Metal particle compaction during drop-substrate impact for inkjet printing and drop-casting processes

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Direct coating methods using metal particles from aqueous solutions or solvent-based inks become central in the roll-to-roll fabrication processes as these methods can lead to continuous or pre-defined conductive layers on a large variety of substrates. For good electrical conductivity, the metal particles have to be brought into contact, and traditionally, additional sintering treatments are required. Such treatments can degrade the sensitive substrates as paper or polymer films. In this study, the possibility of obtaining conductive layers at room temperature is investigated for direct coating methods with an emphasis on drop-casting and inkjet printing. Thus, it is shown that electrical conductive layers can be achieved if the metal particles can compact during the drop-substrate impact interaction. It is theoretically shown that the compaction process is directly related to the particle and ink drop size, the initial fractional particle loading of the ink, solvent viscosity, and drop velocity. The theoretical predictions on compaction are experimentally validated, and the particle compaction’s influence on changes in the electrical conductivity of the resulting layers is demonstrated. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4941344]

I. INTRODUCTION

The enhanced development and the dynamic growth of flexible/paper electronics applications in medical to energy sectors have led to an increased demand for thin metallic or metallized layers as continuous or patterned coatings on a variety of substrates. In energy applications, such coatings are used as electrodes or current collectors in photovoltaics, flexible batteries, or supercapacitors.1–4 Typically, these layers can be obtained by coating (pouring, spraying, casting, or smearing ink over the surface) or by printing (i.e., the ink layer is transferred from a stamp by a reverse action) metal based conductive inks onto desired substrates.5–8 Drop-casting and inkjet printing (Figure 1) are two technical processes that can be implemented independently (or in-series) in roll-to-roll manufacturing processes for coatings or patterned conductive layers without or with minimum substrate alteration.4,8

Experimentally, ink drop-casting can be performed with a simple equipment (Figure 1(a)), but a good horizontal leveling of the substrate is essential.5 The ink can be cast onto the substrate as isolated drops (Figure 1(c)) or as continuous liquid films that are further cured (or dried) at room or elevated temperature.5 The procedure leads to relatively thick continuous films, but drop-casting provides only limited control of the film thickness and pattern geometry. The wetting properties of the inks and the substrate are important because a dewetting process can occur during drying, leading to inhomogeneous coatings.4,5

In the drop-on-demand (DOD) configuration, inkjet printing (Figures 1(b) and 1(d)) can deliver the ink onto the substrate in controlled small (from pl to pl) amounts, the ink waste being minimized when compared with other printing and coating techniques. The desired patterned or continuous layer is then created with minimal or no influence exerted onto the substrate.3–8 Typically, the common commercial inkjet printers utilizing the DOD technology are based on thermal, piezoelectric, or acoustic heads for droplet generation.6–8 In a classical DOD printing configuration, an electrical signal excites a thermal or a piezoelectric element that induces a transient pressure pulse in the ink reservoir. This pulse leads to droplet ejection by forcing a small volume of ink out of the nozzle.6,8

An alternative is represented by the electromagnetically (EM) actuated printing heads that minimize ink heating and reduce the complexity of the printing procedures3,4,7 In this configuration, the nozzle of the printing head has a fixed aperture size. A compressed-air flow provides a constant pressure allowing the drops production as a solenoid driven plunger opens and closes the nozzle orifice.3,4,7 The size of the jetted drops can be controlled by varying the pressure, the opening time, and/or the rheological properties of the ink. In the EM-DOD printing configuration, the movement of either the nozzle or the substrate is allowed, where the relative positions of the printing head and substrate are accurately adjusted using a controlled X-Y stage (see Sec. II).3,4,7 Upon contact with the substrate, the liquid drop begins to spread as the droplet inertia causes a forced wetting. The droplet starts to deform, and the liquid is pushed radially outwards from the initial contact point. During spreading, the droplet velocity normal to the

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surface decreases from the initial impact velocity to zero as the spreading finishes (Figure 2).4,5,8

In a recent study,4 we have experimentally shown that for a water-based ink with silver micron-sized flakes of narrow-size distribution (among drop-casting, doctor blading, flexographic, and ink-jet printing), conductive layers can be obtained without a subsequent sintering process 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 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 (see also Figure 1(e)), the flakes did not compact under the applied pressure.4 In contrast to these methods, the inkjet printing leads to a complete flake compaction into an almost solid block (Figure 1(f)) without further sintering treatment being required. As all printing methods were performed on the same paper substrate, 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.4

In general, the printability is directly linked with ink–substrate interactions, their wetting properties, the surface roughness, and the porosity of the substrate. Consequently, the printed layer’s conductivity is also affected, but its final value is also related with the ink’s composition and the printing method. The initial metal particle loading and the initial particle size distribution within the ink will influence the ink flow during the printing or coating processes, and therefore, it is expected that the resulting layers will have different composition and physical or electrical properties. To obtain the desired conductive layers, typical sintering treatments (e.g., high temperature, UV exposure, etc.) are employed after the printing or coating processes.8–10 For flexible/paper electronics, such sintering processes can degrade the substrate, and consequently, they should be avoided or minimized.

