Inkjet printing of silver and carbon conductive functional coatings

A thesis submitted to the University of Limerick in fulfilment of the requirements of the degree of Masters of Science

By

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Declaration

I, Cian Nash, hereby confirm that the content of this thesis is a product of my own research. Where use has been made of the work of other people it has been fully acknowledged and referenced in accordance with University regulations. This material has not been previously submitted to any other University or higher education institution for an academic award of any kind.

Signed: ______________________  Date: ______________________

Cian Nash
Abstract

The direct inkjet printing of conductive silver and/or carbon suspension inks on flexible substrates is a promising route for the direct manufacture of printed and functional electronics. In this thesis silver flake inks designed for flexography were modified for inkjet printing. The effect of the printing parameters on the properties of the printed silver layers was examined using a Taguchi design of experiments which allowed for the electrical conductivity to be optimised.

It was shown that dynamics of the inkjet deposition had a strong influence on the compaction of the silver flakes in the printed layers. The compaction observed led to conductivities which were only 1/100 of the conductivity of bulk silver. The impact of the deposition dynamics on the compaction in the silver layers was modelled and was found to be dominated by the properties of the ink droplet. The model was found to be in agreement with my previous measurements and it allows for the prediction of the compaction behaviour as a function of the drop size, rheology and the volume loading of the ink.

Carbon nanoform powders from the plasma splitting of natural gas were tailored by pyrolysis to improve their electrical conductivity and porosity. These powders were formulated into a water based ink suitable for inkjet printing, on printing conductive layers were formed with only printed layer without any further thermal treatment. The resistance of the coatings was demonstrated to decrease as the number of printed layers was increased.
Acknowledgements

I would like to express my immense gratitude to my supervisor Prof. Bartek Glowacki for his invaluable advice and guidance. I would not have been able to perform this research without the financial support which I received from the Bernal Energy Group led by Prof. Glowacki.

I would like to thank the other postgraduate members of the Bernal Energy Group, Emma and Niall for their advice and assistance in both writing this thesis and for creating a positive work environment.

I would like to thank Dr. George Amarandei in particular for his enormous assistance in coming up with ideas and methodologies for the interpretation of my data. The long discussions we had improved my understanding of the underlying physics behind drop wetting.

I am extremely grateful to the Department of Physics and Energy and the Bernal Institute at UL for the excellent facilities and technical support I received. In particular I would like to thank the technical staff who were always quick to help when I encountered technical problems in my project.

I want to thank my family and friends especially for the support (and much needed distractions) which they gave me throughout my MSc.
### List of Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\ddot{x}$</td>
<td>Acceleration</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett Joyner Halenda adsorption isotherm</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller adsorption isotherm</td>
</tr>
<tr>
<td>$R_c$</td>
<td>Capillary radius</td>
</tr>
<tr>
<td>CNF</td>
<td>Carbon nanoform</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>$d$</td>
<td>Change in inter-particle spacing</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
</tr>
<tr>
<td>A</td>
<td>Cross sectional area</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>DB</td>
<td>Denka Black</td>
</tr>
<tr>
<td>$\rho_{air}$</td>
<td>Density of air</td>
</tr>
<tr>
<td>$\rho_{Ag}$</td>
<td>Density of silver</td>
</tr>
<tr>
<td>DTGA</td>
<td>Differential thermogravimetric analysis</td>
</tr>
<tr>
<td>DCFC</td>
<td>Direct carbon fuel cell</td>
</tr>
<tr>
<td>DOD</td>
<td>Drop on demand</td>
</tr>
<tr>
<td>$a$</td>
<td>Droplet acceleration</td>
</tr>
<tr>
<td>H</td>
<td>Droplet diameter</td>
</tr>
<tr>
<td>$\rho_d$</td>
<td>Droplet line density</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>$p_d$</td>
<td>Dynamic pressure</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>R</td>
<td>Electrical resistance</td>
</tr>
<tr>
<td>$P_e$</td>
<td>External pressure</td>
</tr>
<tr>
<td>$D_f$</td>
<td>Final diameter of droplet</td>
</tr>
<tr>
<td>F</td>
<td>Force</td>
</tr>
<tr>
<td>F</td>
<td>Fraction of particles compacted</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
</tr>
<tr>
<td>$H_0$</td>
<td>Initial droplet diameter</td>
</tr>
<tr>
<td>$D$</td>
<td>Inter-particle spacing</td>
</tr>
<tr>
<td>$P_j$</td>
<td>Jetting pressure</td>
</tr>
<tr>
<td>LB</td>
<td>Larger the better signal to noise ratio</td>
</tr>
<tr>
<td>$d_t$</td>
<td>Layer thickness</td>
</tr>
<tr>
<td>l</td>
<td>Length</td>
</tr>
<tr>
<td>h</td>
<td>Length of fluid column</td>
</tr>
<tr>
<td>$L_f$</td>
<td>Loading fraction</td>
</tr>
<tr>
<td>L</td>
<td>Loading of particles</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>Mass density</td>
</tr>
<tr>
<td>$m_d$</td>
<td>Mass of droplet</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of particles</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of particles</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Opening time</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Particle radius</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>PC</td>
<td>Plasma carbon</td>
</tr>
<tr>
<td>$x$</td>
<td>Position</td>
</tr>
<tr>
<td>PPC</td>
<td>Pyrolysed plasma carbon</td>
</tr>
<tr>
<td>C</td>
<td>Particle contact radius</td>
</tr>
<tr>
<td>RC</td>
<td>Residual polymer carrier</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>S</td>
<td>Scalloping factor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SN ratio</td>
<td>Signal to noise ratio</td>
</tr>
<tr>
<td>SB</td>
<td>Smaller the better signal to noise ratio</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific surface area</td>
</tr>
<tr>
<td>$P_s$</td>
<td>Stagnation pressure</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface tension</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>$\dot{x}$</td>
<td>Velocity</td>
</tr>
<tr>
<td>$v$</td>
<td>Velocity of drop</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_d$</td>
<td>Volume of drop</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffractometry</td>
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Motivation

Additive manufacture is of rapidly growing interest and it is the key class of technologies in development for the 'third industrial revolution'[1]. Additive manufacturing marks a divergence from the classical types of manufacturing such as the assembly line of the ‘second industrial revolution’ which is responsible for the production of huge amounts of identical products. 3D printing allows for the production of customised components at a low cost allowing it to compete with and surpass traditional techniques. Additive manufacturing allows for on-demand manufacture which is highly flexible compared to traditional techniques [2].

Additive manufacturing is the term used to describe processes in which material is deposited only where it is needed in a layer by layer fashion, there are a number of techniques which can be used to accomplish this such as extrusion and selective solidification of liquid or powder beds to produce a finished part [3], [4]. This process can be used to create entire objects or it can be used to manufacture moulds for casting, enabling the use of materials which are not yet compatible with additive techniques. Traditional or subtractive manufacturing relies on the selective removal of material from a larger piece to produce a finished part an example of this is CNC milling. This has the disadvantage of being costly and wasteful of material as well as introducing geometrical limitations because the cutting head has to be able to fit inside the geometry being produced, because of this manufacturers turning to 3D printing as an alternative for traditional manufacturing processes. The number of materials which are compatible with additive manufacturing technologies is growing at a rapid rate. Materials such as metal and polymers can be selectively sintered by laser irradiation or deposited as suspensions and sols [5]–[7].

Nanomaterials have significantly different physical, chemical and electrical properties than the bulk properties of the material, this has led to the use of nanomaterial inks and nanomaterial filled composites for additive manufacturing. Nanomaterials are added to alter the physical properties of materials such as the mechanical strength, electrical and thermal conductivity, optical properties or the surface chemistry [8]. Additives such as carbon nanotubes and carbon black are added to polymer and rubber compounds to increase their resistance to wear and
thermal conductivity [9], [10]. Carbon nanotubes and graphene platelets also display semiconducting properties making them suitable materials for developing the next generation of electronic devices. These carbon nanoforms are an extremely interesting and promising area of research so research into economically viable methods of production such as microwave plasma processing of methane is of high importance[11].

Metal nanoparticles display significantly lower melting points than the bulk metal due to their increased surface to volume ratio, making it is possible to sinter them at far lower temperatures (~100°C) [12]. Sintered metal nanoparticles offer a route to the inkjet printing of conductive tracks and coatings. The small particle size and ease of dispersing metal nanoparticles into inks makes them highly compatible with additive manufacture by inkjet printing on a huge variety of substrates. To avoid damage to sensitive substrates, flash photonic sintering, selective laser sintering or microwave sintering can be utilised in which the printed nanoparticle layer is exposed an extremely bright flash of light which it absorbs strongly, this can heat the particles enough to enable sintering without excessive heating of the underlying substrate[13]–[15].Silver nanoparticle based inks in conjunction with photonic sintering have been used to manufacture printed tracks with conductivities reaching approximately 66% of bulk silver[16].

Inkjet printing of carbon nanoforms presents exciting opportunities for the manufacture of conductive coatings and tracks in addition to energy storage devices[17], [18]. Carbon nanoforms include carbon nanotubes, buckyballs and graphene in addition to other allotropes of carbon. These materials remain expensive due to their difficulty of manufacture but the plasma splitting of methane presents an opportunity to manufacture carbon nanoforms at an industrial scale at a low cost while also liberating hydrogen which can be used as a fuel or for cryogenics applications [19].
Research Objectives

The initial research in this project concerns the inkjet printing of commercially available silver flake inks (DZP Technologies). These commercial inks are designed for flexographic printing making them too viscous to be compatible with inkjet printing without modification. To reduce the viscosity of these inks into the range which is compatible with inkjet printing the inks were diluted with water and the effect of the dilution and the printing parameters on the conductivity of the obtained tracks was studied.

The direct inkjet printing of conductive silver inks (D38NV and F50NV, DZP technologies Ltd.) led to conductive silver tracks with electrical conductivity approximately 100 times lower than bulk silver by drying the printed ink at room temperature. During the course of this study it became clear that the inkjet printing process itself was having an effect on the microstructure of the printed layers which resulted in higher than expected conductivity in the layers.

Conductive carbon nanoforms produced from microwave plasma processing of methane are promising materials for manufacturing functional and conductive coatings for printed electronics. The availability of a supply of these plasma derived carbons (PC) from Professor Glowacki’s research group in Cambridge prompted research into the use of these carbons in inkjet printable suspensions for conductive and functional coatings[19], [20].

The experimental work presented in this thesis consists of two main parts:

1. Inkjet printing of commercial silver ink on paper substrates which was done to investigate the effect of the substrate and the inkjet printing parameters on the microstructure and the electrical conductivity of obtained layers. A Taguchi design of experiments was used to extract the main factors responsible for the properties of the printed layers. The effect of particle size distribution on the electrical conductivity will be compared between the two commercial inks and the effect of the inkjet printing process on the compaction of the printed layers will be investigated by mathematical modelling.

2. Carbon suspensions suitable for inkjet printing containing commercially available carbon powders and plasma derived carbons will be examined. The
effect of the particle properties, dispersing media and surfactant concentration on the suspension properties and on printed layers was investigated. The effect of thermal treatment on the carbon powders was looked at as a means to tailor the properties of printed carbon layers for applications.
1 Background

For electronic components the direct printing of metals from aqueous solutions or solvent-based inks is an important technique because it can be used to produce continuous metallic patterns in a pre-defined manner on large variety of substrates [21]. Conductive inks find applications in the areas of printed and plastic electronics as conductive connectors in printed (rigid or flexible) circuit boards, flexible aerospace and automotive components, conductive grids for flexible displays screens, medical devices and bio-sensors as well as energy related components such as electrodes in organic light-emitting diode applications, photovoltaics, current collectors in flexible batteries and supercapacitors printed on paper or nano-cellulose substrates [22]. These inks have to meet strict requirements in terms of performance and stability, processing temperatures, cost, energy efficiency, and manufacturability.

The metal precursor inks can be composed either of dissolved organometallic compounds and polymers or colloidal suspensions of metal micro- and/or nano-particles suspensions [21]. Over the years a significant effort was devoted to the production and utilization of silver particles of different morphologies (e.g. nanoparticles, nanowires, flakes etc.) due to their high electrical conductivity, resistance to oxidation, excellent solderability and reasonable price [23]. Therefore, silver conductive inks are used in plastic and printed electronics where electronic devices require multiple layers of conductive interconnects or electrodes [21]–[23]. Metal particle inks have the disadvantage of requiring extra post processing to obtain highly conductive lines and coatings, this post-processing introduces limits on the possible substrate choices available as typical inks require harsh solvents and thermal sintering. The use of conductive and water based silver inks which don’t require sintering (such as those discussed in this thesis) presents a huge advantage because it allows for conductive coatings and tracks to be printed directly on to almost any substrate without damage [24], [25].

