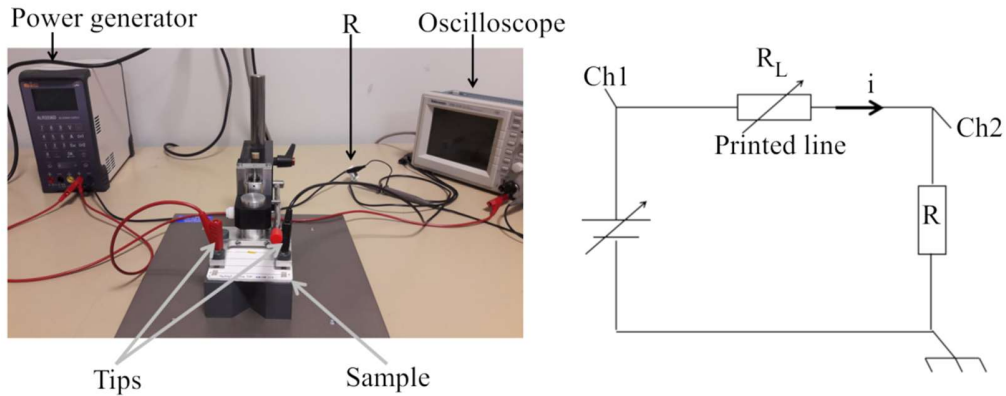


Figure 2: Picture of the homemade electrical assembly to operate ohmic curing and the corresponding electrical diagram

In order to obtain the most efficient ohmic curing, i.e to reach the best conductivity without damaging thermoplastics, a trial-and-error process was made. Since the higher the current intensity and applied time, the more intense the Joule effect the objective was to find the highest current intensity and applied time that could be used without damaging samples. Both a constant intensity current for a given time and variable current intensities for different times were explored. The selected parameters of this process are summarized in Table 1. For all samples, the applied signal had a square wave profile with a period of 65 s.(Figure 3). The current intensity increased between each stage and a duty cycle of 54% (corresponding to a rest time of 30 seconds) was imposed. For the curing of inks printed on the PC+ABS substrate, two sets of curing parameters, labeled as [P1] and [P2], were selected since preliminary tests highlighted a limited substrate damage. Parameters [P1] lead to a curing process without sample deformation, whereas parameters [P2] lead to a curing process causing slight local deformation. Concerning the curing of inks on PA6 MD25 FR(30), only one set of parameters was studied since the damaging limitation was never reached.

	Applied current intensity (A) and time (s)	
	Henkel Ink	CM ink
PC+ABS [P1]	1.5 A 35 s + 1.8 A 35 s + 2 A 15 s	1.8 A 35 s + 2 A 35 s + 2.3 A 15 s
PC+ABS [P2]	1.8 A 35 s + 2 A 35 s + 2.3 A 15 s	2 A 35 s + 2.5 A 35 s + 2.8 A 15 s
PA6 MD25 FR(30)	2 A 35 s + 2.7 A 35 s + 3 A 15 s	2.5 A 35 s + 3 A 35 s + 3.2 A 15 s

Table 1: Selected parameters for the ohmic curing of samples according to the ink and the substrate

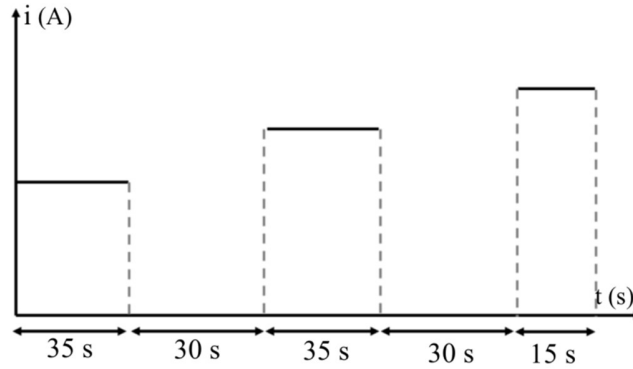


Figure 3: Structure of the current signal applied on all samples

Characterization. Electrical characterization. The homemade electrical assembly presented in Figure 2 permitted to follow the evolution of the applied voltage and the current intensity during the curing process. According to the electrical diagram, the channel 1 of the oscilloscope measures the voltage at the generator output whereas the channel 2 measures the voltage at the resistance R. The value of the resistance was 1Ω , the intensity of the current is then deduced by using the Ohm's law using (Ch1-Ch2) voltage. The resistivity of printed lines (ρ) is defined by Equation 1. Thanks to the measurements made with the oscilloscope and knowing the size of the printed lines, their resistivity during the curing was calculated.

$$\rho = R_L \frac{A}{L} \quad \text{Equation 1}$$

where ρ is the resistivity ($\Omega \cdot m$), R_L is the resistance (Ω), A is the section of the lines (m^2) and L is the length of the line (m).

