The Importance of Surface Characteristics for Structure Definition of Silver Nanoparticle Ink Patterns on Paper Surfaces

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Abstract

Silver nanoparticle inks are printed on nine papers as well as a polyimide film. Structure width and edge raggedness is evaluated on each substrate for both polar and non-polar ink. The substrates are characterized in terms of material content and various physical surface properties. The aim of this study is to establish relevant correlations between printed structure measurables and surface properties, in order to expand the understanding of the mechanisms involved in nanoparticle ink - paper surface interaction. A multivariate analysis is presented which reveals correlations between print performance and paper properties, as well as relations between different paper properties. The results suggest that besides surface energy considerations, absorption rate and surface roughness play important roles for achieving well behaved print structure definition in paper electronics applications.

Introduction

Printing of functional materials is an expanding field of interest as a complement to traditional deposition methods. Compared to common patterning methods such as photo-lithography, printing has the obvious advantage of being an additive method, leading to less material consumption and therefore economic and environmental advantages. Printing can also be adapted to a wide range of substrates including flexible and environmentally attractive materials such as paper[1].

A combination of ink and substrate properties together with the process requirements usually influence the choice of printing method. Inkjet is suitable for low viscosity fluids and due to its non-contact nature it can be used for surfaces of various geometry including pressure-sensitive surfaces. When high conductivity is needed, metal nanoparticle dispersions are typically used, among which silver is the most commonly used metal due to high performance and comparably low reactivity under ambient conditions[2, 3].

The possibility of using paper as a substrate for printed electronics is of considerable interest due to cost efficiency and environmental considerations. However, some inherent properties of paper such as porosity, surface roughness and water absorption make functional printing on paper non-trivial. These non-ideal properties may be overcome or even used to advantage for certain applications, as in the case of a printed moisture sensor [4].

In this paper, print definition is examined on nine different papers as well as a reference polyimide film, using silver nanoparticles dispersed in both polar and non-polar carrier solution.

Materials and Methods

Printing and inks

A Dimatix 2831 piezoelectric inkjet printer was used to print 20 mm long lines with the smallest possible width (single nozzle). The drop volume was 10pL and the nozzle voltage 24V. Drop spacing was set to 20µm; the nozzle and platen temperature was set to 28ºC.

Two silver nanoparticle dispersions from Advanced Nano Products were used; DGP40LT with polar dispergent (triethylene glycol monoethyl ether) and DGH55LT with non-polar dispergent (n-tetradecane). The inks have similar particle size distributions and mass loading. Viscosity and surface tension of the dispersions were measured with a Brookfield LVDV-+ and a Kruss K9, respectively. Viscosity and surface tension was measured to 12.9 cP, 37.3 mN/m for the polar ink and 9.75 cP, 29.4 mN/m for the nonpolar ink.

Paper characterization

Material analysis was performed using both energy-dispersive spectroscopy (SEM/EDS, Jeol JSM-5800 LV / Oxford Link ISIS) and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One/AutoImage) on the top layer of the surfaces.

Contact angle measurements were performed according to test method Tappi T558 om-07, using a Fibro DAT 1100 drop absorption tester with 4µL of water and 2.5 µL of diiodmethane. Measurements were made as a function of time with first readings taken at 0.02s (initial contact angle, immediately after reasonable geometrical stabilization of the drops). Surface energy components were calculated using the geometric-mean equation[5]:

$$(1+\cos(\theta_l))\gamma_l = 2\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \qquad (1)$$

where γ_l is the surface tension of the liquid and γ_s is the surface energy of the substrate. Superscripts d and p denotes dispersive and polar component respectively, where $\gamma = \gamma^d + \gamma^p$.

Note that measurements of contact angles are not trivial on heterogeneous, absorbing and rough surfaces; initial contact angle is influenced also by surface roughness and absorption rate[6]. Nevertheless, in this study we use equation 1 with the initial contact angles and refer to the result as apparent surface energy.

Absorption was measured using a Bristow absorption tester [7] with water as test liquid and contact times in the range of 0.01 to 2 seconds.

Surface roughness was measured with an optical profilometer (FRT MicroProf with CRT H0 sensor). The profilometer data was post-processed in custom FFT software to extract wavelength-dependent surface roughness information.

The porosity was characterized with a Mercury porosimeter (Micromeritics Autopore IV 9500) according to ISO 15901-1. A pore size range of 10µm down to approximately 5nm (corresponding to the maximum pressure limit of 230 MPa) was examined.

