Low-cost Ink-Jet printing for Electrical Functionalization of Rigid Substrate Materials

Marcus Reichenberger, Oleksandr Kravchuk, Andreas Mühlbauer; Georg-Simon-Ohm University of Applied Sciences Nuremberg; 90489 Nuremberg, Germany

Abstract

Digital printing processes are gaining more and more interest as an approach to implement electrical functionality (conductive patterns, sensors etc.) on different types of substrate materials. Focusing on the inkjet-printing process, the paper presents results that were gathered with-in the research project "FKIA", funded by the Bavarian Research Foundation. In the paper, the applicability of inkjet printing of silver nanoparticle ink on technical thermoplastics substrate materials commonly used in automotive applications such as glass fiber filled PA, but also on phenolic paper substrates (FR-2) is investigated. In this context, the influence of the surface roughness of the molding tool on the printing results was examined. Besides thermal sintering of nano-particles, photonic sintering as one alternative approach is discussed. In addition, the long-term behavior of the produced conductor tracks was investigated. Parts were exposed to thermal cycling between -20°C and +100° for 1500 cycles. Besides the stability of the electrical properties also the mechanical stability of the metallic layers on the different substrates was compared with the findings prior to any exposure.

Introduction

As an emerging technology, digital printing processes are a promising approach for the additive metallization of Molded Interconnect Devices (MID) and other substrate materials. MIDs are injection molded three-dimensional devices, which integrate mechanical as well as electrical functions in one thermoplastic part [1]. Most research investigations focus on the applicability of expensive substrate materials such as Liquid Crystal Polymer or polyimide as carriers for printed electronics [2-4]. This material selection is mainly driven by the sintering temperatures needed to achieve high and reproducible conductivity. The investigations presented in this paper were initiated to demonstrate the capabilities and opportunities of ink-jetting silver ink based conductors tracks onto cost-effective injection molded thermo-plastic substrates, which are commonly used in high volume automotive applications. In parallel, a low invest printing process with common or only mechanically adapted office ink-jet printing equipment for fabricating conductor tracks is presented.

Materials, equipment and test conditions

Used substrates and ink

Out of four different thermoplastic substrate materials commonly used in automotive applications, plate specimen (dimensions 60mmx60mmx1mm) with three different levels of surface quality according to molding tool variations were molded.
In parallel, phenolic paper substrates (thermosetting material) with the same dimensions were used. Glass substrates were selected for some basic evaluations as a reference material. Details regarding the chosen materials can be found in Table 1.

Table 1. Substrate Materials

Abbreviation	Material& Filler	Heat deflection temperature	Water absorption
A	PA6.6 30% GF	234°C	5,6%
B	PA6 40% MF	186°C	5,4%
C	PA6 30% GB/GF	170°C	6,5%
D	PBT/ASA 20% GF	160°C (VST)	<1%
E	FR-2	-	-

Specially treated steel-inserts in the injection molding tool gave the opportunity to investigate the influence of the surface roughness on the inkjet printing behavior and the results. With these three different inserts, the surface roughness of the tool is transferred during the molding process to the thermoplastic specimen, thus resulting in different surface qualities of thermoplastic specimen. Figure 1 lists the surface qualities, depending on the insert type and the substrate material.

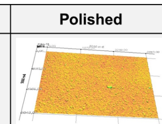
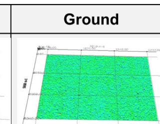
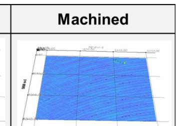
		Polished	Ground	Machined
Roughness value (Thermoplastics: in Flow direction)	Material			
R_a / R_z	A	0,37µm / 2,40µm	0,60µm / 3,38µm	0,68µm / 4,25µm
	B	0,27µm / 1,74µm	0,57µm / 3,30µm	0,54µm / 4,46µm
	C	0,17µm / 1,11µm	0,56µm / 3,14µm	0,64µm / 4,01µm
	D	0,29µm / 2,57µm	0,61µm / 3,94µm	0,65µm / 4,66µm
	FR-2	0,44µm / 2,49µm		
Remark: Measured according to DIN 4228 with optical laser-profilometer (verified by tactile measurement)				

Figure 1. Surface roughness of thermoplastic and thermo-setting specimen

As expected, the polished insert results in the lowest roughness values both for R_a and R_z, whereas the milled insert resulted in highest roughness values. Material E shows values similar to values obtained with polished insert.