The final resistivity of the cured patterns was assessed after a couple of hours after the curing. Each extremity of printed tracks was in contact with a probe. The two probes were linked to a Jandel RM3000 Test unit. Several currents were applied on samples and corresponding voltages were measured. The Ohm's law permitted to deduce the lines resistance and the resistivity was calculated according to Equation 1.

Thermal characterization. The variation of temperature during the ohmic curing was also studied. To evaluate the temperature reached by the printed lines, a thermocouple (T type, $25 \mu m$ wire diameter) linked to a data logger was fixed on the surface of each printed pattern at the middle of the line. The data logger permitted to save the temperature each 31 ms during the curing process. Besides, pictures taken with an infrared camera (Flir i7) at different stages of the curing process gave information about the increase of temperature of the printed lines and the surrounding thermoplastics. The emissivity of the substrate and the apparent temperature was taken into account to make this measurement.

Inks adhesion on substrates. The adhesion of the inks on the two thermoplastic substrates was evaluated after the ohmic curing using the tape test following the ISO 2009-2007 2013 standard.

Microscopic ink characterization. To evaluate the effect of the curing process on inks morphology, four kinds of samples were produced on glass substrates for each ink: (a) not cured, (b) cured at

110°C/90min in an oven, (c) cured at 500°C/15min in an oven, (d) ohmic cured. Their surface was examined thanks to an Environmental Scanning Electron Microscope (ESEM) (Quanta200, FEI, the Netherlands). Images were performed with a working distance of 10 mm and a voltage of 15 kV.

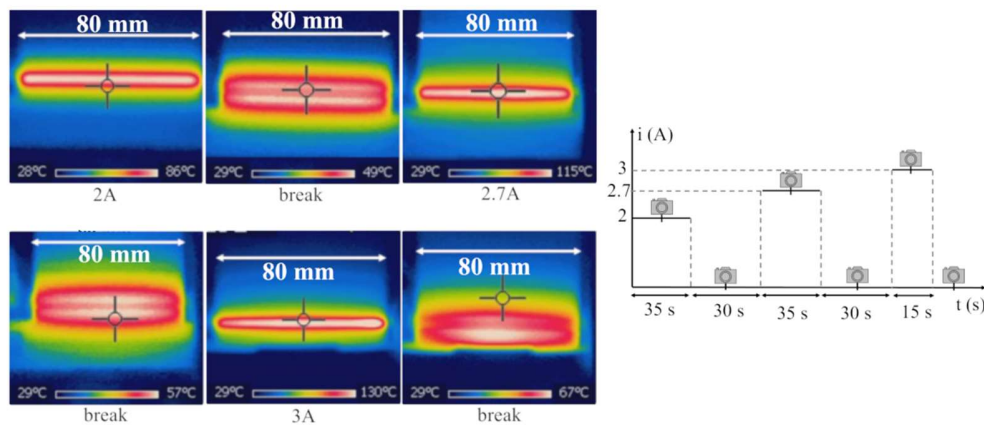
Substrate characterization. The deformation of the substrates caused by the ohmic curing was evaluated using an Alicona InfiniteFocus optical profilometer (magnification x 50) and the Profile Form Measurement function of the corresponding software IF Measure Suite.

Results and Discussion

Temperature variation caused by the ohmic curing

Approximation of the heating area on samples. The applied ohmic curing process was composed of three steps with different current intensities and separated by a break of 30 s (see Table1). Some pictures (see Figure 4) have been taken at each step during the curing of Henkel ink on PA6 MD25 FR(30) thermoplastic.

Figure 4: Pictures taken with infrared camera of a sample composed of a Henkel ink line printed on PA6 MD25



FR(30) substrate. The instant of picture capture was illustrated on the graph for each curing process step.

Several results were highlighted:

- The ohmic curing induces an increase of temperature for which the printed line is the starting point.
- The break between each step is adequate to limit the increase of temperature, in particular of the surrounding substrate. A thermal diffusion is observed during this stage.
- The higher the applied current intensity, the higher the reached temperature of the silver line. Applied current intensities lead to line temperature superior or equal to advised temperature for a thermal curing. Reached temperatures are summed up in Table 2.

	Step 1, 2 A	Break	Step 2, 2.7 A	Break	Step 3, 3 A	Break
$T_{\text{line}} (^{\circ}\text{C})$	86	49	115	57	130	67
$T_{\text{surrounding substrate}} (^{\circ}\text{C})$	64	49	79	57	88	67

Table 2: Reached temperatures of the printed line and of the surrounding substrate during the different steps of the curing process (Henkel ink line printed on PA6 MD25 FR(30) substrate).

Those results suggest the efficiency of the ohmic curing to improve the electrical conductivity of printed lines without damaging the global substrate, as the temperature increase remains localized on printed tracks. However, local thermoplastics deformation could appear at the close surrounding of printing patterns due to the local temperature elevation. To deeply investigate this point, the printed line temperature evolution was followed during the curing thanks to a thermocouple and final samples were analyzed by means of an optical profilometer.