***Table 1.** Substrates in the study. Classification based on data from manufacturers, Hg-porosimetry and SEM-EDS/FTIR material analysis.*

	Substrate	Coating Type	Main Surface Composition
1	Semigloss Photopaper	Mesoporous	Al_2O_3
2	Glossy Photopaper1	Mesoporous	Al_2O_3
3	Glossy Photopaper2	Mesoporous	Al_2O_3
4	Glossy Photopaper3	Mesoporous	Silica
5	Swellable Photopaper	Water Soluble Polymer	Gelatin
6	LWC1	Lightweight coating	$CaCO_3$, Caolin Clay
7	LWC2	Lightweight coating	$CaCO_3$, Caolin Clay
8	Matte Inkjet Paper	Macroporous	Silica
9	Copy Paper	Uncoated	Cellulose, $CaCO_3$ filler
10	Polyimide film	Uncoated	Polyimide

Structure definition evaluation

The ISO13660 standard definitions of line width and raggedness[8] were used as measures of structure definition. Printed lines were scanned at 2400 dpi with an Epson 10000XL fladbed scanner and the images were fed into a custom software, calculating the line width and raggedness according to the ISO definitions.

Multivariate Analysis

A Principal Component Model (PCA-XY) [9] was constructed in Simca-P software(version 11.5, Umetrics Inc.) and fitted to the data. Four components were used, resulting in a cumulative R2X of 0.98 and a cumulative Q2 of 0.89.

Results

Paper characterization

Results from the surface material analysis and porosimetry can be seen in table 1. Table 2 shows data on some of the measured physical properties of the ten substrates.

Paper 1-4 are commercially sold as high performance inkjet photo papers. This group of papers had narrow pore size distributions and a characteristic pore size in the 10 nm range. Absorption rate was very high, and this group also had the highest total pore volumes. Surface roughness values were low for papers 2-4 but a factor five or higher for paper 1. This was also the group were the apparent surface energy values were the largest.

Paper 5 is coated with a water soluble protein gel. It's typical application area is as photo paper for dye based inks in which the coating layer 'swells' and encapsulates the dye, thereby prolonging the lifetime of the print[10]. Surface roughness was low and absorption rate in the middle range.

Papers 6-7 are lightweight coated papers typically used for high quality offset printing. These were characterized as having low absorption rate, low surface roughness and low surface energy.

Paper 8 and 9 both have low energy, high roughness surfaces. Paper 8 (matte inkjet paper) has higher absorption rate and pore volume than paper 9 (copy paper).

Substrate 10 is non-porous/non-absorbing and has the smoothest surface. While the surface roughness of the transparent polyimide film in this study was not possible to measure with the optical profilometer, additional measurements with the Parker Print Surf (PPS) method confirmed it to be smoother than any of the paper surfaces.

***Table 2.** Surface measurements. Neither dispersive- and polar surface energy components nor mid- and low frequency surface roughness contributions are explicitly shown here, but are used in the multivariate analysis.*

	App. total surface energy (mN/m)	Absorption Rate ($cm^3/m^2\sqrt{t}$)	Pore V/A (cm^3/m^2)	HF Surface Roughness (μm^2)
1	53	105	113	0.027
2	71	90	84	N/A
3	64	50	71	0.0037
4	54	105	82	0.0044
5	60	18	51	0.0028
6	44	8	28	0.0027
7	36	9	28	0.0041
8	33	22	79	0.110
9	32	15	47	0.112
10	51	1	3	N/A

Line Definition

Figure 1 shows data on line width and raggedness as well as images of printed lines on the ten substrates. The print definition is highest on the inkjet photo papers (paper 1-4).

Raggedness is particularly large on the roughest substrates (paper 8 and 9), and has a characteristic appearance known as feathering (figure 1 and 3). Generally the substrates with the slower absorption rates show lower print definition, and on the polyimide film, which is the only non-absorbing substrate in the study, lines have the lowest definition.

Substrate	Polar ink		Non-polar ink	
	Line Width	Raggedness	Line Width	Raggedness
1. Semigloss photopaper	38.4	0.83	40.2	1.38
2. Glossy Photopaper1	36.4	0.63	34.6	0.75
3. Glossy Photopaper2	46.9	0.72	40.8	0.92
4. Glossy Photopaper3	39.9	0.82	39.4	0.79
5. Swellable Photopaper	110	4.6	61.7	2.4
6. LWC1	56.0	2.8	89.6	5.1
7. LWC2	49.2	1.8	99.6	5.3
8. Matte Inkjet Paper	58.9	1.7	60.7	3.4
9. Copy Paper	99.5	9.6	123	9.7
10. Polyimide film	105	7.3	300	14.9

Figure 1. *Print definition with polar and non-polar nanoparticle ink on the different substrates. All images are at equal magnification. Values in µm.*

Figure 2 shows a roughly linear relationship between the raggedness and the line width for the nine papers. It may be argued that the raggedness and the line width both are influenced by the absorption rate, where a fast absorption (table 1) prevents the ink spreading and feathering.