Energy storage is a key limiting factor in using the green electricity and power from solar and wind resources. Ideally, a highly efficient energy storage device should provide high instantaneous power combined with high energy density and have a long operational life with the ability withstand a large number of charge-discharge cycles. These energy storage devices must be able to fulfil application specific
requirements for discharge time, endurance of harsh conditions such as large variations in temperature and mechanical shocks and vibrations encountered in practical devices [26]–[28]. Super-capacitors, redox flow batteries and fuel meet most of the above criteria representing exciting alternatives to conventional battery technology. The key factors reducing their efficiency is poor electrode kinetics and high electrical resistance which can lead to a high ohmic drop across a battery or supercapacitor electrode. Poor electrode kinetics lead to slow charging and discharging cycles reducing the compatibility of an electrode for high power applications. Many of the existing problems with electrochemical electrodes can be addressed by using environmentally friendly low-resistance carbon electrodes with large surface area for ions to cling onto[26]–[28].

Carbonaceous materials resulting from processing hydrocarbons like natural gas, methane or acetylene can fulfil these conditions. The resulting carbon powders can contain valuable carbon allotropes (e.g. nanotubes, fullerenes, and mesoporous carbon structures [20]) that can provide the required surface area, porosity and/or electrical properties. By coating these valuable carbons onto different substrates, electrodes with enhanced properties can be obtained. The carbons deposition can be achieved by incorporating them in liquid dispersions i.e. inks. These inks can be printed using electro-magnetically actuated print heads (inkjet printing) avoiding substrate damage and making the process suitable for large scale manufacturing.

To obtain the desired patterns, the inks can be applied on a variety of substrates using different methods of coating (i.e. the ink layer is transferred to the substrate by pouring, spraying, casting or smearing it over the surface) or printing (by which the layer of ink is transferred from a stamp to a substrate by a reversing action) [29]. Coating techniques include spin, spray, curtain, casting, painting, knife-over-edge coating, doctor blading etc., while printing techniques are the screen, pad, gravure or flexographic printing. Inkjet printing is a standalone technique that could be placed in both categories as it can apply uniform coatings but also offers the possibility to reproduce a complex pattern in a one step process [29]. In the areas of flexible and paper electronics the coating and printing techniques can be used either individually or combined in order to reduce the number of processing steps.
Casting (Figure 1-1 a) is the simplest experimental technique that can be employed for substrates coating [30]. No sophisticated equipment is needed but a good horizontality of the substrate surface is essential. The ink is simply cast onto the substrate in the form of isolated drops or liquid portion and then dried at room or elevated temperature. This simple procedure allows for thick films with good quality of the coating to be obtained, but it lacks in the precision of the film thickness control. Also, the wetting properties of the inks are important as dewetting can occur during drying leading to inhomogeneous coatings.

Doctor-blading (Figure 1-1 b) allows for the formation of films with a well-predefined thickness ranging from 10 µm to 500 µm while the ink loss during coating can be minimized to less than 5wt% [30], [31]. This technique uses a sharp blade placed at a fixed distance above the surface of the substrate and it can be applied for both grooved and flat surfaces. The ink is placed in front of the blade that is then moved linearly across the substrate. The thickness value of the coated layer depends on the meniscus between the blade and the wet film on trailing edge of the blade as this is related to shear field (proportional to the speed of the blade). Other factors that can influence the film thickness are the surface energy of the substrate and/or its porosity, but also the surface tension and the viscosity of the ink. The final dry thickness of the film will be proportional to the gap width and the concentration of the solid material present in the solution [30]. The linear speed during the doctor-blading can vary between 1 – 100 mm·s\(^{-1}\). Therefore, this leads to relatively small shear stress applied during coating [30], [31]. An alternative to this technique is represented by bar-coating that has a similar working principle, but in this case a bar rolls the ink over the substrate [22], [32].

Flexographic printing (Figure 1-1 c) has been demonstrated to be a reliable technique for organic electronics, photovoltaic and battery applications [33]. Its working principle is based on the transfer of the desired image using relief plates that impose a low pressure onto the substrate [33], [34]. During the printing procedure the ink is transferred from a reservoir to an anilox (micro-engraved cylinder) by a doctor blade and then onto a printing plate. The anilox micro-cells are always filled with a constant ink volume. The printing plate defines the pattern information. While the inked pattern is pressed between the printing plate and printing cylinder against the substrate the ink transfer is made by ink film scission. When a solid pattern is printed its thickness depends on the ink volume in the anilox cells, on the ink-substrate
affinity and on the number of ink layers [33]. The roller pressure during flexographic printing is typically around 100 Pa and it will depend on parameters such as the nature of the roller material that will influence its hardness, the impression distance, the substrate material, the printing speed (e.g. for hand flexo-proofer this is ~ 0.1 m·s\(^{-1}\)). Flexographic printing can be used to deposit silver nanoparticle ink coatings with a conductivity of approximately 2% of bulk silver with track dimensions of the order of 50 µm [35], the reel to reel compatibility of flexographic techniques lend themselves to the large scale manufacture of patterned devices such as RFID tags and solar cell electrodes[13], [30].

Inkjet printing (Figure 1-1 d) is a relatively new technique to be used in energy and electronics industrial applications [4]. In the drop-on-demand mode (DOD) the inkjet printing has the advantage of delivering controlled small amounts of ink onto substrate creating the desired pattern with minimal ink waste [36], [37] and minimal influence on and without direct contact with the substrate [38]. Nowadays, the majority of commercial inkjet printers are based on DOD technology utilizing thermal, piezoelectric, electrostatic or acoustic methods of droplets generation [5]. Alternatively, the electromagnetically actuated print head (Figure 2-1) can be used as DOD method in order to minimize ink heating and to reduce the procedure complexity [39]. The nozzle aperture can be machined to the desired tolerance whilst exhibiting resistance to wear and corrosion, but its size is fixed. A constant pressure is provided by an external air compressor allowing the production of drops as a solenoid driven plunger opens and closes the nozzle orifice. The drop size can be controlled by varying the opening time and/or the rheological properties of the ink. The method allows for the movement of either the nozzle or the substrate. Thus, the relative positions of the print head and substrate may be adjusted accurately and rapidly by using computer controlled X-Y stage. An advantage of inkjet printing over other manufacturing techniques is that it is a digital printing technique in which the desired pattern can be printed at will without the need for masks or patterned rollers. The resolution of inkjet printing is also quite high ~50 µm however self-aligning techniques can be used to decrease the minimum feature size to the order of 0.1 µm [40].
Figure 1-1 Schematic representation of the different techniques used to create layers of conductive inks on paper substrate. Pictured are the corresponding optical images of the layers obtained by: (a) Casting – ink drops attached to the dispensing nozzle are brought into contact with the substrate and transferred due to capillary action. (b) Doctor-blading – an ink drop is placed on the substrate in front of a blade. By moving the blade small shear fields are applied and the substrate is coated. (c) Flexographic printing – the ink from a reservoir is transferred to the anilox and then to the plate cylinder (this can be flat or engraved). Then the ink is impregnated on the paper against the impression cylinder. The amount of ink at the contact point between the plate cylinder and the paper is exaggerated for illustration purpose (d) Inkjet printing – in drop-on-demand (DOD) the ink is released in small quantities from a nozzle at high speeds. The drops impact with the substrate and/or with the previous deposited droplets leading to the desired coating thickness.

It can be anticipated that, if one particular ink composition is used, the methods presented in Figure 1-1 will lead to different properties of the coatings deposited onto the substrates as the ink flow dynamics are dependent on the method of deposition. Therefore finding the differences that can occur and determining the technique that can deliver a particular set of specifications (e.g. target conductivity, film thickness etc.) for a particular ink composition is important as this will influence the success and the efficiency of chosen deposition method. Optimizing the technique that deliver the required quality of the ink layer it is important from technological perspectives.
2 Silver printing: The conductive properties of coated and printed silver layers on a paper substrate

The effect of the coating and printing methods presented in chapter 1 on the micro-structure and on the conductivity of the resulting silver layers formed on proofing paper substrates. In the experiment a specially formulated water-based ink with silver micron-sized flakes of narrow-size distribution was used in an attempt to determine the optimum silver printing process for paper electronics. Commonly used silver-nanoparticles based inks are not suitable for this application because they typically require thermal treatment to sinter the nanoparticles and use solvents that can deform or degrade the paper substrates.

It is shown that for this particular ink composition, only the inkjet printed coatings revealed high conductivity after deposition at room temperature with no further sintering process being required. Using a Taguchi optimization method the influence of the different process parameters like ink thinning, pressure, opening time and drop density on the conductivity of the inkjet printed layers were evaluated and discussed.

2.1 Materials and Methods

2.1.1 Materials

A water-based silver flake ink formulated by DZP Technologies Ltd, UK was used for the printing experiments. The silver content of D38NV ink was 52 wt% and the ink viscosity was quoted as 10 Pa·s. The silver flakes had a narrow size distribution with 10% < 1.1 µm, 50% < 2.1 µm and 90% < 3.9 µm. For some of the printing experiments the ink was thinned with deionised water (18 MΩ.cm). A predefined shaking and stirring procedure was performed before deposition to ensure a homogenous mixture. A coated proofing paper (KPP/SHC from RK Print Coat Instruments, UK) with a Brunauer-Emmett-Teller (BET) surface area of 23.5 m²·g⁻¹ was used as a substrate in all the coating and printing experiments discussed in chapters 2 and 4. A scanning electron microscopy (SEM) image of this substrate is presented in Figure 2-1 a. The effect of the ink–substrate interactions (e.g. substrate wettability, porosity) was maintained constant and, therefore, not discussed in this thesis. Thus, the final results should be influenced only by the method used to deliver the ink onto the substrate.
Figure 2-1 (a) The SEM image of coated proofing paper revealing the microstructure of the paper. Scale bar represents 2 µm. (b) Schematic diagram and (c) Optical image of the DOD inkjet printing head used in this study. The printing head was attached to a Roland plotter DXY 1150 to allow for X-Y movement with a step resolution of 25 µm.

Casting consists of applying a fixed amount (~100 µL) of as-received or thinned ink as a drop onto the paper substrate. The distance between the dispensing nozzle and the substrate was minimized until the ink drop was deposited mainly due to capillary action. The liquid deposition led to drops of 4 – 7 mm diameter (Figure 2-2 a). The coated surface was then dried at room temperature. However, even after few days the core of the coated layers remained wet.

In the doctor-blading procedure ink drops with similar sizes as for casting were used. The drops were placed between two tape tracks. This simple configuration allowed for a constant gap between the blade and the substrate during coating. A sharp laboratory blade was then moved across the substrate at a speed of approximately 0.01 m·s$^{-1}$. The procedure was then repeated with bar coating, thus mimicking the bar methods described in [2, 6]. In the present case a cylinder with a non-porous rubber shell and metal inner core was used. Between the rubber shell and the metal core a soft foam material was present. The method led to similar results as doctor-blading.
Figure 2-2 Optical images of (a) a typical ink-drop deposit by casting; (b) a layer coated using the doctor-blading. The speed of the blade was kept at ≈ 0.01 m·s⁻¹. (c) a typical flexographic printed layer. The printing speed was 0.1 m·s⁻¹. (d) typical silver tracks obtained using the DOD inkjet printing. The drop speed varies with the printing parameters but the typical values are 1 – 2 m·s⁻¹. The scale bar in all images represents 5 mm.

For flexographic printing only as-received ink was used. The printing was performed at a speed of 0.1 m·s⁻¹ leading to smooth layers as seen in Figure 2-2 b. The films were printed using a hand flexographic proofer with 200 LPI and Q type cell (quad anilo engraving) with a volume of 9.0 BCM. In a control experiment, the same flexographic printing arrangement was used to print silver films using a commercial flexographic ink containing silver powders of wide-size particle distribution (ink F50NV formulated by DZP Technologies Ltd.) and this led to a fully conductive film, no sintering process being required (data not shown).

Inkjet printing was performed using thinned ink as the as-received ink was too viscous for direct use in the inkjet printing head. The print chamber (Figure 2-1 b and c) was emptied and cleaned by purging water and isopropyl alcohol before a fresh ink was used.

The electromagnetically actuated inkjet system was controlled by hardware (Macrojet X–Y controller) and software developed within TEMPRI project [14]. This allows for the printing of custom raster scan patterns. The nozzle aperture was defined by a ruby orifice of 100 µm in diameter (Figure 2-1 b). The jetting pressure
was provided by means of compressed air controlled by a high precision adjustable regulator (SMC IR3000-04). The print nozzle was moved over the substrate by a Rolland X–Y plotter with a step resolution of 25 µm. For all inkjet experiments presented in this paper the inter-drop wait time was fixed at 250 µs, this means that a drop is deposited and the nozzle is moved to the next location while the next drop.