Evolution of the printed lines temperature during the curing. For each couple ink/thermoplastic, the temperature evolution during the ohmic curing was recorded. Figure 5 shows the recorded temperature variation for silver tracks on PC+ABS substrate. Whatever the ink, the same trend was observed for printings on the PA6 MD25 FR(30) substrate with a maximal temperature up to 170°C. That temperature remains inferior to the phase transition temperature (225°C) of that thermoplastic. Consequently, the ohmic curing cannot damage this substrate.

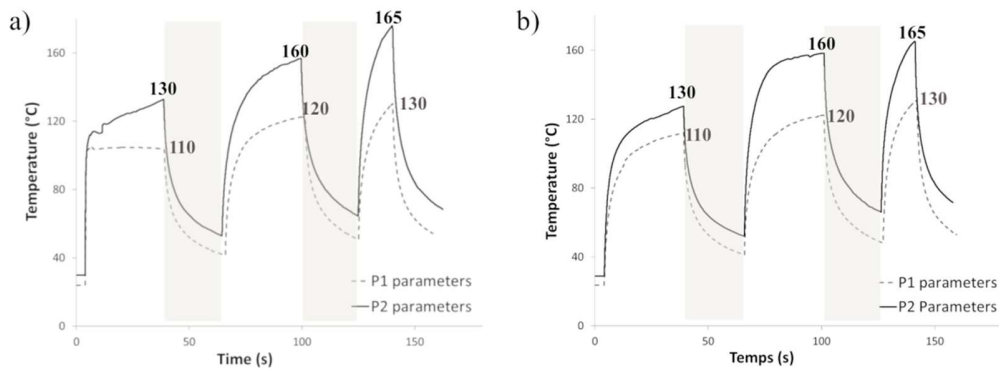


Figure 5: Evolution of the printed line temperature on PC+ABS substrate during the ohmic curing performed with P1 parameters and P2 parameters for a) Henkel ink and b) Creative Material ink. (the definition of P1 and P2 is given in table 1). Grey areas represent the 30 s time breaks of the curing process.

The ink nature seems not to influence reached temperatures during the curing. However, it is supposed that this phenomenon cannot be generalized since the characteristics of the two studied inks are similar.

For all conditions, the two first curing steps are characterized by a temperature increase with two kinetics. 75% of the final temperature is reached during the 10 first seconds or less. The increase in the third step is more regular. The first step represents the main increase of temperature, superior of 340% of the initial value. The 30 second breaks permit to reduce the reached temperature at the end of a step to 60% and therefore constitute an effective limitation of the temperature to avoid damaging the substrate.

The phase transition temperature of PC+ABS substrates has been evaluated to 110°C. Although the weak difference of current intensity values between P1 and P2 parameters (see Table 1), a significant effect is observed. With P2 parameters, the phase transition temperature is overtaken at each step of the curing since final temperatures are 130°C, 160°C and 165°C for the two inks. On the contrary, P1

parameters permit to limit the temperature of the first step to 110°C. In the two following steps, the temperature reaches respectively 120 and 130°C whatever the considered ink.

Silver tracks punctually reach temperature superior to the phase transition temperature of the PC+ABS substrate. However, considering results of figure 4, the thermal diffusion from the center of printed lines to the surrounding thermoplastics is accompanied from a decrease of temperature. The combination of these results suggests that the ohmic curing with P1 parameters process could prevent the substrate damage. Applying P2 parameters should affect the substrate. This is why further experiments are performed.

Effect of the temperature increase on substrates. Near to the printed line, the substrate is subjected to a thermal diffusion coming from the silver pattern. Observations with a profilometer were made to evaluate the effect of ohmic curing on the substrate on the surrounding of the printed line. Figure 6 represents the reconstruction of the PA6 MD25 FR(30) surface containing a cured line printed with Creative Material ink. The same trend was observed with lines printed with Henkel ink. The Ra roughness of the virgin substrate is of $0.65 \pm 0.13 \mu\text{m}$.

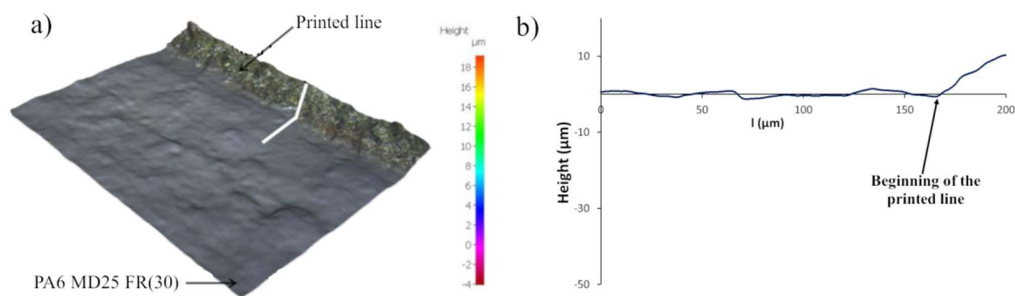


Figure 6: Profilometer analysis of Creative Material ink printed and ohmic cured on PA6 MD25 FR(30): a) 3D view of the edge of the printed line, b) Profile of the black line marked on the 3D view.