For drop casting, doctor-blading, and flexographic printing, the pressure acting on the ink and the ink flow are well-studied.2,5,11,12 However, despite the fact that the drop-substrate impact during inkjet printing of a homogenous liquid droplet is also well established,8,9 the understanding of the metal particle movement during the drop-substrate impact for multi-component liquids, like conductive silver inks, is still in its infancy. Here, a theoretical study is employed to understand and predict the (complete) compaction of the metal particles due to the drop-substrate impact. The influences of the particle size, ink solvent viscosity, and density as affected by the metal loading, drop size, and velocity in the compaction process are explored. Thus, the possibility of contact between the metal particles and the extent of the particle compaction are theoretically foreseen and confirmed by the experimental results.

II. EXPERIMENTAL

A. Materials

An aqueous-based silver ink formulated by DZP Technologies, UK, was used for the coating and printing experiments. The silver content of D38NV ink was 52 (wt. %), and the ink viscosity \( \mu = 10 \text{ Pa s} \). The silver flakes had a narrow size distribution with 10% < 1.1 \( \mu \)m, 50% < 2.1 \( \mu \)m, and 90% < 3.9 \( \mu \)m. In all coating and printing experiments, proofing paper sheet (KPP/SHC from RK Print Coat Instruments, UK)
was used as the substrate. Thus, the effect of the ink–substrate interactions (e.g., substrate wettability, porosity) was maintained constant and so is not discussed. Therefore, the final results will be influenced only by the ink delivery onto the substrate.

As-received, D38NV ink has a large viscosity ($\mu \sim 10$ Pa s) prohibiting its direct use in the inkjet printing head where the requirement for the viscosity upper limit is $\mu \sim 10$ mPa s. Therefore, for all experiments, the ink was thinned (see Table I) with deionized water (18 MΩ cm) in the desired ratios. Thus, the water-ink ratios employed were 40/60; 50/50; and 60/40 (v/v).

B. Coating and printing methods

The drop-casting coating method involved applying a fixed amount ($\sim 100 \mu l$) of thinned ink onto the paper substrate. The distance between the dispensing nozzle (here, represented by the tip of a micropipette (see also Refs. 4 and 5)) and the substrate was minimized until the ink drop was deposited mainly due to capillary action. The ink deposition led to drops of 4–7 mm diameter that were dried at room temperature. The surface of the drops dried completely within 2 h, but their core required over 10 days until a complete drying was achieved.

In the present work, the ink-jet printing system used has an electromagnetically driven printing head. This technology was chosen not only because of its simplicity and reliability but it also offers a wider range of ink/suspension compatibility. The printing head works on a magnetic piston/solenoid mechanism (Figure 1(g)) where the ink is loaded into the reservoir and a pressure is applied onto it. The main advantage of this mechanism is that the applied field is away from the ink, and thus, no heating occurs. The printing head is provided with an outlet valve (Figure 1(g)); this is opened prior to printing, thus ensuring that all air pockets are removed. An electrical pulse controlled by the computer interface passes through the solenoid, and the electromagnetic field lifts the piston off the surface of the nozzle (Figure 1(g)) for a certain amount of time (i.e., the “opening time” parameter). In these experiments, a 100 μm Domino ruby nozzle is used as it exhibits resistance to wear and corrosion. A plunger is attached to the piston to ensure secured closing of the nozzle and to avoid damaging the piston and the nozzle. An external air compressor provides constant pressure that forces the ink to be ejected from the nozzle, leading to the production of a constant drop size (see Table I). The printing head is attached to an x–y planar positioning system (Rolland X–Y plotter with a step resolution of 25 μm). The computer interface is controlling the opening time, the printing speed, and inter-drop wait time, while the pressure is adjusted using a high precision adjustable regulator (SMC IR3000–04). Here, the printing speed and the inter-drop wait time are maintained constant at 100 mm s$^{-1}$ and 250 μs, respectively.