For printing, a commercially available ink from ANP (DGP 40TE-20C) was used as received. According to the suppliers information, it consists of nano-silver particles in a TGME solution. The supplier recommends "curing temperatures" of around 180°C…200°C, without giving further information about the recommended curing time. Therefore it was necessary to determine the appropriate sintering process settings in the first step of the investigation program.

Test structures

To investigate the behavior of the Ag-filled ink during printing and sintering as well as the electrical resistance after sintering and accelerated ageing, a simple test structure was defined. The layout consists of several parallel tracks with nominal width of 1mm and 0,4mm and an effective length of 44mm. In addition, squares were printed onto selected substrates in order to evaluate the mechanical adhesion of the sintered ink to the substrate using the cross cut test according to ISO 2409 [5].

Used equipment

For printing, commercially available office inkjet printers from EPSON were used:

- EPSON R200
- EPSON R1800 (modified by Printolux: printing head can be lifted to enable printing onto three-dimensional parts)

It needs to be mentioned that using common office printers for printing Ag-nano-inks results in some constraints regarding process control and tuning. Adaption and optimization of the printing results using features such as drop space, waveform etc. is not possible. Therefore, it is crucial, that the chosen ink is compatible in terms of viscosity etc. with the selected printer. Additionally, office printers do not provide the position accuracy which is necessary for multiple printing of overlaying ink layers.

Thermal curing (sintering) of the inks was done in a preheated batch convection oven in normal air atmosphere.

Accelerated Ageing

To determine the effect of the different factors such as surface roughness, substrate material and conductor track width on the long term behavior, accelerated ageing tests were performed. The selected test conditions were slow thermal cycling between -20°C and +100°C with dwell times of 30 minutes each for 1000 cycles in an air system. This thermal cycling condition was chosen as it corresponds to automotive industry qualification requirements for electronic/mechatronic parts in passenger compartment. Resistance values of printed conductor tracks were recorded offline by four-point-measurement at room temperature after defined intervals.

Results

Printing Process

Prior to printing, all substrate were dried for 4h/80°C to achieve a reproducible and low water content and hereafter cleaned with lint-free clothes soaked with isopropyl alcohol.

After adjusting the printing program using the appropriate software, test structures were printed onto the dried and cleaned substrates. For getting sufficient and stable conductivity, multiple-printing up to 6 times was necessary, interrupted by 10 minute drying at 70°C. With these settings, conductor thicknesses of 2µm-3µm after sintering were achieved.

After printing, the structures were investigated using microscopy. Here it was found that substrate surfaces produced with the milled tool insert were not suitable due to un-controlled "bleeding" of the Ag-ink, following the surface structures induced by the milling process. For further investigations, this type of surface was not considered any longer. On the remaining surface qualities, relatively accurate lines can be printed. The line widths of dried conductor tracks independent from the substrate material were within a tolerance window of +/-20%, which is comparable to results achievable for conventionally etched traces on PCBs.

Sintering process evaluation

As mentioned above, determination of the appropriate curing (sintering) process for the ink was the first step of the investigation program. In order to get further information about the interaction between sintering conditions (temperature, time) and properties of the thermally treated Ag-ink-layers such as resistance, test structures were printed onto glass substrates. Due to the good thermal stability of this material, even higher curing temperatures will not influence the dimensional stability of the substrate.

Results showing the effect of the curing temperature (duration 1h) on the measured resistance values and the micro hardness of the cured Ag-layers can be seen in Figure 2.