### 2.1.2 Conductivity measurements

The electrical resistance of the patterns was measured using a Jandel 4 point probe with a Matt TC tip (radius ~ 100 μm, probe spacing ~1 mm). The probes were placed on each of the lines and the resistance per unit length was measured. The current between the outer pins was set to $I = 100$ mA and the voltage $V$ across the inner pins was measured. Five values were measured for each pattern. The resistance ($R$) per unit length ($l$) was calculated using:

$$ R = \frac{V}{I} \quad \text{(Eq 2.1)} $$

The conductivity was calculated by:

$$ \sigma = \frac{A}{Rl} \quad \text{(Eq 2.2)} $$

where (A) is cross sectional area (as determined from the SEM images). The conductivity values were then employed to determine the signal to noise (S/N) ratios and the average conductivity for each trial in the Taguchi analysis as it is described in section 2.2.4. When no conductivity was measured the zero values were assigned.

In all cases, the ink layers and tracks were used “as printed” without any post-treatment or sintering.

### 2.1.3 Image analysis

The microstructure of the ink layers was inspected by scanning electron microscopy using a Hitachi S4800 FESEM operating at 5 kV. Images analysis was performed using the Open Source image processing package FIJI, which is based on ImageJ (National Institutes of Health, USA). Low magnification top-view SEM images gave information on the quality of inkjet printed layers surface. At larger magnification the shape and the 2D projected area of the silver flakes could be determined. Using this information the surface coverage (defined as being the total 2D projected area of silver divided by the total area of the image) was evaluated. However, the surface coverage would reflect only the flakes visibility as these were found to be oriented
predominantly in a horizontal plane, but in some cases they tended to have a 3D orientation. The SEM investigation of the layer cross-section allowed to estimate the relative amount of silver present in the layers as represented by the filling ratio (defined in a similar manner as coverage) and also to observe the flakes vertical distribution and their connectivity. The thickness of the printed layers was also estimated from the SEM cross-sections.

2.2 Results and Discussion

Casting the silver ink onto the paper substrate led to formation of uniform and relatively thick layers (Figure 2-2 a) with thicknesses of ~ 200 µm or larger. The layers exhibited an inner wet structure present after days of drying at room temperature as result of the substantial thickness that prevented water removal in the absence of further thermal treatment. For doctor-blading similar drops were first cast on the substrate and then bladed. This led to uniform coatings (Figure 2-2 b) of silver ink on the paper. The doctor-blading experiments were performed for as-received and thinned (in a ratio of 40% ink and 60% water) inks resulting into coatings with thicknesses of 27 and 38 µm, respectively. Flexographic printing of the as-received ink led to a film thickness of 7 µm while the inkjet printing of the thinned ink (40% ink and 60% water) produced tracks which are approximately 19 µm thick.

Conductivity measurements were performed on all the layers. Only the tracks obtained by inkjet printing the thinned ink were conductive. No conductivity values were obtained for the 4-point probe measurements of the other samples.

As different techniques were used it was expected that the difference in the conductivity of the silver layers would be related to the inner morphology as an effect of the silver flakes connectivity and the formation of conductive percolating paths.

2.2.1 Microstructure

Both doctor-blading (Figure 2-3 a) and flexographic printing (Figure 2-3 b) were revealed to produce a uniform distribution of the flakes within the layer when the as-received ink was used. The visual distribution of the flakes doesn’t seem to differ significantly when the water-thinned ink is coated by doctor-blading (Figure 2-3 c). Therefore in these samples a significant number of brighter regions (due to overcharging with electron beam) containing the residual polymer carrier (RC) can be observed in the SEM images (Figure 2-3 a–b). These RC regions kept the flakes
apart. Therefore, the flakes could not form a conductive path. For the layer obtained by inkjet printing, however, the top-view SEM images (Figure 2-3 d) were dominated by the silver flakes presence forming a continuous network.

The cross-sections of the layers (Figure 2-4) showed similar distribution of the flakes within the layers. Thus, after blading (Figure 2-4 a and c) and flexographic printing (Figure 2-4 b) the silver flakes remain isolated by the RC while after inkjet printing the flakes are oriented in-plane and compacted (Figure 2-4 d).

![Figure 2-3 Top-view SEM images of the silver ink (D38NV) layers using: (a) doctor blading of the as-received ink; (b) flexography of the as-received ink; (c) doctor blading of a thinned ink (40% ink and 60% water); (d) inkjet printing of a thinned ink (40% ink and 60% water). The printing parameters were opening time \( \tau = 275 \, \mu s \), jetting pressure \( P_j = 0.6 \) bar, drop density \( \rho_d = 2 \) drops-mm\(^{-1}\). The presence of the residual polymer carrier (RC) and of the silver (Ag) flakes is indicated by arrows. The scale bar represents 10 µm in all the images.

The printing parameters were opening time \( \tau = 275 \, \mu s \), jetting pressure \( P_j = 0.6 \) bar, drop density \( \rho_d = 2 \) drops-mm\(^{-1}\). The presence of the residual polymer carrier (RC) and of the silver (Ag) flakes is indicated by arrows. The scale bar represents 10 µm in all the images.
Figure 2-4 Cross-section SEM images of the silver ink (D38NV) layers using: (a) doctor blading of the as-received ink, (b) flexography of the as-received ink, (c) doctor blading of a thinned ink (40% ink and 60% water), (d) inkjet printing of a thinned ink (40% ink and 60% water). The printing parameters were opening time $\tau = 275\, \mu s$, $P_j = 0.6\, \text{bar}$, $\rho_d = 2\, \text{drops/mm}^2$. The presence of the residual polymer carrier (RC) and of the silver (Ag) flake nest is indicated by arrows. The dotted lines show layers with a thickness of (a) 27µm, (b) 7 µm, (c) 38 µm and (d) 19 µm, respectively. The scale bar represents 5 µm in all the images.

The SEM analysis of the layers (Figure 2-3 and Figure 2-4) suggests that the silver flakes are randomly distributed within the layer and separated by large areas of residual carrier regions, but the flakes are connected locally leading to small isolated clusters or nests. These nests were far apart and there is no percolating path that can allow for electrical conductivity occurring.

### 2.2.2 Electrical conductivity
The electrical conductivity data measured (Figure 2-5) were analysed in relation with the flakes surface coverage from the top view images (Figure 2-3) and the filling
ratio from the cross-section images (Figure 2-4). It was observed (Figure 2-5) that for small coverage and filling ratios (corresponding to isolated nests of flakes) the conductivity was zero, while for enhanced flake compaction (as reflected by the larger coverage and filling ratios) the layers became electrically conductive. Only the inkjet printed coatings were conductive. The samples coated using doctor-blading (i.e. samples a and c) have similar coverage and filing ratio independently of their thinning. This suggests that the ink-thinning might play a secondary role in the final morphology.

Although the thinnest layers were obtained by flexographic printing, the highest compaction of the flakes was observed in the inkjet printed layers. The thinned ink was utilized in inkjet printing and doctor-blading experiments. In the latter case no significant difference in the flake distribution within the layer was observed when compared with as-received ink experiments (compare to Figure 2-3 a and c with Figure 2-4 a and c, respectively). This observation suggests that the changes in the conductivity are not related to the variation of the ink mass load percentage but to the dynamics of the suspended silver flakes during the coating or printing processes.
2.2.3 Ink flow dynamics and its influence on the conductive properties of the layers

The dynamics of ink transfer inherent to the different coating and printing methods are complex processes that depend on the ink properties e.g. viscosity and surface tension (both parameters are also directly related to the solid content of the ink), the paper properties (roughness or porosity) and on the paper-ink interactions. Due to the complexity of the processes involved it is not a trivial task to determine the individual influence of each parameter because they are not independent. Here, as for all methods the same ink (or its thinned variants) and the same paper substrate were used, the importance of these factors becomes secondary to the influence exerted by the coating and printing methods. Significant efforts have been made in the last decades to model the different types of ink flows and it is beyond the scope of this thesis to give a complete fluid dynamics description of the ink-flow for different methods employed. Therefore, I will limit the discussion only to the description of the main kinetic factors that could lead to the observed changes in the conductivity of the silver layers.

The paper-ink interaction depends on the coating and printing method used. Nevertheless this interaction could be divided into three common stages. In the first stage the ink makes contact with the substrate and the liquid carrier starts to be absorbed by the paper. In the second stage the flakes tend to agglomerate and a partially dried film forms. As the flakes aggregate they also start to reach the paper and block the pores. Consequently, the residual liquid carrier will be trapped within the deposited layer. In the third stage a consolidation of the dried film occurs. At this stage the liquid carrier loss can happen only through evaporation as the permeation through the paper pores is obstructed. The in-plane motion of particles is expected to be small under typical drying conditions, while the motion of the particles into the paper pores is prevented by a bridging mechanism [41]. For inks with a relatively high initial volume fraction flakes (used in this study with the exception of inkjet ink) the pores can be blocked by a group of particles trying to enter the pore simultaneously. Usually the pores are blocked almost immediately. This blocking mechanism provides an explanation for the wet core of the casted layers persisting days after coating as well as for the presence of the RC in the layers deposited by doctor-blading or flexographic printing. The duration of each stage will depend on
the ink properties e.g. the initial solid volume of the ink, but also on the capillary-driven process taking place during the coating and printing.

The Bosanquet model can be applied for studying this capillary-driven process [42]. Thus, providing that the Poisseuille’s law applies the effects of the force due to momentum exchange of ink fluid in a capillary tube and the circumstances under which these effects become negligible can be investigated. In its mathematical form the Bosanquet model can be written as:

\[
\frac{d}{dt} \left( \pi R_c^2 \rho_m h \frac{dh}{dt} \right) + 8\pi \mu \frac{dh}{dt} = P_e \pi R_c^2 + 2\pi R_c \gamma \cos \theta
\]

(Eq 2.3)

where \( R_c \) is the capillary tube radius, \( \rho_m \) is the mass density, \( h \) the length of the fluid column, \( \mu \) the dynamic viscosity of the liquid, \( \gamma \) the liquid surface tension and \( \theta \) the contact angle. The first term on the left-hand side accounts for the force due to the momentum exchange of the liquid in a capillary tube (here represented by the paper pore) and the second term is the viscosity drag of the liquid. On the right-hand side the first term corresponds to the external pressure \( P_e \) exerted by the ink on the paper surface while the second term corresponds to the capillary force. Thus, it can be observed that a significant increase in the external pressure can render the capillary forces inappreciable since they are constant for a given ink-paper system.

In the casting procedure no external pressure is applied (\( P_e = 0 \)) and therefore, the entire flow is driven only by the capillary forces (Figure 2-6a). Therefore, compaction of the flakes is minimal and the thick layers deposited are not conductive. The liquid carrier is not fully absorbed as the pores will be blocked by the flakes nests, preventing the inner core of the coating from drying quickly.

During doctor-blading the liquid flows in the gap between the blade and the substrate (Figure 2-6 b). As liquid is dragged by the wedge, a pressure gradient is formed, in opposition to the drag flow. Therefore, the blade removes the excess of coating and acts as self-metering smoothing system [43]. The pressure distribution under the blade is a strong function of the blade operating angle, and whether or not the blade is stiff or if the blade erosion takes place [43], [44]. The coating speed used was small (~ 0.01 m·s\(^{-1}\)) so the expected values for the pressure are small. When blading is applied to liquid dispersions containing particles as the present ink, structures of particles can form in shear fields. The size of these structures varies with the shear
fields and they can even span the gap between the paper and the blade [45]. However, these large bridging structures were not observed confirming the existence of small shear fields.

In flexographic printing the external pressure $P_e$ is due to the printing nip and it varies with the pulse, vanishing when the pulse finishes [42]. In the present paper a hand held flexographic proofer (with no impression cylinder) was used. The roller pressure during the flexographic printing is typically below 100 Pa, and it will depend on a range of parameters such as nature of the roller material, the impression distance, the substrate material, the printing speed, etc. The dynamic nip pressure (see Figure 2-6 c) used in the present case is estimated to be about 0.1 - 0.2 MPa. This larger pressure accounts for the thinner films seen after flexographic printing. The pressure profile (Figure 2-6 b) for the blading [46] is similar to that for the flexographic printing (see Figure 2-6 c) leading to similar morphologies (compare Figure 2-3 a and b).