Water thinning leads to changes in the solvent viscosity $\mu_S$ and/or on the ink surface tension. The ink thinning also

<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>$\mu_S$ (mPa s)</th>
<th>$H$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>0.4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>9</td>
<td>576</td>
</tr>
<tr>
<td>D2</td>
<td>0.5</td>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>7</td>
<td>576</td>
</tr>
<tr>
<td>D3</td>
<td>0.6</td>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>5</td>
<td>576</td>
</tr>
<tr>
<td>T1</td>
<td>0.4</td>
<td>0.45</td>
<td>255</td>
<td>2</td>
<td>9</td>
<td>157</td>
</tr>
<tr>
<td>T2</td>
<td>0.4</td>
<td>0.5</td>
<td>275</td>
<td>2.2</td>
<td>9</td>
<td>241</td>
</tr>
<tr>
<td>T3</td>
<td>0.4</td>
<td>0.6</td>
<td>300</td>
<td>2.5</td>
<td>9</td>
<td>340</td>
</tr>
<tr>
<td>T4</td>
<td>0.5</td>
<td>0.45</td>
<td>275</td>
<td>2.5</td>
<td>7</td>
<td>233</td>
</tr>
<tr>
<td>T5</td>
<td>0.5</td>
<td>0.5</td>
<td>300</td>
<td>2</td>
<td>7</td>
<td>254</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>0.6</td>
<td>255</td>
<td>2.2</td>
<td>7</td>
<td>210</td>
</tr>
<tr>
<td>T7</td>
<td>0.6</td>
<td>0.45</td>
<td>300</td>
<td>2.2</td>
<td>5</td>
<td>149</td>
</tr>
<tr>
<td>T8</td>
<td>0.6</td>
<td>0.5</td>
<td>255</td>
<td>2.5</td>
<td>5</td>
<td>190</td>
</tr>
<tr>
<td>T9</td>
<td>0.6</td>
<td>0.6</td>
<td>275</td>
<td>2</td>
<td>5</td>
<td>175</td>
</tr>
</tbody>
</table>

FIG. 2. 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.
contributed to the changes in the droplet (as jetted) diameter \( H \) that is primarily influenced by the applied pressure and the opening time of the nozzle (see Table I). Consequently, the properties of the inkjet-printed silver layers (e.g., electrical conductivity \( \sigma_{\text{el}} \), layer thickness \( d_L \), etc.) can be influenced by factors such 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-number line-density \( N_d \) (i.e., the number of drops per mm). The influence of these factors was investigated, and a Taguchi optimization method was employed. For each of these four control factors, three levels were chosen (for complete experimental details, see Ref. 4). In all cases, the ink layers were dried at room temperature for 2 h before investigations were performed. No other thermal or other types of post-treatment or sintering process was used.

C. Microstructure analysis

The layers microstructure was investigated in top-view and cross-sections by scanning electron microscopy (SEM) using a Hitachi S4800 FESEM operating at 5 kV. Image analysis was performed using the open source image processing package FIJI, which is based on ImageJ (National Institutes of Health, USA). Low magnification SEM images gave information on the continuity of the ink-jet printed layers, while larger magnification allows identification of the shape and the 2D projected area of the silver flakes.

D. Electrical conductivity

The resistance (and, consequently, the conductivity) of the layers was measured using a Jandel 4 point probe (Matt TC tip, radius \( \sim 100 \mu m \), and probe spacing \( \sim 1 \text{mm} \)). The probe was placed on the lines, the current between the outer pins was set to \( I = 100 \text{mA} \), the voltage \( V \) across the inner pins was measured, and the resistance per unit length was calculated. The electrical resistivity (and, consequently, the conductivity) was calculated by multiplying the resistance per unit length by the cross-sectional area (as determined from the SEM images). The measurement was performed in five different points on the layer, and their mean value was considered (see Ref. 4 for further details).

III. THEORETICAL MODEL

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 2(a)). Upon contact with the substrate, the droplet does not retain its spherical shape and it starts to deform (Figures 2(b) and 2(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 2). This consideration remains valid for a large section of the central area of the droplet if one considers the dimensions of the particles (see Sec. II) 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.

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

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

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 the following equation:

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

At an 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 2(a)). There are \( N_L - 1 \) intervals between particles with a length given by the following equation:

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

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 the following equation:

\[
\frac{nm \ddot{x}}{6\pi \mu_S R} = -6\pi \mu_S R \dot{x}.
\]

Integrating yields the composite particle’s velocity, which decays to zero according to Eq. (5), we should receive an expression for \( d \), Eq. (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 \( d = D \)

\[
n = \frac{9\mu_5 D}{2R^2 \rho_{Ag} v_0}. \tag{7}
\]

Combining Eqs. (3)–(7), the fraction of particles to compact is given by the following equation:

\[
F = 1 - \frac{n}{N_L} = 1 - \frac{(1 - 2N_l r)}{\beta N_l (N_L - 1) r^2}, \tag{8}
\]

where \( r = R/H \) and \( \beta = 2\rho_{Ag} v_0 H/9\mu_5 \).

If \( N_L \gg 1 \) and using Eqs. (2) and (8), we obtain an expression for \( F \) that is dependent on \( \beta \) and the loading fraction \( L_f \) only

\[
F \approx 1 - 4 \frac{1 - L_f^{1/3}}{\beta L_f^{2/3}}. \tag{9}
\]

The fractional loading \( L_f \) and the parameter \( \beta \) will influence the compaction factor \( F \) as given by Eq. (9), where \( \beta \) is determined by the initial drop velocity, its diameter, and the ink carrier viscosity (see also Figure 3).