No deformation was observed. This result is in accordance with the study of the temperature evolution during curing. Indeed, on PA6 MD25 FR(30) substrate, the highest reached temperature was about 170°C (Figure 5) inferior to the phase transition temperature about 225°C. For patterns printed on PA6 MD25 FR(30) substrate, the ohmic curing with the selected parameters kept the substrate intact even for the surface closely adjacent to the printed line.

As concerns printings on PC+ABS substrate, Figure 7 illustrates the trend for both inks.

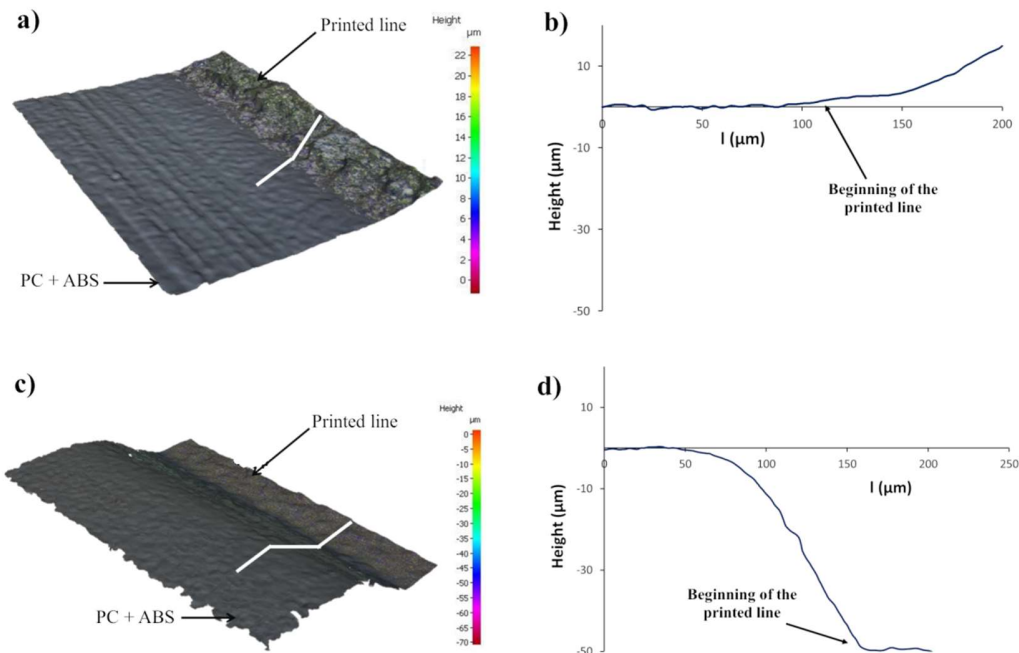


Figure 7: Profilometer analysis on Henkel ink printed and ohmic cured on PC+ABS: a) and b) are respectively the 3D view and the profile of the black line for samples cured with the set of parameters P1. c) and d) are respectively the 3D view and the profile of the black line for samples cured with the set of parameters P2.

Results are in accordance with the previous observations. The ohmic curing applied with P1 parameters process (Figure 7 a. and b.) does not damage the substrate. As the temperature of the silver line is equal to the phase transition temperature, the decrease of temperature due to thermal diffusion permits that the temperature reached by the substrate is just inferior to the phase transition temperature. Consequently, no deformation of the sample occurs. However, when considering the curing process with P2 parameters, the temperature on the silver line is significantly superior to the polymer phase transition temperature. The decrease of the temperature gradient is not enough to protect the parts of the substrate closely adjacent to the printed pattern. That is why Figure 7 c. and d. exhibit a deformation of the thermoplastic along the printed line. According to the picture, a brief and local change of state of the substrate surrounding the conductive path induces a local thickness decrease of about 50 μm .

Nevertheless, despite of a local deformation for some ohmic curing process conditions, the mechanical adhesion of the printed ink on substrates was not affected. For all samples, an excellent adhesion was evaluated since 0% of the ink was removed during the tape test. Consequently, even if the ohmic curing process could cause some local deformations of the substrate, this process is compatible with printed electronic applications on temperature sensitive thermoplastics. This is a very promising result in light of the development of applications such as Plastronics. Besides, it is essential to evaluate the electrical performance of ohmic cured samples in order to conclude on the interest of this process.

Resistivity evolution of printed lines cured by ohmic process

Evolution of the resistivity during the curing. Figure 8 shows the evolution of resistivity and temperature during the ohmic curing of printed lines on PA6 MD25 FR(30). The same trend was observed on PC+ABS substrate.