In inkjet printing, after the contact with the substrate the drop starts to spread as the inertia of the droplet causes a forced wetting. Upon contact with the substrate the droplet starts to deform and the liquid is pushed radially outwards from the initial contact point. During spreading the velocity normal to the surface will decrease from the initial impact velocity to zero as spreading finishes. This velocity reduction can lead to changes in droplet dynamics that is governed by the balance between the surface energy, the viscous dissipation and the inertia[47].
Figure 2-6 Schematic representation for flow and pressure profile during the different methods used for coating and printing. (a) Casting coating – the ink flow is dominated by the capillary forces as the external pressure $P_e = 0$; (b) Doctor-blading coating – the ink flow and pressure profile during blading. The arrows indicate the typical mass flow lines during the coating. (adapted from [43], [44], [46]); (c) Flexographic printing – the printing nip and the pressure pulse. The arrow indicates the rotation direction of the nip during printing. (adapted from [42]); (d) Inkjet printing – the droplet shape and diameter changes during the impact with the substrate (adapted from [47]). The ink absorption into the paper substrate is represented for illustration purpose only.

The impact-pressure of the inkjet droplets can be determined using the droplet mass, the initial velocity and contact diameter of the droplet. The mass, the diameter and the velocity of droplet can be estimated from previous drop-watcher experiments [37], [39], [48], [49] while the diameter of the droplet relics can be measured from optical micrographs. This implies that the ink droplet has a mass $m_d$ of $\sim 6\mu g$, an impact velocity $v_0 = 1\, m/s$ and contact diameter $C$ impacting with a rigid substrate. The initial droplet diameter $H_0 = 200\, \mu m$ represents the diameter of the droplet in flight. The final diameter of the droplet after impact with the substrate $C_f$ is measured to be approximately 600 $\mu m$ with a film thickness of 20 $\mu m$. The pressure is then estimated by assuming that the deceleration of the droplet on impact (as reflected by the changes in the droplet acceleration $a$) is the deceleration required to stop the topmost portion of the droplet as it collapses to the final film thickness of 20 $\mu m$. Assuming a circular contact area with diameter $C$ the pressure is given by
\[ P_e = \frac{4ma}{\pi C^2} \]  

(Eq 2.4)

The pressure varies (Figure 2-7) from 300 MPa at a contact diameter of 20 µm to 0.3 MPa at a contact diameter of 600 µm i.e. the final droplet diameter. It was assumed that it takes the droplet approximately 0.4 ms to stop which gives rise to a deceleration of \(~2.8 \text{ km s}^{-2}\).

![Figure 2-7 The decrease in applied pressure as the droplet reaches the maximum spreading and its final diameter.](image)

The estimated impact-pressures representing the external pressure term \( P_e \) are shown in Figure 2-7. It is obvious that during the most of the drop-spreading time the pressures are significantly higher than the ones applied for any of the other techniques. It should be noted that this analysis is presented only to show that inkjet printing can lead to extremely high instantaneous pressures compared to the other methods presented which in turn leads to higher compaction being observed in the inkjet printed samples. These high pressures cause the liquid component of the ink to be forced into the paper substrate. Thus it can be speculated that inkjet printing of the as-described silver ink leads to highest compaction of the silver flakes (see Figure 2-4). The significant shear forces experienced by the elongated flakes will tend to
orient the particles in-plane and to compact them. The radial spreading of inkjet
drops can cause shear alignment of the silver flakes leading to some compaction. The
high impact pressure which forces of the liquid component of the ink into the paper
will tend to further compact the flakes which are already aligned. The pressure of
deposition is the most significant driving force behind the removal of the liquid
carrier between the silver flakes which will result in compacted and aligned flakes.
The result is the appearance of percolation paths consisting of silver-flake nests and
the observed increase in the conductivity without any additional sintering.

2.2.4 Taguchi method
To understand the influence of the process parameters on the formation of
conductive layers when using inkjet printing, an optimization by the Taguchi method
was performed. The ability of Taguchi’s technique to determine the optimal
parameters to achieve a desired characteristic has been proved in the past especially
when the final result was determined by unrelated parameters [37]. Therefore, the
method is well suited for analysing complex sets of interdependent process
parameters as those in the inkjet printing process.

In the present case, the quality of inkjet-printed silver layers will be influenced by
factors as the proportion of water added to the ink defined by the water/ink ratio, the
opening time of the nozzle, the jetting pressure and the spacing between ink droplets
as reflected by the drop density (i.e. the number of drops per mm). For each of these
four control factors three levels are chosen as shown in Table 2-1. The levels were
chosen to ensure the ink printability. For example, a significant thinning of the ink
was not feasible as the high-water content tended to deform the paper due to water
absorption. An $L_9(3^4)$ orthogonal array is employed to study the system response to
the control factors. This results in a series of nine experiments as tabulated in Table
2-2

Table 2-1 Chosen factors and levels for the inkjet printing experiments.

<table>
<thead>
<tr>
<th>Level</th>
<th>Water/ink ratio (v/v)</th>
<th>Pressure (bar)</th>
<th>Opening Time (µs)</th>
<th>Drop density (drops/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Factor A 0.4</td>
<td>Factor B 0.45</td>
<td>Factor C 255</td>
<td>Factor D 2</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
<td>275</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.6</td>
<td>300</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The effect of each experimental factor on the conductivity, filling ratio, surface coverage and on the thickness of the printed layers is examined by calculating an appropriate signal-to-noise ratio $S/N$ that is defined as the ratio of the signal power (the mean) to the noise power corrupting the signal (the standard deviation) [37]. In this work I am optimising the process to provide the maximum conductivity (as a function of filling ratios and surface coverage) and thinner layers. Therefore, the larger-the-better ratio ($S/N_L$) and smaller-the-better ($S/N_s$) ratio, respectively, are used. These are defined as:

$$S/N_L = -10\log\left(\frac{1}{n}\sum_{i=1}^{n} \frac{1}{y_i^2}\right)$$  
(Eq 2.5)

$$S/N_s = -10\log\left(\frac{1}{n}\sum_{i=1}^{n} y_i^2\right)$$  
(Eq 2.6)

To optimise a process using the Taguchi method one attempts to maximise the appropriate signal-to-noise ratio as defined above. Control factors which have the greatest impact on the $S/N$ ratio can be considered to be the most important. The average $S/N$ ratio for each control factor and level can be calculated to examine how the $S/N$ ratio varies [37].

As used, the Taguchi approach allowed the optimization of the chosen printing parameters: water/ink ratio, the opening time of the nozzle, the jetting pressure and the spacing between ink droplets as reflected by the drop density. The inner array and the response of the conductivity used in the Taguchi approach are presented in Table 2-3 and Table 2-4 respectively. Analysing the data in Table 2-3 a-c one can
conclude that a linear dependence between the measured conductivity and the estimated filling ratios and surface coverage cannot be established. The results in Table 2-4 suggest that the least influential factor for the conductivity is the ink thinning (as reflected by the water/ink ratio) while the strongest influence is exerted by the pressure, followed at equal distance by the opening time and drop density.
Table 2-3 Taguchi inner arrays for the (a) conductivity (LB); (b) filling ratio (LB); (c) surface coverage (LB) and (d) thickness (SB of the printed layers)

(a)

<table>
<thead>
<tr>
<th>Exercise</th>
<th>Water/ink ratio (v/v)</th>
<th>Pressure (bar)</th>
<th>Opening Time (µs)</th>
<th>Drop Density (drop/mm)</th>
<th>Conductivity (S/m) x10&lt;sup&gt;5&lt;/sup&gt;</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
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<td>255</td>
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<td>0.00041</td>
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<td>2.2</td>
<td>1.38</td>
<td>116.86</td>
</tr>
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<td>300</td>
<td>2.5</td>
<td>2.25</td>
<td>121.15</td>
</tr>
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<td>2.5</td>
<td>1.91</td>
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<td>0.5</td>
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<td>2.09</td>
<td>117.66</td>
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<td>0.6</td>
<td>255</td>
<td>2.2</td>
<td>1.53</td>
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(b)

<table>
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<th>Pressure (bar)</th>
<th>Opening Time (µs)</th>
<th>Drop Density (drop/mm)</th>
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<th>S/N ratio</th>
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</thead>
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<td>2.5</td>
<td>0.70</td>
<td>-3.09</td>
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<tr>
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<td>2</td>
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### (c)

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<th>Pressure (bar)</th>
<th>Opening Time (µs)</th>
<th>Drop Density (drop/mm)</th>
<th>Surface coverage</th>
<th>S/N ratio</th>
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<td>Factor A</td>
<td>Factor B</td>
<td>Factor C</td>
<td>Factor D</td>
<td></td>
<td></td>
<td></td>
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<td>300</td>
<td>2</td>
<td>0.72</td>
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<td>-1.57</td>
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<td>0.45</td>
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<td>2.2</td>
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<td>0.63</td>
<td>-3.97</td>
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### (d)

<table>
<thead>
<tr>
<th>Exercise</th>
<th>Water/ink ratio (v/v)</th>
<th>Pressure (bar)</th>
<th>Opening Time (µs)</th>
<th>Drop Density (drop/mm)</th>
<th>Thickness (µm)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor A</td>
<td>Factor B</td>
<td>Factor C</td>
<td>Factor D</td>
<td></td>
<td></td>
<td></td>
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<td>31.4</td>
<td>90.01</td>
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<tr>
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<td>42.8</td>
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<td>2.5</td>
<td>35.5</td>
<td>89.00</td>
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<td>0.5</td>
<td>0.45</td>
<td>275</td>
<td>2.5</td>
<td>24.5</td>
<td>92.17</td>
</tr>
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<td>0.5</td>
<td>0.5</td>
<td>300</td>
<td>2</td>
<td>24.9</td>
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<td>90.71</td>
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<td>0.45</td>
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<td>2.2</td>
<td>30.1</td>
<td>90.42</td>
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<tr>
<td>8</td>
<td>0.6</td>
<td>0.5</td>
<td>255</td>
<td>2.5</td>
<td>24.2</td>
<td>92.27</td>
</tr>
<tr>
<td>9</td>
<td>0.6</td>
<td>0.6</td>
<td>275</td>
<td>2</td>
<td>19.7</td>
<td>93.99</td>
</tr>
</tbody>
</table>
Table 2-4 Taguchi response tables of the (a) conductivity (LB); (b) filling ratio (LB); (c) surface coverage (LB) and (d) layer thickness (SB).

(a)

<table>
<thead>
<tr>
<th>Level</th>
<th>Water/ink ratio</th>
<th>Pressure</th>
<th>Opening Time</th>
<th>Drop Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (low)</td>
<td>94.60</td>
<td>84.37</td>
<td>96.08</td>
<td>97.07</td>
</tr>
<tr>
<td>2 (medium)</td>
<td>117.40</td>
<td>118.81</td>
<td>121.48</td>
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</tr>
<tr>
<td>3 (high)</td>
<td>112.38</td>
<td>121.20</td>
<td>108.76</td>
<td>120.96</td>
</tr>
</tbody>
</table>

S/N variation (maximum-minimum) 22.80 36.83 25.40 23.89
Ranking 4 1 2 3

(b)

<table>
<thead>
<tr>
<th>Level</th>
<th>Water/ink ratio</th>
<th>Pressure</th>
<th>Opening Time</th>
<th>Drop Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (low)</td>
<td>-4.09</td>
<td>-4.85</td>
<td>-4.44</td>
<td>-4.30</td>
</tr>
<tr>
<td>2 (medium)</td>
<td>-3.42</td>
<td>-3.40</td>
<td>-3.06</td>
<td>-3.25</td>
</tr>
<tr>
<td>3 (high)</td>
<td>-3.93</td>
<td>-3.19</td>
<td>-3.35</td>
<td>-3.89</td>
</tr>
</tbody>
</table>

S/N variation (maximum-minimum) 0.66 1.65 1.38 1.05
Ranking 4 1 2 3

(c)

<table>
<thead>
<tr>
<th>Level</th>
<th>Water/ink ratio</th>
<th>Pressure</th>
<th>Opening Time</th>
<th>Drop Density</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-7.15</td>
<td>-5.12</td>
<td>-4.66</td>
<td>-5.07</td>
</tr>
<tr>
<td>2 (medium)</td>
<td>-3.40</td>
<td>-3.72</td>
<td>-5.58</td>
<td>-3.21</td>
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<tr>
<td>3 (high)</td>
<td>-2.17</td>
<td>-3.88</td>
<td>-3.34</td>
<td>-4.44</td>
</tr>
</tbody>
</table>

S/N variation (maximum-minimum) 4.98 1.40 2.24 1.86
Ranking 1 4 2 3

(d)

<table>
<thead>
<tr>
<th>Level</th>
<th>Water/ink ratio</th>
<th>Pressure</th>
<th>Opening Time</th>
<th>Drop Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (low)</td>
<td>88.80</td>
<td>90.87</td>
<td>91.57</td>
<td>91.64</td>
</tr>
<tr>
<td>2 (medium)</td>
<td>91.26</td>
<td>90.19</td>
<td>91.18</td>
<td>89.50</td>
</tr>
<tr>
<td>3 (high)</td>
<td>92.23</td>
<td>91.24</td>
<td>90.11</td>
<td>91.15</td>
</tr>
</tbody>
</table>