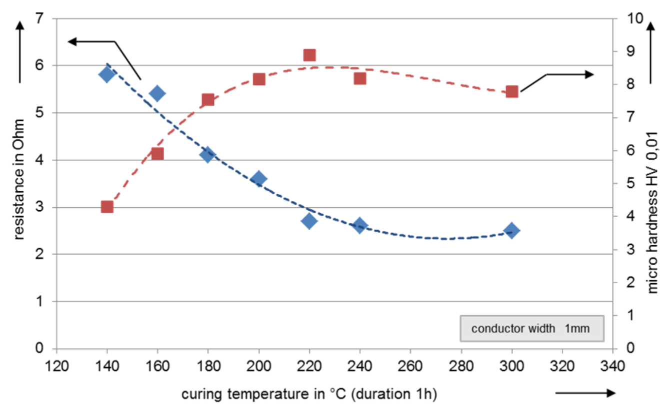


Figure 2. Development of resistance and micro hardness as a result of curing conditions

As expected, higher curing temperatures result in better conductivity. In the other hand, best conductivity was achieved with curing temperatures between 220°C…300°C, which is significantly higher than recommended by the supplier. In addition, micro hardness measurement indicates increasing hardness of the sintered Ag-layer up to curing temperatures of around 240°C. Taking these results into account, best curing conditions would be 240°C for 1h.

Unfortunately, the selected thermoplastic substrates are not able to withstand curing temperatures of 240°C. Therefore, it was necessary to define curing conditions providing a compromise between reasonable electrical performance and hardness on the one and reduced thermal stress for the substrates on the other hand. Finally, a curing profile of 180°C/1h was used for all further investigations. However, processing substrate material C and D with these conditions resulted in significant loss of dimensional stability with extreme bow and twist, therefore these materials were not used for further tests.

Initial resistance and adhesion values

After printing and sintering at 180°C/1h initial characterization of the samples was performed. Results displaying the influence of the selected substrate material A and B, the conductor width and the surface roughness can be seen in Figure 3. As expected, the polished tool surface results in the lowest resistance values, especially for broader conductor traces of 1mm width. For track width 0,4mm mean resistance values and variances are increasing by a factor of 3…4. Significant differences between the two substrate materials cannot be detected. In general, good results can be achieved even with ground tools. On material E (not shown in Figure 3), slightly higher resistance values of around 5Ohm for conductor width 1mm were measured. The variance of the values was comparable to the results gained on polyamide substrates.

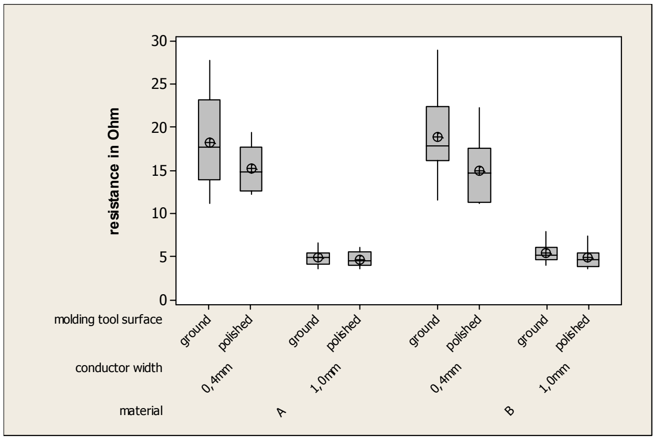


Figure 3. Initial resistance values of conductor tracks

The adhesion of the cured Ag-layer on both thermoplastic as well as on the thermosetting material is excellent. After cross cut testing ISO grading GT 0 was observed in the initial stage. No difference between the surface qualities could be observed.