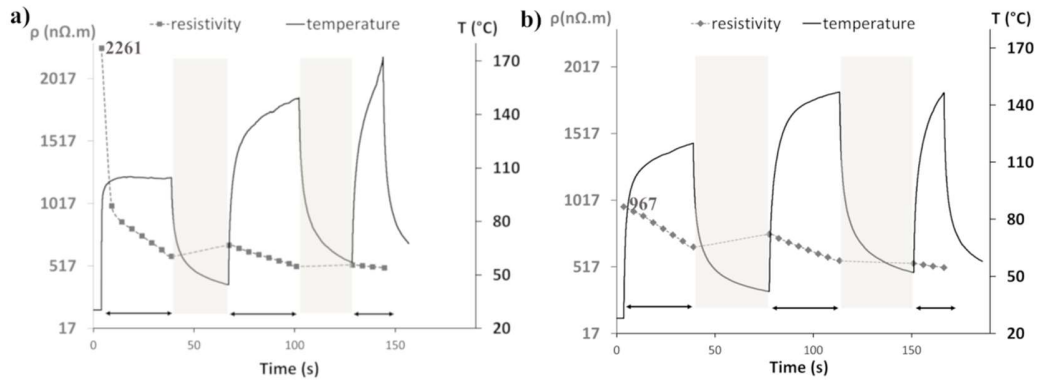


Figure 8: Evolution of temperature and resistivity of the printed lines on PA6 MD25 FR(30) substrate during the ohmic curing for a) Henkel ink and b) Creative Material ink. Grey areas represent the 30 s time breaks of the curing process.

The printings of the two inks showed a similar trend except in the first five seconds of the curing process. Lines printed with Henkel ink had a huge initial resistivity of 2261 nΩ.m that is 2.3 times superior to the initial resistivity of samples printed with Creative Material ink. However, this initial high value dropped to ca. 1000 nΩ.m after five seconds curing. A major resistivity loss, about 40% of the initial value, occurred during the first curing step. The influence of the third step is not significant since only a decrease of 5% of the resistivity was recorded. It has to be outlined that the break between steps 1 and 2 causes a slight increase of 15% of the resistivity. This can be due to the decrease of the temperature as this parameter can improve electrons mobility in metals. This phenomenon is nearly inexistent between steps 2 and 3 and suggests the stabilization of samples. Consequently, steps 1 and 2 are necessary to obtain samples with optimized electrical performances whereas the step 3 is optional. These results show that conductive samples can be obtained after 30 s of ohmic curing, whereas thermal curing needs 30 minutes to reach the same performance. The ohmic curing duration could be minimized by determining the optimum couple: "Intensity of the current through the printed pattern/Time of appliance". In the case of a maximized conductivity is required, an ohmic curing of 2 minutes permits to reach better performances than thermal curing.

Resistivity of final samples according to the curing method. Calculated resistivity values of samples after ohmic and thermal curing are summarized in table 3.

Substrate	Resistivity of Henkel ink (nΩ.m)		Resistivity of Creative material ink (nΩ.m)	
	Ohmic curing	Thermal curing 110°C 90 min	Ohmic curing	Thermal curing 110 °C 90 min
PC+ABS P1	310 ± 37	332 ± 41	360 ± 32	481 ± 51
PC+ABS P2	286 ± 31		292 ± 26	
PA6 MD25 FR(30)	321 ± 42	445 ± 56	407 ± 42	536 ± 63

Table 3: Comparison of resistivity values of the two inks on the different substrates according to the curing process

The most important result is that for all samples the ohmic curing leads to a lower resistivity value than the thermal curing. The ohmic curing is more efficient than the conventional thermal curing since it permits to obtain better electrical performances in a shorter time. It is an alternative compatible with printed electronics industrial processes. The obtained resistivity values are in accordance with several papers of the literature [8,21]. However, they remain higher than values comprised between 75 and 145 nΩ.m recorded in [23]. That can be due to the difference of printed lines thickness. In this study, printed lines had a thickness from 35 to 75 μm that is 7 to 15 times superior to lines printed by Roberson et al in [23].

The second observation concerns the influence on the resistivity value of the two sets of parameters applied on PC+ABS substrates. As it has been discussed earlier, these parameters significantly affect the deformation of the substrate near the silver line. However, regarding values in Table 2, the influence on the resistivity value is not significant. Even on the thermal sensitive PC+ABS substrate, the ohmic curing can be applied with parameters allowing obtaining better electrical performance than thermal curing without any damaging.