S/N variation (maximum-minimum) 3.43 1.05 1.46 2.14
Ranking 1 4 3 2
The increase of the processing pressure led to an initial increase in S/N ratio followed by a saturation to a level where maximum compaction was already reached (Figure 2-8 a). For opening time (Figure 2-8 b) the second level seems to be the optimal with a decrease in the S/N ratio observed afterwards, probably due to the extended spreading of the resulting bigger droplets and emerging of secondary factors such as paper substrate non-uniformities. An increase in drop density led to the expected linear increase in the conductivity (Figure 2-8 c). One might expect this as the higher the density the longer compaction pressure within the coalescing drops was sustained leading to better connectivity between the silver flakes and, therefore, a higher conductivity. The data summarized in Table 2-4 and Table 2-5 clearly determines the pressure as the most important factor for the conductivity and the filling ratio of the deposited tracks reflecting the role of the compacting pressure exercised by the landing drops. The least influential factor was found to be the ink thinning described by the water/ink ratio ( Figure 2-8 d) and ranked 4 in Table 2-4 a and b. A similar effect was observed for the doctor-blading (Figure 2-3 a and c Figure 2-4 a and c) where the surface coverage and filling ratio remained similar after thinning (Figure 2-5). Water/ink ratio appeared to be the most influential factor for the surface coverage and the thickness as it was strongly affecting the ink rheology and consequently the spreading characteristics of the drops.
2.3 Conclusions

It has been demonstrated that conductive silver layers can be deposited onto paper substrates using inkjet printing at room temperature without a further sintering process. The presented results were obtained using specially formulated aqueous-based ink containing micron-sized silver flakes with narrow size distribution. The results indicate that inkjet printing is uniquely positioned among several other printing and coating methods for the deposition of this type of ink, leading to the formation of highly conductive percolated material. It was found that there was no linear relationship between the measured conductivity and the estimated filling ratio and surface coverage. This suggests that the variation of the impact pressure of the drops results in a change of the flakes compaction mechanism. These findings open interesting avenues for further investigation of the fluid dynamics associated with inkjet deposition technology, in which drops may vary in size from the pL to the nL range depending on the inkjet printing technology used and the requirements for the ink formulation. Understanding the dynamics of the inkjet deposition method can provide insight into ink and substrate design which will result in the acceleration of the development of paper-based electronics.
3  Metal particle compaction experiments during drop-substrate impact

The compaction behavior of the DZP silver flake inks discussed in the previous chapter in which the impact of the ink droplet on the paper substrate forces the silver flakes together leading to a high electrical conductivity of $4.86 \times 10^5 \text{ S m}^{-1}$. It is clear that the inkjet printing process is responsible for this compaction effect because the compaction isn’t observed in the samples prepared by flexography, doctor blading or drop casting. This observation hasn’t been explored previously making a study into the effect of the droplet impact velocity on the compaction of metal particle suspensions when deposited by inkjet printing an interesting area of research.

3.1  Proposed experimental method

![Image of drop slowing experiments with the important parts labelled a-e. (a) Centrifugal fan, (b) Pitot tube and pressure sensor, (c) Inkjet controller and strobe controller, (d) GyGer printhead, (e) Dropwatcher, f) Substrate](image)

The drop impact velocity can be controlled by changing the inkjet printing parameters such as the pressure applied and the opening time of the inkjet nozzle.
Changing these parameters will achieve the desired effect but the drop size would be altered which can have a large impact on the compaction (as discussed in chapter 4) to avoid this I have attempted to slow down the droplets in flight by applying a counter flow of air to the falling droplets which will slow the droplets.

Slowing the droplets with counter flowing air requires a low Reynolds number <3000 to achieve low turbulence flow. Fully developed laminar flow is not desirable in this situation because that implies a parabolic distribution of the air speed in the system with a maximum in the centre, a drop falling through a tube with laminar air flow will tend to be deflected towards the walls where the air speed is lowest. For practical reasons an acrylic tube with an inner diameter of 19 mm was chosen as the ‘wind tunnel’, A centrifugal fan (EBM Pabst) was mounted to a 40 mm internal diameter tube with a pitot tube connected to a digital differential pressure sensor (omron). The pressure differential between the dynamic pressure and the stagnation pressure is related to the air speed by the following relationship:

$$v_{air} = \frac{\sqrt{2(P_d - P_s)}}{\rho_{air}}$$  \hspace{1cm} (3.1)

Where $P_d$ and $P_s$ are the dynamic and stagnation pressures respectively, $v_{air}$ is the velocity of the air flow and $\rho_{air}$ is the density of air. The cross section of the two tubes are different so the continuity equation is used to calculate the velocity in the lower tube where the inkjet nozzle is situated. The velocity of the drops was measured using the dropwatcher system in which the position of the ink drops as a function of time was recorded. An image of the system with the critical components labelled is shown in Figure 3-1.

3.2 Results

The dropwatcher system is used to determine the velocity of the falling droplets in flight, the inkjet nozzle used is an electromagnetically actuated GyGer micronozzle which was chosen as it fits the size restraints of the experimental setup. Inks without particles added were used to characterise the effect of slowing drops without clogging the nozzle, their properties were tuned to be similar to previous particle laden inks. The velocity of the falling droplets was calculated by measuring the displacement of the falling drops as the delay on the strobe is increased, this gives the position of the droplets versus time. The data is plotted and the slope is used to
calculate the velocity of the falling droplets. Results of initial testing of the system are presented in Figure 3-2, the results show that as the counter flow velocity increases the droplet velocity is indeed retarded. As the counter flow velocity the Reynolds number transitioned into turbulent flow since $\text{Re} \propto v_{\text{air}}$. When the flow in the tube becomes more turbulent the falling droplets will be deflected in an uncontrollable manner which make it difficult to measure the falling droplets with the dropwatcher as drops won’t fall through the field of view. This limits the practical counter flow velocity to $3 \text{ m s}^{-1}$ in the current configuration.

Figure 3-2 (a) Plot of droplet Position vs Time for 0 to 3 m s$^{-1}$ counter flow. Best fit lines for each set of data have been plotted in the same colour as the data points. The slope of the best fit lines is used to calculate the velocity of the falling drops. The velocity of the droplets decreases as the counter flow velocity is increased. The experiment was conducted with a particle free ink which was 50/50 v/v Ethylene Glycol to Ethanol giving a viscosity of 6 cP. A pressure of 400 mbar was applied to the printhead and an opening time of 300 µs was used. (b) Image from dropwatching experiments, the position of the drop from the top of the image is recorded as a function of time, this data is used to generate the graphs in (a).
3.3 Conclusions

While it is possible to slow down droplets in flight by applying a counter flow of air it becomes difficult to control the position of the droplets which makes it unsuitable for correlating the impact velocity of the droplets with the conductivity of tracks and coatings. It isn’t possible to print well defined tracks and layers with the setup presented in Figure 3-1. Therefore during my study to characterise the effect of impact velocity and droplet size on the compaction of suspended particles it was essential to conduct modelling of the composite drop impact with a solid substrate. Modelling of the impact of a suspension droplet with a solid substrate provides insight into the effect of the dynamics of inkjet deposition which is a crucial component in maximising the impact of this technology in the additive manufacture of printed electronics. Modelling of the compaction of silver particle suspensions is presented in chapter 4.
4 Modelling of the drop-substrate impact

4.1 Introduction:

As discussed in chapter 2 it has been experimentally shown that for a water-based ink with micron-sized flakes of silver with a narrow-size distribution (among drop-casting, doctor blading, flexographic and inkjet printing) conductive layers, without employing a subsequent sintering process, can be obtained only by inkjet printing. The flexographic printing led to the thinnest layers but, despite this effect, the coatings were not conductive as complete flake compaction was not taking place; the non-conductive polymeric carrier was still present in the layer cross-section preventing the silver particles from creating a conductive path. In fact, for all the other techniques, including drop-casting the flakes did not become compacted under the applied pressure[25]. In contrast to these other methods, inkjet printing leads to complete flake compaction into an almost solid block (Figure 2-4 Error! Reference source not found. d) without further sintering treatment being required. All of the aforementioned printing methods were performed on the same substrate minimising the role of other influences (e.g. paper porosity, wetting properties etc.) was minimized. It was concluded that the observed compaction effect is directly associated with liquid flow and particle movement in the different coating and printing techniques used [25].

4.2 Experimental

The experiments were conducted as described in chapter 2 and are summarised in Table 4-1.

Table 4-1. The input parameter values for the drop casting (D1-D2) and inkjet printing (T1-T9) experiments.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Water/Ink Ratio (v/v)</th>
<th>Pressure (bar)</th>
<th>Opening Time (µs)</th>
<th>Drop Density N_d (drop/mm)</th>
<th>μ_s (mPa·s)</th>
<th>H (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
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<td>N/A</td>
<td>N/A</td>
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<td>576</td>
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<tr>
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<td>N/A</td>
<td>N/A</td>
<td>7</td>
<td>576</td>
</tr>
<tr>
<td>D3</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<td>576</td>
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<td>------</td>
</tr>
<tr>
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<td>2</td>
<td>7</td>
<td>254</td>
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<td>2</td>
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</table>

**Theoretical Model**

![Figure 4-1 Schematic representation of an ink droplet of diameter H and the axial distributed spherical particles of radius R during the different stages of the impact and compaction: (a) at t = t_0 the initial contact of the droplet with the substrate is made, but the drop deformation is not initiated yet. Colloidal particles are evenly dispersed throughout the droplet being separated by a distance D. (b) At any intermediate time (t_0 < t < t_f), as the droplet deformation progresses, the particles begin to compact near the substrate. (c) In the final stage (t = t_f) the droplet deformation and the particle compaction processes are completed and, ideally, the full particle compaction is obtained.](image)

As delivered from the nozzle and prior to impact, an ink drop can be considered to be a sphere of diameter H travelling at the velocity v_0. The metal particles are considered to be homogenous and uniformly distributed in space within the travelling droplet (Figure 4-1 a). Upon contact with the substrate, the droplet does not retain its spherical shape and it starts to deform (Figure 4-1 b and c) as its inertia causes a forced wetting. The liquid drop starts to spread and it is pushed radially outwards from the initial contact point. As the droplet deformation progresses it is expected that the silver particles will not retain their initial distribution and they will tend to compact. The compaction requires the particles to move through the ink solution (i.e. the ink carrier) until they make contact. Here, for simplicity, it is assumed that the silver particles are spherical and that Stokes flow arises around the
particles leading to a resistance given by Stokes’ law. Only the central axis of the spherical drop in the direction of the initial droplet velocity is considered (Figure 4-1). This consideration remains valid for a large section of the central area of the droplet if one considers the dimensions of the particles and the size of the drop. However, more complicated motions are expected to arise off axis. These are neglected to reduce the model to a one dimensional problem. Moreover, experimentally, the influences of these complicated flows (e.g. different particle distribution at the edges) were not seen in the SEM cross-sections of the investigated drops confirming the generality of the assumption.