Longterm behavior – resistance and adhesion

As already mentioned, printed test specimen (substrate A, B, E) were subject to slow thermal cycling between -20°C and +100°C up to 1500 cycles, 500 cycles more than originally planned. Despite of the relatively high thermal expansion coefficients for the thermoplastic materials between 30ppm/k up to 65ppm/k depending on the filler material type and orientation of the filler, the average values for the resistance of the conductor tracks for all materials, surface qualities and tracks widths remained stable or slightly dropped. Additionally, no increase of the variation could be observed. As the results for track width 1mm on both thermoplastics show (Figure 4), up to 1500 cycles no degradation of the electrical performance can be detected.

Similar observations were made for the adhesion strength. After 1000 cycles, no degradation of the adhesion strength can be detected during cross cut testing for all tested variations. The grading GT 0 remains unchanged. The edges of the cuts are completely smooth, none of the squares of the resulting lattice is detached.

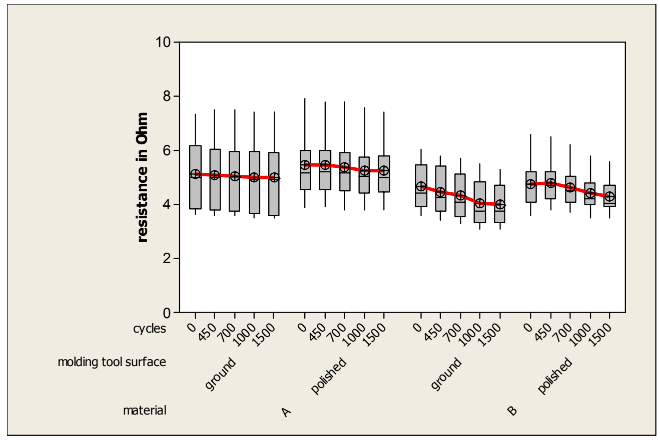


Figure 4. Effect of thermal cycling on the resistance values of conductor tracks (width 1mm)

Alternative Sintering Processes

To fabricate conductive tracks on substrates with low thermal stability, sintering is a crucial step. Due to the low thermal stability of the selected substrate materials, a process window with reduced thermal stress for the substrates needed to be identified. As a drawback of the reduced process temperatures, the achieved conductivity does not reach the optimum values. Therefore as a potential alternative among others [6], photonic sintering with intense pulsed light as a low temperature sintering alternative for temperature sensitive substrates was investigated to sinter the silver nanoparticle ink patterns.

Photonic sintering is a low thermal exposure sintering method using short light pulses (around 1ms) of a wavelength provided by a xenon flash lamp. The emitted light is absorbed by the nanoparticles to some extent, which heats them up and results in sintering to larger particles. To achieve good conductivity of the printed Ag-layers, the sintering process window defined by energy density and pulse duration needs to be set properly. For the experiments described in this paper, a photonic sintering system (Xenon Sinteron 2000, provided by Polytec, Waldbronn) equipped with a xenon spiral flash lamp was used. The pulse energy of the system can be set between 450Joule and 2000Joule, the duration can be adjusted between 100µs and 2000µs. The distance between the lamp and the substrate surface was kept fixed at 50mm.

To assess the potential of photonic sintering for substrates with lower thermal stability, only experiments on small scale basis were done so far. Printed substrates were subject to flash-light sintering with different pulse energies and durations. For the thermosetting material E, multiple flash sintering (25 respectively 12 repetitions) with pulse energies of 900 respectively 1350 Joule results in resistance values which are comparable or even lower than the corresponding values for thermal sintering (Figure 5). The resulting conductor traces were formed regularly, without indicating any blistering or surface cracks. Summing up, the process window for this type of material seems to be very robust and has room for further reduction of flash light pulse repetitions.