Effect of the ohmic curing on inks

Figure 9 shows ESEM pictures of samples printed with Henkel ink (D50 particle diameter = 8 μm), not cured or cured according to different processes. Whereas the curing at 500°C causes the melting of silver particles and partially closes the porosity, the microstructural change induced by ohmic curing or curing at 110°C is not significant. These two processes could suggest a coalescence of some silver particles since some flakes appears bigger than on the picture of not cured sample. The micro-surface appearance of the three samples is very similar. That is consistent with remarks reported in the literature. [8,19,21,23,24]

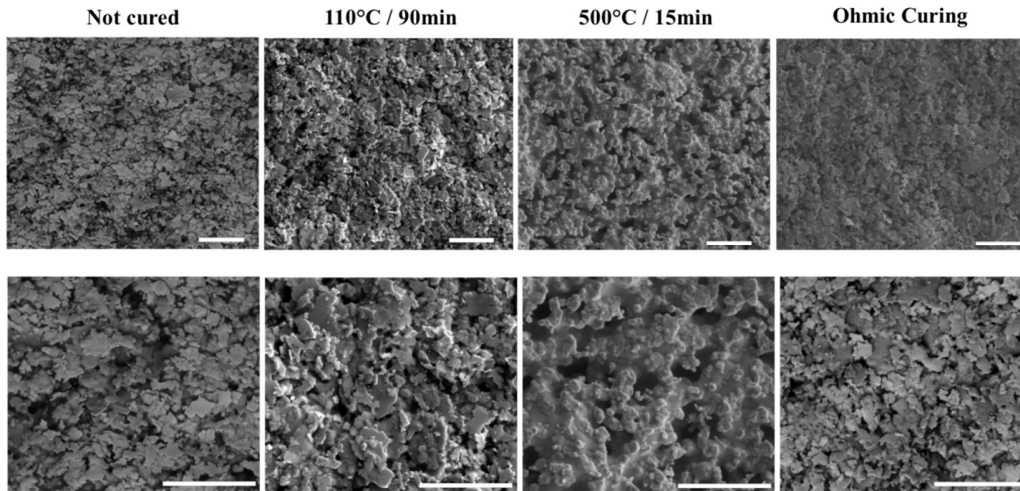


Figure 9: ESEM pictures of the surface of patterns printed with the Henkel ink according to different curing processes.

Scale bar = 20 μm

Observations were quite different for samples printed with Creative Material ink (D50 particle diameter = 2 μm) as it is highlighted by Figure 10. With that ink, the thermal curing at 500°C permits to melt all particles since the micro surface appears like a film with pine holes. The later could be due by the damaging and the extraction of organic compounds initially in the ink. The difference of microstructure with Henkel ink samples can be explained by the different of size of silver particles. More differences are observed between not cured samples and samples cured at 110°C and with ohmic curing for Creative Material ink printings than Henkel ink printings. The not cured sample exhibit at least two kinds of objects: small silver particles and bigger blocks. Considering that the silver particles size is relatively homogeneous, it is most likely that those blocks are other materials such as organic compounds. The 110°C curing process modifies the microstructure samples by reducing the porosity of the printed layer thanks to thin and homogeneous connection between silver particles. The ohmic curing process leads to a different modification. In that case, the porosity remains and the particles connection are wider but less homogeneous. The difference in the microstructure modification of the two inks induces by curing process probably comes from the difference on particles size and concentration and on the used organic compounds.

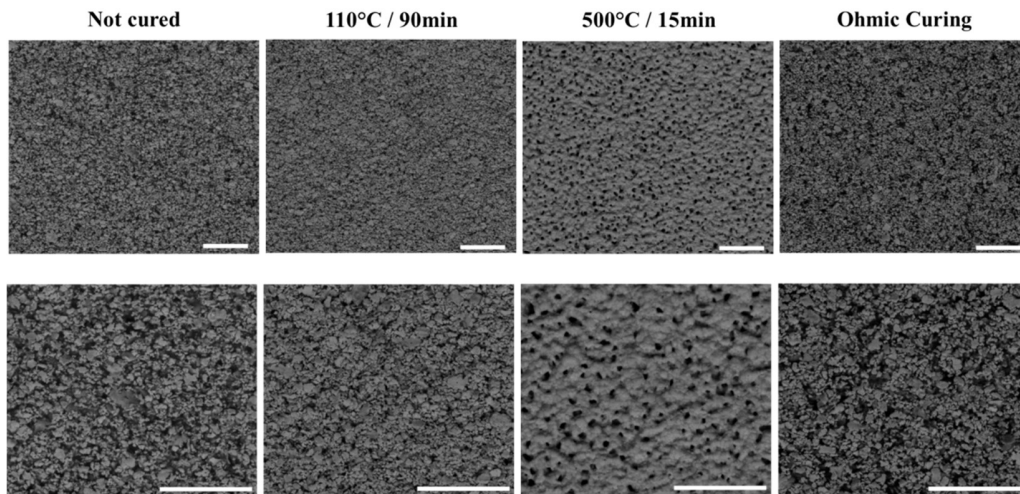


Figure 10: ESEM pictures of the surface of patterns printed with the Creative Material ink according to different curing processes. Scale bar = 20 μm

Conclusion

The efficiency and the effect of ohmic curing of silver micro-particles inks on thermoplastic substrates were studied. Two kinds of ink and thermoplastic were considered. A trial and error process was implemented to find optimized parameters process. The results of the ohmic curing process applied with those parameters were discussed.