In general, a droplet of volume \(V\) contains \(N\) particles, each of mass \(m\) and radius \(R_p\), leading to a loading \(L\) of the silver particles in the droplet given by Eq (4.1),

\[
L = \frac{Nm}{V} = N \frac{4}{3} \pi R_p^3 \rho_{Ag} = N \left( \frac{2R_p}{H} \right)^3 \rho_{Ag}
\]  

(4.1)

where \(\rho_{Ag}\) is the density of the silver. If the silver particles are assumed to be uniformly dispersed in the droplet then the number of particles expected along an axis of the droplet is \(N_L = N^{1/3}\) and the loading fraction will be given by Eq. (4.2).

\[
L_f = \frac{L}{\rho_{Ag}} = \left( \frac{2N_L R}{H} \right)^3
\]  

(4.2)

At initial impact where \(t = t_0\), the \(N_L\) silver particles are positioned at regular intervals and entirely enclosed in the droplet such that the boundary particles are assumed to be making contact with the inner surface of the droplet (see Figure 4-1a). There are \(N_L - 1\) intervals between particles with a length given by Eq. (4.3).

\[
D = \frac{H - 2N_L R}{N_L - 1}
\]  

(4.3)

The droplet impacts at a velocity \(v_0\). Subsequently, the first particle makes contact with the surface and stops. The remaining particles still have inertia that is being depleted by the viscous drag due to the fluid represented by the dynamic viscosity of the carrier solution \(\mu_s\). This drag is only experienced when there is a relative motion between the particles. Hence the remaining \(n\) moving particles may be thought of as acting as a single composite particle at position \(x\) and experiencing a force due to Stokes’ law given by Eq. (4.4)
\[ nm \ddot{x} = -6\pi \mu_s R \dot{x} \]  

Integrating yields the composite particle’s velocity which decays to zero according to Eq. (4.5) an expression for \( d \) is obtained, Eq. (4.6)

\[ \dot{x} = -\frac{6\pi \mu_s R}{nm} d + v_0 = 0 \]  

\[ \Rightarrow d = \frac{nmv_0}{6\pi \mu_s R} = \frac{2nR^2 \rho_{Ag} v_0}{9\mu_s} \]  

where \( d \) is the change in relative position between the particles. If \( d \geq D \) then the particles make contact and a compacted layer is formed. The minimum number of particles, \( n \), that have enough inertia for compaction occurrence can be found by letting \( d = D \):

\[ n = \frac{9\mu_s D}{2R^2 \rho_{Ag} v_0} \]  

Combining Eq. (4.3)-(4.7) the fraction of particles to compact is given by Eq. (8)

\[ F = 1 - \frac{n}{N_L} = 1 - \frac{(1 - 2N_lr)}{\beta N_L(N_L - 1)r^2} \]  

where \( r = R/H \) and \( \beta = 2\rho_{Ag} v_0 H/9\mu_s \)

If \( N_L \gg 1 \) and using Eq. (4.2) and (4.8), an expression for \( F \) is obtained that is dependent on \( \beta \) and the loading fraction \( L_f \) only,

\[ F \approx 1 - 4 \frac{1 - L_f^{1/3}}{\beta L_f^{2/3}} \]  

4.3 Results and discussion

The three stages of droplet impact with a substrate are described in section 2.2.3. Typically, the particle movement into the paper pores is prevented by a bridging mechanism i.e. the pores are blocked by particles trying to enter simultaneously [25]. For inks with relatively high initial flakes loading the pores can be blocked in the initial stages of the ink-paper interaction. Such a blocking mechanism can explain both the persistence of the wet core of the drop-casted layers days after coating as well as the residual liquid carrier (RC) presence in the layers. In the present study the same substrate and similar flakes size are used for all experiments. Therefore, these complex flows, taking place after the initial drop-substrate contact, are considered to
play a secondary role in the extent of the flakes’ compaction (Figure 2-4 c and d) [25].

The fractional loading $L_f$ and the parameter $\beta$ will influence the compaction factor $F$ as given by Eq. (4.10) and shown by the contour plots in Figure 4-2, where $\beta$ is determined by the initial drop velocity, its diameter and the ink carrier viscosity. Note that no compaction occurs for the following parametric condition given by Eq. (4.10):

$$\beta < 4L_f^{-2/3} \left( 1 - L_f^{1/3} \right), \quad \text{or equivalently} \quad L_f < \left[ \frac{2}{\beta} \left( \sqrt{1 + \beta} - 1 \right) \right]^3$$  \hspace{1cm} (4.10)

Figure 4-2 Contour plots of the compaction factor $F$ calculated using Equation (4.9) as a function of the dimensionless quantities $L_f$ and $\beta$. The white region indicates that $F$ is negative and, consequently, no compaction of the particles can occur. The solid black curve represents the compaction boundary from Equation (4.10). The white square boxes represent the calculated $F$ values based on the experimental data. Panel (a) shows $F$ on a logarithmic scale of $\beta$ and $L_f$. No compaction occurs for conditions of low loading fraction and high dynamic viscosity or low impact velocity. The drop-casting layers are corresponding to this situation. Compaction occurs for large impact velocity during inkjet printing (red square box). (b) Zoom-in of (a) on a linear scale in the area corresponding to the inkjet printed layers as described in Table 4-1. The degree of compaction $F$ differs due to the variations in the initial loading, viscosity, droplet diameter and velocity as controlled by the thinning water/ink ratio, pressure and opening time.

For very low $\beta$, particle compaction can only be achieved (see Figure 4-2) by increasing the initial loading fraction $L_f$ to values close to unity. However, such an increase in particle loading can lead to a significant increase in viscosity and the inks can become less suitable for casting or inkjet printing at room temperature. As the loading increases, the distance $D$ between the particles decreases and the interactions
(e.g. long and short range van der Waals interactions, electrostatic repulsion, if any, etc.) between the particles (here neglected) should be considered as they can enhance or retard the particles aggregation and, therefore, their compaction. For very low loadings, the compaction occurrence requires either very low viscosity or high jetting velocities (i.e. large $\beta$ values). In this case which was not studied experimentally here, one has to add other factors (like Marangoni flow etc.) because the particle distribution on the substrate will be influenced by the solvent (liquid carrier) flow. Consequently, for these limiting cases the present model would have to be adjusted.

The direct comparison of the theoretically predicted compaction factors and the values calculated for the experimental conditions presented in Figure 4-2 show that, indeed, no compaction should occur in the drop casted layers (see Figure 2-4 Error! Reference source not found.c and D$_1$ – D$_3$ points in Figure 4-2 a). For the drop casted layers $F$ has negative values and fall beneath the theoretical compaction boundary Eq. (4.10) and solid black curve in Figure 4-2). For the inkjet printed layers the calculated compaction factor $F$ falls above this boundary. The extent of compaction will be controlled by the printing parameters, but, for the data presented here, the variation in $F$ is not large and all the points are positioned within the contour regions corresponding to large compaction factors (Figure 4-2 b). Thus, for the majority of experimental data (excepting T$_1$ and T$_7$ samples) the compaction factor is close to unity ($F \geq 0.8$). Such large $F$ values can allow the formation of solid silver layers as seen in the SEM cross-section (Figure 2-4 d).

The differences in compaction level are also reflected in the electrical conductivity $\sigma_{el}$ of the layers. For the inkjet printed layers a good overlap of the printed drops is very important as continuity of the layers is required to maximise the conductivity for a given level of compaction. Once a high level of compaction is achieved ($F \geq 0.8$) then the conductivity of the printed lines becomes more strongly dependant on the other printing parameters such as the jetting pressure and the water content of the ink. T9 presents the highest conductivity due to its increased water content which dilutes the amount of silver and polymer binder being delivered on to the substrate leading to tracks with a higher proportion of compacted silver relative to the binder. Alignment of the silver flakes during drop coalescence can be another factor which leads to the high conductivity observed in T9.
The variation of the printing parameters can lead to a series of geometries of inkjet printed lines on solid non-porous substrates such as individual drops, scalloped, continuous, bulged and stacked coined lines being reported in the literature [47], [50]. If the particle density $N_d$ is small (i.e. distance between two drops is too large) then isolated drops are formed. As the particle density increases (the drop spacing decreases) the drops overlap and merge. During this process the drops retain their individual rounded contact lines, and a scalloped pattern emerges. Further increases in $N_d$ result in a decrease in the drop spacing that can eliminate the scalloping effect and leads to smooth (straight) lines. Because the fluid expansion is partially arrested the scalloped lines are narrower than an isolated drop but larger than the uniform smooth edge and top lines [47], [50]. For very large $N_d$ the printed drops tend to form discreet bulging along the line’s length, separated by regions of uniform narrow lines. If the evaporation time of a single drop is less than the drop jetting period (here, controlled by the opening time) then lines with a stacked coin geometry are obtained [47], [50].

In this study, for the printing parametric range, only individual drops (sample $T_1$) and scalloped lines (sample $T_2$ – $T_9$) were observed, the contact line being influenced by the liquid carrier flow into the porous substrate. The intrinsic paper porosity allows for liquid to flow both in the vertical and horizontal planes, influencing the scalloping effect. Describing these flows and their influence on the line-edge smoothness are beyond the scope of the present study. However, in a simple approximation, the scalloping effect can be characterized by a scalloping dimensionless factor $S = 2d_S/H_f$ where $d_S$ is the scalloping depth and $H_f$ is the final diameter of the landed dried drop (see the inset in Figure 4-3 a). As defined, the scalloping factor suggests that $S \rightarrow \infty$ corresponds to isolated drops (sample $T_1$) while $S = 0$ characterizes the uniform smooth edge and top lines (not seen for the printed parameters used here). The case $S = 1$ implies that two drops make a tangential contact. For $S$ close to unity (here, $S = 0.8$ for sample $T_7$ in Figure 4-3 a) it is expected that the drops are not overlapping properly leading to a poor connectivity between them. Therefore, only the samples for which a good overlapping between the printed drops ensures good continuity (i.e. $S \leq 0.5$) are considered in order to observe the possible dependences of $\sigma_{el}$ on the compaction factor $F$ (Figure 4-3). It should be remembered that these experiments were designed to observe the dependence of the electrical conductivity of printed tracks on the ink
and printing parameters (see chapter 2) and not specifically on the scalloping factor \( S \) or the compaction factor \( F \). This leaves the possibility of further enhancement of the electrical conductivity by tuning the deposition parameters with respect to \( \beta \) and \( S \) using another set of Taguchi trials.

\[ \sigma_{el} \] as influenced by (a) the scalloping factor \( S \) and (b) the calculated compaction factor \( F \) for the different inkjet printed and drop-casted layers. The inset in (a) represents a schematic of the scalloping effect where \( d_s \) is the scalloping depth and \( H_f \) the final diameter of the landed drop. The dashed lines in (b) have guideline purposes only.

Results presented in Figure 4-3 b show that there is a threshold in the compaction layer \( F \) above which the layers become conductive as the compacted silver flakes form a conductive path. This threshold will be determined by the variations in the initial loading, viscosity, droplet diameter and velocity. For small initial velocities or low particle loading the compaction is not achieved and, consequently, the resulting layers are not conductive. Above this threshold the electrical conductivity increases steeply as, most likely, the particles form a percolating path but further experiments are required to determine the analytical dependence of the electrical conductivity on the compaction factor \( F \).

### 4.4 Conclusions

Printing of flexible electronics has been undergoing enhanced development over the last decade. However, understanding and controlling the physical processes have not exhibited a similar trend. These physical processes are complex and require not only
predicting the ink fluid dynamics as a whole but also understanding the behaviour of the metal particles dynamics during printing. The electrical conductivity of the printed layers is determined by the degree of particle compaction and their ability to form a conductive path or layer. To date the particle compaction is realized by further sintering processes that can damage the substrate. To avoid this, the compaction process should and can be enhanced during the drop-substrate impact interaction. The theoretical predictions and experimental validation presented here confirm that particle compaction can be achieved at room temperature as long as the particle and ink drop size, the initial fractional particle loading of the ink, solvent viscosity and jetting velocity are in the required parametric range. The changes in the compaction factor affect the electrical conductivity of the resulting layers. For no or a limited compaction occurrence the printed layer will need sintering treatments, but for a large compaction factor a conductive path is formed.
5 Carbon printing: The properties of carbon originating from hydrocarbon processing as powders and ink ingredients: structure, morphology and electrical properties

5.1 Introduction
In this chapter I discuss the thermal treatment of carbon materials originating from the plasma splitting of natural gas and their behaviour as ink ingredients. Their influences on ink properties like the stability and printability on different substrates will be researched and discussed in detail.

![Diagram showing hydrocarbon decomposition and plasma reactor](image)

*Figure 5-1 Schematics of (a) the ideal hydrocarbons (here, methane CH4 and acetylene C2H2) decomposition route leading only to hydrogen that can be stored for later usage in “hydrogen economy”, and carbon that can be incorporated in water based inks for creating conductive coatings; (b) the schematics of a typical 3 kW microwave plasma reactor for natural gas/methane processing. The inset shows a typical plasma flame of the microwave discharge.*

In hydrocarbon processing either hydrogen or carbon black generation (Figure 5-1a) is typically enhanced. In the last decade, as the trends towards a green economy are accelerated, the use of hydrocarbons for hydrogen generation increased significantly [20]. The resulting hydrogen is usually filtered and stored for further applications but the resulting carbonaceous material is typically seen as waste material (soot) and,
therefore, discarded. Here, it is shown that resulting carbonaceous materials can possess valuable properties and can represent an added value product of the hydrogen generation process.