Note that no compaction occurs for the following parameter condition given by the following equation:

\[
\beta < 4L_f^{-2/3} \left(1 - L_f^{1/3}\right), \quad \text{or equivalently,} \quad L_f < \left[\frac{2}{\beta} \left(\sqrt{1 + \beta} - 1\right)\right]^3. \tag{10}
\]

IV. RESULTS AND DISCUSSION

Independently of the coating or printing method, the paper–ink interaction proceeds in three stages. Initially, as the ink makes contact with the substrate, the liquid carrier starts to be absorbed by the paper. In the second stage, as a partially dried film forms, the flakes tend to agglomerate, form aggregates, and compact. As the flakes reach the paper, the pores are blocked. As a result, the liquid carrier is trapped within the deposited layer. Finally, in the third stage, the dried film consolidates, and as the permeation through the paper pores is impeded, the evaporation is the only mechanism that can allow for the liquid carrier loss. The extent of each stage not only depends on the ink properties (e.g., the initial ink loading) but also on the capillary-driven process taking place during the casting and printing. Thus, the first two stages can exist independently, or alternatively, their occurrence cannot be distinguished due to their short duration. In the drying conditions presented in this study, it is expected that the particles in-plane movement is small as no significant changes in the particles, spatial distribution were observed in the SEM cross-sections when the central drop region and the triple contact point were investigated.

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. 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 presence of residual liquid carrier (RC) in the layers. 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 (Figures 1(e) and 1(f)). Consequently, these flows are not considered in the theoretical model employed here.

The compaction factor \( F \) is influenced by the parameter \( \beta \) and the fractional loading \( L_f \) (see the contour plots in Figure 3). Thus, for very low \( \beta \), particle compaction can be achieved (see Figure 3) only 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.

![Contour plots of the compaction factor](image-url)

**FIG. 3.** Contour plots of the compaction factor \( F \) calculated using Eq. (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 Eq. (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 corresponding to the drop-casting layers. 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 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.
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, not studied experimentally here, one has to add other factors (such as Marangoni flow) as the surface particles distribution onto 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 compaction factor \( F \) is determined by the \( \beta \) parameter that can be influenced by the velocity \( v_0 \) and the size \( H \) of the droplets ejected from the nozzle (Eqs. (8) and (9)). These are controlled by the applied pressure and the opening time, respectively. However, finding the printing parameters that will emphasize the transition between the points presented in Figure 3 is not trivial. Thus, a lower applied pressure can lead to a lower velocity, but it results in increased dot positioning errors or insufficient kinetic energy to break free from the printing head. A higher velocity can result in splashing of the droplet upon impact with the substrate.

The size of the droplets can influence the compaction factor \( F \), but this influence is not a linear dependence as it appears in both \( \beta \) and \( r \) factors in Eq. (8). Experimentally, the size of the droplet is controlled by the rheology of the ink, the applied pressure, and the opening time. For a given viscosity and applied pressure, a larger opening time can lead to bigger droplets, but such droplets can adhere to the nozzle affecting the printing. Therefore, further work is required to establish the influence of each experimental parameter.

The direct comparison of the theoretically predicted compaction factors and the values calculated for the experimental conditions presented in Figure 3 show that, indeed, no compaction should occur in the drop casted layers (see Figure 1(e) and D1–D3 points in Figure 3(a)). For the drop casted layers, \( F \) has negative values and falls beneath the theoretical compaction boundary (Eq. (10) and the solid black curve in Figure 3). 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 3(b)). Thus, for the majority of experimental data (excepting \( T_1 \) and \( T_7 \) samples), the compaction factor is close to unity (\( F \approx 0.8 \)). Such large \( F \) values can allow the formation of solid silver layers as seen in the SEM cross-section (Figure 1(f)).

The differences in compaction level are also reflected in the electrical conductivity \( \sigma_{\text{ij}} \) 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.

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. 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. For very large \( N_d \), the printed drops tend to form discrete 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 coins geometry are obtained.

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(a)). As defined, the scalloping factor suggests that an \( S \rightarrow \infty \) 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(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 a 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(b)).

Results presented in Figure 4(b) show that there is a threshold in the compaction layer $F$ above which the layers become conductive as the silver flake compaction can form a conductive path. This threshold will be determined by the variations in the initial loading, viscosity, droplet diameter, and velocity. Thus, 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 experimental tests are required to determine the electrical conductivity’s analytical dependence on the compaction factor $F$.

V. CONCLUSIONS

Printing 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 limited or no compaction, the printed layer will need sintering treatments, but for a large compaction factor a conductive path is formed.

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