First, the analysis of the temperature variation and its influence on substrates has highlighted the key points:

- The ohmic process leads to a silver tracks curing by thermal effect with a considerable time saving compared to oven curing. The electrical current circulation in printed lines causes a quick increase of temperature because of the Joule effect. The main temperature rise occurs in 10 seconds or less.
- The ohmic curing process is compatible with all kinds of substrates, even thermal sensitive thermoplastics. The control of the applied intensity values and the setup of breaks permit to keep the temperature just below the phase transition temperature of the substrate.
- The ohmic curing process does not affect the mechanical adhesion of the ink on the substrate.

Second, the study of the resistivity evolution generated by the ohmic process leads to promising results:

- Better electrical performances are obtained with the ohmic process than with an oven curing. The treatment being local, higher temperature can be applied without damaging global properties of samples.
- The main resistivity drop is reached during the first 30 seconds and the sample stabilization occurs after 90 seconds of process that considerably reduces the curing time.
- The conductivity improvement is due to slight microstructure modifications. In particular, the ohmic curing causes a coalescence of some silver particles facilitating the electrical current circulation.

In regards to the development of printed electronics on a lot of kinds of substrates and especially on thermoplastics thanks to Plasma applications, the ohmic process can be a very promising curing process. The key points to underline are:

- it is a low cost process. It only needs a power generator and electrodes.
- it is more efficient than thermal curing in an oven : better electrical performances and time saving.
- it can be used in an industrial process since it is compatible with micro-particles inks, substrate with different thermal sensitivities and fast production process.

Nevertheless, some challenges remain but they can be overcome. There are two main drawbacks. Firstly, the electrode tips have to be in contact with printed patterns. That requires designing an adaptable tool, maybe supported by an automatized arm, to insure the contact between electrodes and printed lines. Secondly, the process creates an electrical path between the two electrodes tips. It is well adapted for lines but not for solid print. For instance, this process is well adapted to cure NFC antenna. However, some electronic devices need a ground plane made by a solid print.

To overcome these points and keep the assets of the ohmic process, the exploration of a contactless ohmic curing by means of the appliance of an alternative current should be explored. In literature, some results already exist for nanoparticles inks. However no one deals with micro-particles inks, leaving the way open for new studies.

- [1] Matthew Dyson, Khasha Ghaffarzadeh, *Flexible Hybrid Electronics 2020-2030: Applications, Challenges, Innovations and Forecasts*, IDTechEx, 2020.
- [2] Khasha Ghaffarzadeh, Richard Collins, *In-Mold Electronics 2020-2030: Technology, Market Forecasts, Players*, IDTechEx, 2020.
- [3] W. Wu, Inorganic nanomaterials for printed electronics: a review, *Nanoscale*. 9 (2017) 7342–7372. <https://doi.org/10.1039/C7NR01604B>.
- [4] I. Reinhold, C.E. Hendriks, R. Eckardt, J.M. Kranenburg, J. Perelaer, R.R. Baumann, U.S. Schubert, Argon plasma sintering of inkjet printed silver tracks on polymer substrates, *J. Mater. Chem.* 19 (2009) 3384. <https://doi.org/10.1039/b823329b>.
- [5] B. Polzinger, F. Schoen, V. Matic, J. Keck, H. Willeck, W. Eberhardt, H. Kueck, UV-sintering of inkjet-printed conductive silver tracks, in: 2011 11th IEEE International Conference on Nanotechnology, IEEE, Portland, OR, USA, 2011: pp. 201–204. <https://doi.org/10.1109/NANO.2011.6144541>.
- [6] M.-K. Kim, J.Y. Hwang, H. Kang, K. Kang, S.-H. Lee, S.-J. Moon, Laser sintering of the printed silver ink, in: 2009 IEEE International Symposium on Assembly and Manufacturing, IEEE, Seoul, South Korea, 2009: pp. 155–158. <https://doi.org/10.1109/ISAM.2009.5376912>.
- [7] K.A. Schroder, S.C. McCool, W.F. Furlan, *Broadcast Photonic Curing of Metallic Nanoparticle Films*, (2006) 5.
- [8] V. Thenot, Impression et recuits sélectifs d’encres métalliques sur papier – Optimisation des propriétés électriques de boucles RFID-HF en vue d’une production industrielle, (n.d.) 273.
- [9] M. Allen, A. Alastalo, M. Suhonen, T. Mattila, J. Leppaniemi, H. Seppä, Contactless Electrical Sintering of Silver Nanoparticles on Flexible Substrates, *IEEE Trans. Microwave Theory Techn.* 59 (2011) 1419–1429. <https://doi.org/10.1109/TMTT.2011.2123910>.
- [10] M.L. Allen, M. Aronniemi, T. Mattila, A. Alastalo, K. Ojanperä, M. Suhonen, H. Seppä, Electrical sintering of nanoparticle structures, *Nanotechnology*. 19 (2008) 175201. <https://doi.org/10.1088/0957-4484/19/17/175201>.
- [11] P. Escobedo, M.A. Carvajal, J. Banqueri, A. Martinez-Olmos, L.F. Capitan-Vallvey, A.J. Palma, Comparative Study of Inkjet-Printed Silver Conductive Traces With Thermal and Electrical Sintering, *IEEE Access*. 7 (2019) 1909–1919. <https://doi.org/10.1109/ACCESS.2018.2887113>.
- [12] O. Kravchuk, Y. Bobitski, M. Reichenberger, Electrical sintering of inkjet printed sensor structures on polyimide substrate, in: 2016 IEEE 36th International Conference on Electronics and Nanotechnology (ELNANO), IEEE, Kyiv, Ukraine, 2016: pp. 104–106. <https://doi.org/10.1109/ELNANO.2016.7493022>.
- [13] O. Kravchuk, Y. Bobitski, M. Reichenberger, Laser curing of inkjet printed strain gauge structures, in: 2016 MIXDES - 23rd International Conference Mixed Design of Integrated Circuits and Systems, IEEE, Lodz, Poland, 2016: pp. 343–345. <https://doi.org/10.1109/MIXDES.2016.7529761>.
- [14] H. Lee, D. Kim, I. Lee, Y.-J. Moon, J.-Y. Hwang, K. Park, S.-J. Moon, Stepwise current electrical sintering method for inkjet-printed conductive ink, *Jpn. J. Appl. Phys.* 53 (2014) 05HC07. <https://doi.org/10.7567/JJAP.53.05HC07>.
- [15] J. Perelaer, M. Klokkenburg, C.E. Hendriks, U.S. Schubert, Microwave Flash Sintering of Inkjet-Printed Silver Tracks on Polymer Substrates, *Adv. Mater.* 21 (2009) 4830–4834. <https://doi.org/10.1002/adma.200901081>.
- [16] W. Luo, W. Hu, S. Xiao, Size Effect on the Thermodynamic Properties of Silver Nanoparticles, *J. Phys. Chem. C*. 112 (2008) 2359–2369. <https://doi.org/10.1021/jp0770155>.