A promising alternative for hydrogen generation is microwave plasma processing when hydrocarbons (i.e. methane) are used as working gas [20], [51]–[53]. Thus, the microwave plasma methane dissociation exploits the reaction

\[ \text{CH}_4 \rightarrow \text{C(s)} + 2\text{H}_2 \]

allowing for hydrogen and carbon production in the same time without CO₂ emission[20], [51]–[53]. The microwave plasma can be generated using a waveguide supplied nozzle-less microwave system (see Figure 5-1 b) operating at 2.45 GHz. Such a prototype system allows for a microwave output from 0-6 kW [20], [54] at full-wave. The resulting carbon can be collected and used for energy applications like manufacturing direct carbon fuel cells (DCFC) [54] while the hydrogen can be stored for further usage. Here, I will show that the resulting carbonaceous material, named plasma carbon (PC), can be used as ink ingredient for printing conductive layers. Moreover, it will be shown that by further pyrolysis of the plasma carbon its properties can be improved. This carbon will be called pyrolysed plasma carbon or (PPC). The resulting ink and layers properties will be compared with a commercial available carbon black, Denka Black (DB), obtained from self-heating flame pyrolysis of acetylene gas of acetylene. This process was designed by the manufacturer for carbon generation and uses as acetylene gas as the raw material. The decomposition route used during the acetylene pyrolysis process is:

\[ \text{C}_2\text{H}_2 \rightarrow 2\text{C(s)} + \text{H}_2 \]

Since no oxygen is employed in this reaction, the resulting carbon does not contain oxygen functional groups. DB is electrically and thermally conductive making it suitable for low-temperature fuel cell catalysts [55], or in DCFC [10], as carbon electrode material for Li-air cells [56] or Li-air batteries [57]. Therefore, DB represents a proper reference point for the PC and PPC generated using prototype plasma microwave reactors developed in the TEMPRI laboratories [58, p. www.tempri.eu]. In the present study, the different carbons are expected to have different structure and, consequently, different behaviour as powders or ink ingredients and, therefore, they will influence differently the properties of the printed
layers. Consequently, their powder properties (i.e. conductivity, particle size, surface area, pore size etc.) and their influence on the ink behaviour (i.e. ink viscosity, stability and printability) will be compared. The inks stability will be also discussed in terms of the possible interactions that can appear among the ink ingredients.

5.2 Experimental

5.2.1 Carbon powder generation

*Plasma Carbon (PC)*

The plasma carbon was obtained after processing natural gas–N$_2$ mixture (20:1 volume ratio) in a standard microwave plasma reactor [20], [54]. The gas was supplied from compressed gas cylinders under normal pressure and the flow rates were adjusted using mass flow controllers. Here, a mixture of the carbonaceous materials collected from the different reactor regions (see [20] and [54] for further experimental details) was used.

*Pyrolyzed Plasma Carbon (PPC)*

To improve the graphitic structure of the PC was thermally treated (pyrolyzed) under an inert atmosphere. The pyrolysis was performed in a furnace at atmospheric pressure under constant nitrogen flux. The PC was inserted in a hot tube furnace at 900 °C and held for t = 15 min. Then the sample was cooled without removing it from the furnace or disconnecting the nitrogen feed. The pyrolysis leads to significant changes of the PC structure. This resulting carbonaceous material is referred to as pyrolyzed plasma carbon (PPC).

*Denka Black (DB)*

Denka acetylene black (DB) was received from Denki Kagaku Kogyo K.K. (Japan). As specified by the manufacturer, the DB is typically obtained from the self-heating pyrolysis of acetylene gas, it has large crystallites and low impurity content, its appearance is described as colloid sized particles of carbon black.

5.2.2 Analysis Methods

*Surface area and porosity*
Surface area and porosity of the carbon powders can influence their performance characteristics, but also their behaviour as ink ingredients. Therefore, N\textsubscript{2} gas-volumetric analysis was carried out at 77 K using Autosorb AS-1 Quantachrome (Quantachrome UK) to obtain the absorption-desorption isotherms and to determine the specific surface area (BET model) and the porosity (BJH model). Prior to analysis all the carbonaceous samples were degassed overnight in vacuum at 30 °C to avoid changes in the carbon powder morphology that can appear at larger temperatures.

**TGA**

Thermal analysis was carried out in a TGA Q600 (TA Instruments). The measurements were performed using a heating rate 10 °C/min and the temperature was raised from room temperature to 800 °C. Pure compressed air flux from a cylinder with a flow rate of 100 ml/min was used. Al\textsubscript{2}O\textsubscript{3} open crucibles are used. The sample weight was about 4 mg.

**XRD**

X-ray diffractometry (XRD) \(2\theta\) scans of carbon powder samples were performed in a Philips X'Pert PW1830 diffractometer with Cu–K\(\alpha\) radiation. We used step mode over a 35-95° range, with 1/2° divergence and anti-scatter slits and a 0.2 mm receiving slit. The measurement step size was 0.05°, with integration time of 42 s per step. Diffraction data was analysed using Panalytical Highscore Plus software;

**Electrical conductivity of carbon powders**

The electrical conductivity of the powders was monitored during compression at room temperature following the standard procedures[59]–[61]. In the experimental set-up presented in Figure 5-2 the sample powder was compressed between two aluminium pistons forming the electrodes placed in a thick ceramic (alumina) tube (inner diameter = \(6.89\times10^{-3}\) m). The surface of the aluminium piston is polished and smoothed to improve electrical contact with the carbon powders. The pressure was varied using a non-rotating spindle micrometer screw (Mitutoyo Series 153, Mitutoyo, Japan) connected to the top piston allowing for a linear smooth movement of the top piston. The changes in pressures were measured using a miniature compression load cell (LCM304-2kN, Omega Ltd, UK) placed under the bottom electrode. The cell was connected to a bridge input meter (DP25B-S, Omega Ltd,
(UK) and the force applied was displayed. The two aluminium pistons (diameter 6.88×10⁻³ m diameter) were placed in PVC holders (~ 10 mm thick) that electrically insulate them from the micrometer screw and the pressure sensor, respectively. The initial volume was kept the same for all samples by placing a removable aluminium washer under the ceramic tube. The powder was poured and tapped until the designated volume was filled. The excess powder was blade and the mass for each sample was recorded. To derive the powders conductivities their electrical resistance was measured using the four-point method. The electrical current was provided using a power source (TTi PL154, Thurlby Thandar Instruments, UK), while the current and the voltage values were measured using a digital multimeter (TTi 1604, Thurlby Thandar Instruments, UK). For each sample, the values of the pressure, applied current and the corresponding voltage was repeated, the mean values being used for resistance R calculation. Measuring the changes of the powder column height (l) and the knowing the cross-area of the pistons (A), the conductivity of the powder samples can be estimated as being $\sigma = l/AR$. Monitoring the changes in powder height also allows finding the changes in powder density with the compression pressure.

![Diagram](image)

*Figure 5-2 Experimental setup to measure the conductivity of carbon powders. An ammeter was used to measure the current flowing through the carbon with a variable resistor to limit the current flowing. The potential across the aluminium pistons was measured using a voltmeter connected as shown. The carbon powder was contained between the pistons by a non-conductive ceramic die. The force applied to the material was measured using a load cell and the displacement of the piston was measured using a micrometer.*
5.2.3 Ink formulation
The same ink recipe was used for all three carbonaceous materials. Inks were prepared by adding 5.5 % (w/w) PTFE (powder, Sigma-Aldrich, IE) with respect to the carbon to be added and 3.5% (w/w) Triton X-100 (laboratory grade, Sigma-Aldrich, IE) with respect to the total weight of the ink to ethylene glycol (Fluka, BE). This mixture was stirred for 10 min before the carbonaceous material addition. The carbon powders were hand grinded prior addition. The obtained dispersions were first stirred overnight and then deionised water was added in a ratio of 48% (w/w) with respect to the total mass of the dispersion. The resulting ink was then stirred for another 10 min to homogenise the dispersion.

5.2.4 Particle size measurements
Carbon incorporation into the water based dispersions lead to cluster formation. Despite the surfactant presence the carbon particles will not remain as individual nanoparticles as seen in the TEM images and they will tend to form aggregates. The diameter of these aggregates will influence the ink properties, stability and printability. Therefore, their diameter was measured using dynamic light scattering DLS (Horiba LA920). The prepared inks were diluted by adding 9 parts deionised water in a dropwise manner to one part ink while stirring. The obtained solution was stirred for 30 minutes then used for the DLS analysis. A relative refractive index of 1.9 was chosen for the analysis. The D$_{32}$ diameter was chosen as the particle size measurement.

5.2.5 Viscosity, surface tension and stability
The ink properties were characterized in terms of viscosity, surface tension and stability. The viscosity was measured using a Brookfield DV2T viscometer with an SC4-18 spindle and a small sample adaptor, the spindle speed being raised up to 200 rpm.

The surface tension was determined using the pendant droplet approach, the measurements being carried out using a CAM-100 (KSV Instruments Ltd, FI) contact angle goniometer.

The stability of the suspensions was determined by observing the phase separation of the solid and liquid phases at regular time intervals. The inks placed in closed transparent glass vials were maintained in fixed position at room temperature and no mechanical factors interfered with them. Photographs of the vials were taken at
regular intervals in time to monitor the phase separation of the inks as a function of time.

5.2.6 Printing
The inks were printed using inkjet printing. A Domino macrojet printhead with a single 100 µm nozzle was used to deposit the inks. The inks were printed on a variety of substrates such as office paper, coated proofing paper (RK Print Coat Instruments, UK), kapton film, kapton tape and acetate sheets. The effect of different printing parameters on the printed tracks was investigated by printing at a variety of pressure levels and opening times. The tracks were allowed to dry completely before electrical testing. The resistance of the printed tracks was measured using a 4-point probe (Jandel) with 1 mm tip spacing and 100 µm tip radius. The measurement range of the 4-point probe was adjusted to optimise the accuracy of the measurements.

5.3 Results and Discussion

Pyrolysis of the plasma carbon (PC) results in a number of physical and chemical changes to the carbon material. The volatile organic compounds in the as-received carbon are removed during pyrolysis, TGA and DTGA Figure 5-3 show that the untreated carbon loses 20% of its initial mass upon heating to 300 °C whereas the PPC and DB powders don’t begin to lose mass until approximately 500 °C. The TGA was performed under air to allow for determination of the ash content of the carbon powders. Pyro GC-MS analysis on the as received PC reveals the presence of poly-aromatic hydrocarbons such as naphthalene, the boiling point of these hydrocarbons is in the range of 200 – 500 °C which is in good agreement with the observed mass loss in TGA but the presence of oxygen allowed for combustion to occur simultaneously with evaporation which can cause difficulties in the interpretation of the TGA data. This mass loss can be attributed to the poly-aromatic hydrocarbon contaminants in the carbon. The removal of non-conductive volatile compounds from the carbons will increase their electrical conductivity and expose
Figure 5-3 TGA-DTGA analysis curves for three carbon powders performed under air. The plasma carbon shows a loss of mass from around 100°C to 300°C which is consistent with the evaporation of volatile organic compounds which are not present in the denka black and have been already removed in the pyrolysed sample.

more of the underlying particle surface area. The PPC and DB carbons show very similarly shaped TGA and DTGA curves in which the primary difference is that the PPC begins to lose mass at 500 °C compared to 600°C in the DB, this loss of mass is due to the carbon combusting. The PPC begins combustion at a lower temperature than the DB because the higher surface area of the PPC powder.

The effect of pyrolysis on the microstructure of the PC was examined using TEM, micrographs of each of the carbons are shown in Figure 5-4. The PPC looks very similar to the DB powder as a result of the pyrolysis process removing non-conductive volatile organic compounds. The non-conductive compounds on the surface of the PC are responsible for the lack of detail seen in the TEM images. The carbon materials all have a similar microstructure since they all consist of agglomerated spheroid particles. The untreated PC consists of spherical agglomerates than the more anisotropic morphology seen in the PPC and DB. The organic contaminants present in the PC are responsible for the greater adhesion between the PC particles than either the PPC or DB particles. This would suggest that the PC powder should have a higher apparent density than the PPC and DB powders.
Figure 5-4 TEM images of the three carbons in this study. The scale bar in each case represents 200nm. The PC particles appear blurry due to non-conductive organic compounds adsorbed on the surface of the PC particles.

The BET adsorption isotherm was used to calculate the specific surface area (SSA) of the carbons, the gas adsorption data was also used to calculate the pore size distribution of the powder using the BJH model. The BET surface area of the carbons is displayed in Table 5-1. The PC has the lowest surface area with the pyrolysis serving to increase the surface area of the carbon by approximately a factor of four. This increase in surface area can be attributed to the removal of contaminants from the surface of the PC powder. The DB has a surface area of 64 m²·g⁻¹ which is in between the values for the two plasma derived carbons. The lower surface area of the DB than the PPC shows that the surface of the DB particles is less porous than the PPC. The pore size distribution of the carbons is shown in Figure 5-7. As expected from the specific surface area the PPC has the highest pore volume with a peak pore volume with radius 40 nm. The PC has the lowest pore volume and the shape of the distribution is similar to the PPC, the peak in the pore size distribution of the PC is approximately 30 nm. The increase in the pore size in the PPC can be explained by removal of a layer of volatile material from the surface of the PC resulting in both the increase in

Figure 5-5 HR-TEM image of the PPC. The PPC is highly graphitic and contains a large proportion of few layer graphene flakes. This high degree of crystallinity will give rise to high electrical and thermal conductivity.
surface area and in the mean pore size. The DB shows quite a different pore size distribution with a small volume of mesopores, the distribution is shifted towards macroporosity which are more characteristic of the agglomerate structure than the carbon material itself. Mesoporous carbons are preferable for electrochemical storage devices since mesopores allow for a good trade off between electrochemical surface area and the ability for charge to penetrate the pore structure. A large resistance to charge flow leads to a high electrical resistance which limits the efficiency of an electrochemical device.