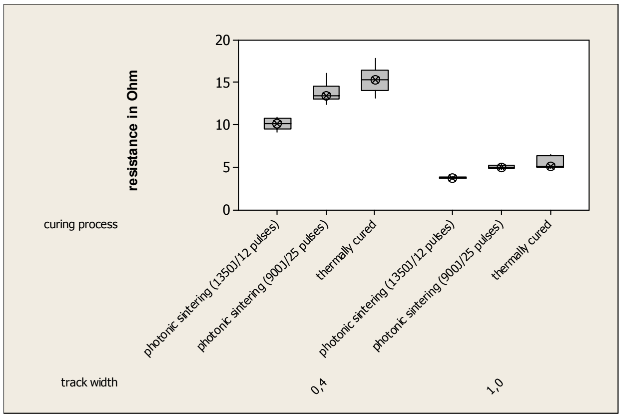


Figure 5. Initial resistance values of conductor tracks on FR-2 after photonic sintering with two different energy levels for both track widths (reference values: thermal curing 180°C/1h)

In contrast, photonic sintering on the remaining thermoplastic materials did not provide a similar robust and broad process window. Blistering of the Ag-layer, crack formation and adhesion loss between the substrate material and the Ag-tracks can be observed, if too much energy is applied. Other investigations describe similar observations [7]. As a result, lower single pulse energy settings and smaller number of pulse repetitions are necessary in order to avoid destroying of the printed conductors. However, the conductivity measured with these settings is remarkably worse than that for thermally sintered conductor tracks.

The reason for the observed blistering is not yet fully understood, but could be due to the high sensitivity of polyamide for water absorption. As there was a delay of 5 days between printing and photonic sintering, this might have caused water absorption from the air and therefore inferior performance during photonic sintering. Another explanation could be the thermal decomposition of organic coatings, which cover the nano-particles and prevent agglomeration prior to printing, during photonic sintering [7]. Further evaluations are on-going to understand the observed behavior and to improve the sintering results.

Conclusion and Outlook

Different manufacturing aspects for low-cost inkjet printing of Ag nanoparticle ink on thermoplastic and thermosetting substrate materials were investigated. The main aspects were print resolution and line width as well as conductivity and mechanical behavior of sintered structures. In the present case, with low cost inkjet equipment line widths down to approximately 400µm can be achieved. Surface roughness of the substrate material influences the spreading behavior in a significant way therefore very smooth surfaces are preferable. Due to the limited thermal stability of the selected substrate materials, sintering temperatures need to be reduced to 180°C, which results the relatively low conductivity compared with the results achievable with optimum curing conditions. Nevertheless, acceptable and stable conductivity can be achieved on all substrates. The adhesion of the cured layers on the different substrates is also not affected by thermal cycling between -20° und +100°C for 1500 cycles. In order to reduce the thermal load for low-temperature substrates, photonic sintering as a potential alternative to thermal sintering was investigated on small scale basis. The conductivity of conductor tracks on material E sintered with xenon flash lamp were slightly higher than corresponding values gained by thermal sintering. Nevertheless, applying photonic sintering to polyamide materials needs further investigation in order to define a robust process window and to determine root-cause and counteractions for the blistering.

In total, ink-jet printing of Ag-nano-inks is a highly promising approach for the functionalization of thermoplastic and other materials with lower thermal resistivity.

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Author Biography

Marcus Reichenberger graduated as a production technology engineer at Friedrich-Alexander-University (FAU) in Erlangen/Germany in 1996.In 2001 he completed his doctorate in electronics production at the same university. From 2001 until 2011 he worked for a globally acting automotive electronics company in several leading functions. Since September 2011 he holds a professorship at the Georg-Simon-Ohm University of Applied Sciences in Nuremberg/Germany.

Oleksandr Kravchuk graduated at Lviv Polytechnic National University in Lviv/Ukraine in 2009. Qualified as a master of laser and optoelectronic engineering, he is currently a postgraduate student at the Department of Photonics at the same university. He is working on a Ph.D. thesis on the theme "The Formation of electronic components using inkjet technology with carbon nanotubes".

Andreas Mühlbauer studies Mechatronic Engineering at the Georg-Simon-Ohm University since 2007.