- [17] Ph. Buffat, J.-P. Borel, Size effect on the melting temperature of gold particles, *Phys. Rev. A.* 13 (1976) 2287–2298. <https://doi.org/10.1103/PhysRevA.13.2287>.
- [18] Fu Liwei, *Laser curing of inks for Plastic Electronic Applications*, University of Liverpool, 2014.
- [19] D.A. Roberson, R.B. Wicker, L.E. Murr, K. Church, E. MacDonald, Microstructural and Process Characterization of Conductive Traces Printed from Ag Particulate Inks, *Materials.* 4 (2011) 963–979. <https://doi.org/10.3390/ma4060963>.
- [20] J. Niittynen, R. Abbel, M. Mäntysalo, J. Perelaer, U.S. Schubert, D. Lupo, Alternative sintering methods compared to conventional thermal sintering for inkjet printed silver nanoparticle ink, *Thin Solid Films.* 556 (2014) 452–459. <https://doi.org/10.1016/j.tsf.2014.02.001>.
- [21] A.J. Lopes, I.H. Lee, E. MacDonald, R. Quintana, R. Wicker, Laser curing of silver-based conductive inks for in situ 3D structural electronics fabrication in stereolithography, *Journal of Materials Processing Technology.* 214 (2014) 1935–1945. <https://doi.org/10.1016/j.jmatprotec.2014.04.009>.
- [22] H.W. Tan, N. Saengchairat, G.L. Goh, J. An, C.K. Chua, T. Tran, Induction Sintering of Silver Nanoparticle Inks on Polyimide Substrates, *Adv. Mater. Technol.* 5 (2020) 1900897. <https://doi.org/10.1002/admt.201900897>.
- [23] D.A. Roberson, R.B. Wicker, E. MacDonald, Ohmic Curing of Printed Silver Conductive Traces, *Journal of Elec Materi.* 41 (2012) 2553–2566. <https://doi.org/10.1007/s11664-012-2140-4>.
- [24] B. Niese, U. Urmoneit, P. Amend, S. Roth, M. Schmidt, *Laser Sintering of Silver Ink for Generation of Embedded Electronic Circuits in Stereolithography Parts*, (n.d.) 12.
- [25] F. Tricot, C. Venet, D. Beneventi, D. Curtil, D. Chaussy, T.P. Vuong, J.E. Broquin, N. Reverdy-Bruas, Fabrication of 3D conductive circuits: print quality evaluation of a direct ink writing process, *RSC Adv.* 8 (2018) 26036–26046. <https://doi.org/10.1039/C8RA03380C>.