Table 5-1 Specific surface area of the carbons

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Specific surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma carbon</td>
<td>34</td>
</tr>
<tr>
<td>Pyrolysed plasma carbon</td>
<td>122</td>
</tr>
<tr>
<td>Denka Black</td>
<td>67</td>
</tr>
</tbody>
</table>

The apparent density of the carbons is shown in Figure 5-6, an equal mass (0.45g) of each carbon powder was added to a vial. The vials were then tapped against the table to cause the powders to settle, the volume of the added carbon was determined and used to calculate the apparent density. The DB has an extremely low apparent density compared to the PC and PPC due to its branched agglomerate structure.

![Figure 5-6 The apparent density of the three carbons. The DB powder shows a significantly lower density than the plasma derived carbons which is indicative of its more branched and open agglomerate structure.](image)
Figure 5-7 BJH adsorption isotherm for the carbon powders. It shows the pore size distribution for the carbons. Mesoporous materials are desirable for electrochemical energy storage since the larger mesopores allow for higher charge transport compared to microporous carbons.

The electrical conductivity of the carbon powders was measured as a function of applied pressure as discussed in section 5.2.2. The carbon powders all display linear behaviour with the applied pressure which is a strong indicator that the carbons weren’t changed structurally by the applied stress, typically it takes pressures very high pressure to modify the structure of the carbon in a non-reversible way. Deformation of the carbon structure will lead to saturation of the conductivity. The PC shows the lowest conductivity of the three carbons which is attributable to a non-conductive organic layer on the surface of the material. Under compression the conductivity of the PC and DB are quite similar but the PPC has an order of magnitude larger conductivity. The increased conductivity in the PPC is primarily caused by the removal of non-conductive material by pyrolysis in addition to a small increase in graphitisation which was observed by TEM (Figure 5-5). A large degree of graphitisation is not expected since the carbon was only pyrolysed for 15 minutes which isn’t sufficient to induce appreciable The PC was only The increased surface area of the PPC can also be responsible because a higher surface area allows for a greater number of inter-particle contacts. The extremely high conductivity of the PPC should lead to highly conductive printed carbon layers.
The conductivity versus the applied pressure for the studied carbons. The pyrolysed plasma carbon shows a significant increase in conductivity compared to the as received plasma carbon and the Denka Black.

The carbon powders were dispersed into an ink as described in section 5.2.3. The viscosity was measured and plotted as a function of the shear rate, this is shown in Figure 5-9. All three of the carbon inks show thixotropic behaviour caused by the breaking down of the initial microstructure in the suspension. The hysteresis in the curves show that the viscosity is lower as the shear rate is reduced from its maximum value towards the minimum shear rate this shows that there is some initial state which isn’t recovered immediately. The PPC and PC inks show very similar behaviour under shear stress with quite similar viscosities being measured. The DB ink has a much higher initial viscosity than either of the plasma derived carbon inks and the viscosity decreases rapidly as a function of the shear rate. The strong shear thinning effect visible in the DB ink is due to the branched agglomerate structure of the DB, the effect is weaker in the PC and PPC as they have more spherical agglomerate structures.
Figure 5-9 The viscosity of the carbon inks as a function of the applied shear rate. The DB ink displays clear shear thinning behaviour but due to the larger relative error in the PC and PPC viscosity it is inconclusive. The large decrease in viscosity as a function of the shear rate is indicative of the more highly structured DB particles.

The size of the agglomerates in the carbon inks is an important characteristic for printing the inks in addition to the time taken for the inks to sediment. The diameter of the carbon agglomerate particles is shown in Table 5-2. The PC and PPC inks have a similar agglomerate particle diameter as observed by DLS (Table 5-2) but there is a difference of 2 cP in their viscosity and the PPC has a 10% higher surface tension. The difference in the surface tension is a result of the different chemical composition of the PC and PPC surfaces induced by the removal of hydrocarbons from the PC surface by pyrolysis. The DB has the highest particle diameter which can be explained by the DB forming more anisotropic agglomerates with a higher aspect ratio, these agglomerates are also responsible for the increased viscosity observed in the DB ink. Longer agglomerates in the ink lead to anisotropic particles which have a lower percolation threshold than the more isotropic PC and PPC particles.
Table 5-2 The particle size (DLS), viscosity and surface tension of the printing inks. The viscosity is recorded at a shear rate of 238s⁻¹

<table>
<thead>
<tr>
<th>Carbon source and properties</th>
<th>Particle Diameter D₃₂ (µm)</th>
<th>Viscosity (cP)</th>
<th>Surface Tension (mN m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>3.44</td>
<td>9.97</td>
<td>34.06</td>
</tr>
<tr>
<td>PP</td>
<td>3.37</td>
<td>7.77</td>
<td>38.64</td>
</tr>
<tr>
<td>B</td>
<td>4.41</td>
<td>13.12</td>
<td>33.93</td>
</tr>
</tbody>
</table>

The sedimentation of the inks as a function of time is an important parameter for the shelf life and usability of an ink. If the ink is very unstable it will have a short shelf life and it will be prone to clogging the inkjet nozzle. The PPC and DB inks are stable for over 24 hours however sedimentation can be seen to be beginning in the PC ink after only 2 hours. The yellow colour of the supernatant is caused by the impurities on the PC particles being brought into solution. On sedimentation the PPC and DB inks leave a colourless supernatant.

![Figure 5-10 The sedimentation of the carbon inks as a function of time from 0 to 24 hours. Only the plasma carbon shows appreciable sedimentation in 24 hours](image)

The PC ink is unstable because the impurities in the carbon material are being brought into solution by the Triton X-100, this results in there not being enough adsorbed surfactant on the particles to provide enough of a steric repulsive force to overcome the attractive Van der Waals forces which act between particles. A schematic of this is shown in Figure 5-11.
The effect of the surfactant concentration on the PC ink was examined by varying the surfactant concentration. Inks were formulated with 1% and 5% w/w Triton X-100 and the sedimentation of thinks was monitored as a function of time and the results are shown in Figure 5-12. The ink with 5% Triton X-100 showed the longest time to begin sedimentation. With a 1% concentration the supernatant appears to be almost colourless compared to the higher surfactant concentrations this is evidence that the surfactant is drawing the contaminants in the carbon into the supernatant solution. These contaminants deplete the carbon particles of surfactant which is responsible for agglomeration of carbon particles and hence sedimentation.
Figure 5-12 Influence of the surfactant concentration on the stability of the PC ink. As the concentration of Triton X-100 is increased the stability of the ink also increases.

The inks were printed as described in 5.2.6 with the opening time set to 275 µs, the pressure set to 700 mbar and the drop spacing set to 0.5 mm. Lines were printed and then allowed to dry at room temperature before making measurements. To print multiple layers of ink the previous layer was allowed to dry completely before the next layer was deposited. The printed layers are shown in Figure 5-13. All three inks show similar coating properties on the less porous substrates i.e. the coated proofing paper, acetate and kapton films. The inks wet these substrates well which causes the printed tracks to spread out over a greater area, this effect is especially prominent for the first printed layers. The inks tend not to spread after the first layer as there is now a carbon layer which can confine the freshly printed inks leading to the centre of the printed tracks being raised up from the extra carbon deposited. The office paper shows the narrowest tracks which corresponds to its high porosity and roughness when compared to the coated proofing paper and polymeric substrates.

The electrical resistance of the printed tracks as a function of the number of printed layers was measured and the results are displayed in Figure 5-14. As it might be expected the resistance of the printed layers decreases rapidly with the number of layers printed for all of the inks. The first printed layer has an extremely high resistance in comparison to the rest of the layers which may be accounted for by the concentration of conductive material being too low to allow electrical current to percolate easily. The printed carbon networks allow some current to flow which implies that the concentration of carbon particles is above the percolation threshold after which a small amount of added conductive material can decrease the
Figure 5-13 Printability on different substrates (coated proofing paper (PP), common office paper (OP), acetate (AS) and Kapton (KS) sheets) of the inks containing different carbons as fillers (a) plasma carbon (PC), (b) pyrolysed plasma carbon (PPC) and (c) acetylene Denka black (DB).

resistance of the coating by an order of magnitude. One would expect that the PPC ink would have the lowest resistance since it had the highest conductivity as a powder but according to my observations the DB ink had the lower resistance by an order of magnitude than the PPC. A plausible explanation is that the more structured and anisotropic DB particles have a higher number of inter-particle contacts the less more spherically agglomerated PPC, these inter-particle connections give rise to printed layers with reduced resistance. High aspect ratio particles such as the DB powder display a lower percolation threshold than the low aspect ratio PC and PPC particles[62]. In the powder conductivity measurements the powders are put under a high external uniaxial pressure which forces the particles to come into contact, this effect isn’t occurring during the inkjet deposition process where suspension drops are being deposited on the substrate. The higher initial number of inter-particle contacts in the DB and the higher particle aspect ratio can give the printed layers lower resistance compared to the less interconnected PPC. The higher aspect ratio structure (Figure 5-4) of the DB particles can be seen in the shear thinning behaviour of the ink, the more interconnected DB particles give the ink a higher initial viscosity which decreases rapidly with the application of a shear stress. The low apparent density of the DB particles is another sign of its highly sparse agglomerate structure. The PC ink presents the highest resistance as would have been expected from the fact that it had the lowest conductivity as a powder.
5.4 Conclusions

Highly conductive carbon nanoform powders were made by pyrolysis of plasma derived carbon material. The conductivity of the dry pyrolysed powder was measured to be 150 S/m at a pressure of 2 MPa compared to approximately 15-20 S/m at the same pressure for the untreated PC and the DB powders. This represents an improvement of approximately an order of magnitude compared to the untreated carbon. The conductivity of graphene flakes at the same applied pressures is in the same range (~150 S/m) [61]. These carbon powders were used to formulate inks suitable for inkjet printing which upon drying provide conductive tracks and coatings without the need for further processing. To draw more accurate conclusions about the effect of the pyrolysis it will be necessary to measure the thickness of the coating so the true electrical conductivity of the tracks can be determined. An experimental method to measure the thickness of thin carbon coatings on flexible and porous
substrates will have to be developed, it is possible that atomic force microscopy (AFM) could be used to measure the thickness of the carbon ink coatings. These carbon inks are suitable for the additive manufacture of conductive tracks and coatings with the high porosity and surface area of the PPC being attractive qualities for electrochemical devices. The DB based ink provided the lowest resistance tracks due to its highly interconnected structure compared to the PC and PPC inks.
6 Summary and Outlook

In this thesis silver flake inks were modified by dilution for inkjet printing and the effect of the printing parameters and the dilution on the conductivity of inkjet printed tracks was investigated using a Taguchi design of experiments (chapter 2). This allowed the effect of each of the chosen parameters to be analysed and optimised. The compaction and hence conductivity in the inkjet printed samples was found to depend most strongly on the pressure applied to the inkjet nozzle. The electrical conductivity of these tracks was approximately 1% of bulk silver, which compares well with other low temperature processes such as NP self-sintering on paper substrates where conductivities up to approximately 2.5% of bulk silver was achieved on porous paper [63]. Higher deposition pressures imply larger impact velocities which is an indication that the speed of impact of an ink drop on a porous substrate can assist in compaction.

The effect of the deposition dynamics on the compaction of silver flake inks is modelled in chapter 4. It was shown that the compaction observed upon impact is possible within the model provided that the particle and ink drop size, the particle loading, solvent viscosity and the jetting velocity are in the required range.

The modification of a plasma derived carbon by pyrolysis and the preparation of water based suspension inks was described in chapter 5. The pyrolysed plasma carbon showed a large increase in specific surface area, pore volume and electrical conductivity. The studied carbons were dispersed in water based suspensions and were printed on a variety of substrates.

I suggest that further investigation of the properties of the aforementioned carbon tracks should be carried out and electrodes constructed utilising the silver and carbon inks as the electrode materials. The combination of silver nanoparticles and the carbon particles into one water based printing ink, The printing of this silver-carbon ink and control of the demixing on deposition might be a promising route for the production of fractally connected silver network tracks in which the volume of silver is reduced but the electrical conductivity remains intact.
7 Bibliography


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