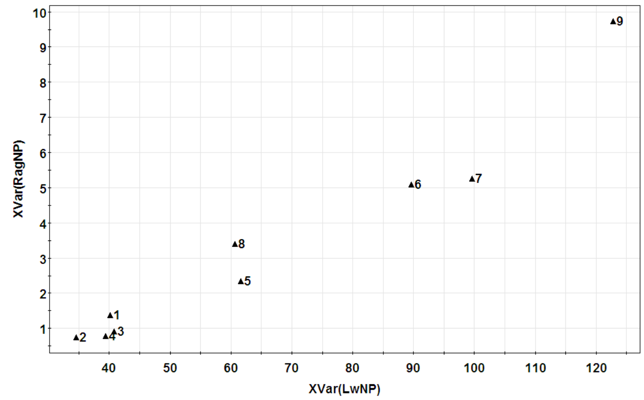

Figure 2. *Raggedness plotted against line width for the nine different papers.*

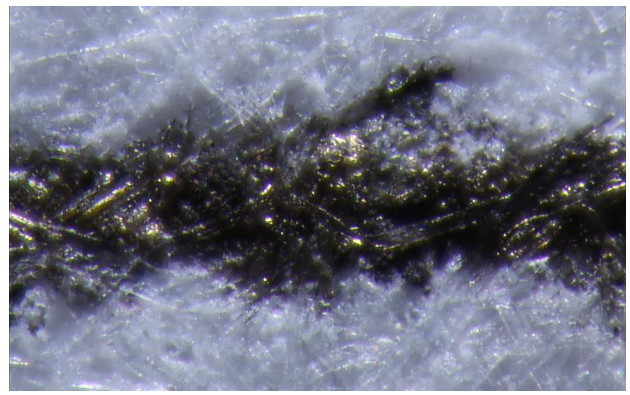

Figure 3. *Microscope picture of substrate 9 (copy paper), showing large surface roughness and ink feathering.*

Multivariate analysis

A 4-component Principal Component Analysis (PCA) model was fitted to all the paper data. The polyimide film was not included in this model due to its different nature. A list of the variables is seen in table 3. The model has high values of goodness of fit (R2X=0.98) and goodness of prediction (Q2X=0.89).

Examining the score plot (figure 4) reveals a cluster structure corresponding well with the coating composition according to table 1. The relations of different variables are indicated in the loadings plot (figure 5). Close variables are correlated and opposing variables negatively correlated. In the same way correlations also exist with papers at similar areas in the corresponding score plot. For instance, high surface roughness is associated with the copy- and matte inkjet paper, and large line width/raggedness is inversely correlated with the mesoporous group of papers.

Table 3. *Variables defined in the PCA model. Three variables of surface roughness are incorporated; HF, MF and LF, corresponding to a spatial wavelength of 7.5, 30 and 190 µm respectively.*

Type	Variable	Quantity
Y	LWP	Line width(polar)
Y	LWNP	Line width(non-polar)
Y	RagP	Raggedness(polar)
Y	RagNP	Raggedness(non-polar)
X	AbsRate	Absorption rate
X	Pore V/A	Pore volume/surface area
X	SEdisp	Apparent dispersive surface energy
X	SEpol	Apparent polar surface energy
X	SR_HF	Surface roughness (HF)
X	SR_MF	Surface roughness (MF)
X	SR_LF	Surface roughness (LF)

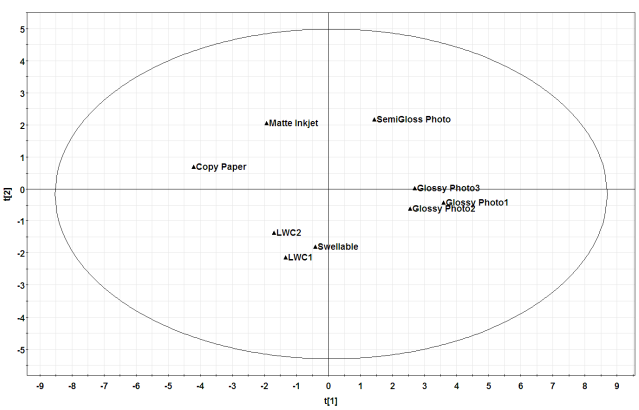

Figure 4. *Score plot. Clustering is seen for the glossy photo papers and the lightweight-coated papers, indicating similar properties.*

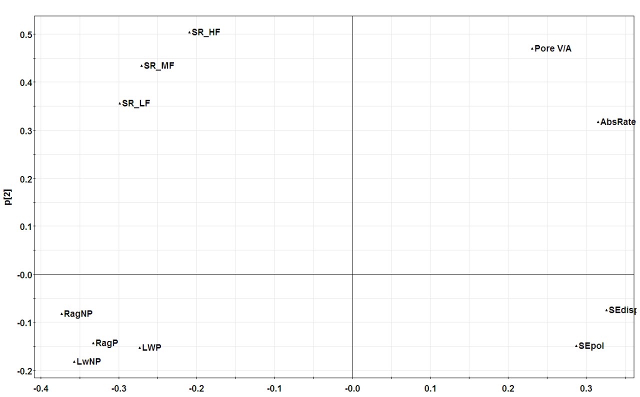

Figure 5. *Loadings plot. Absorption rate and pore volume inversely correlated to line width and raggedness for both polar and non-polar ink.*

Discussion

The multivariate analysis(figure 4, 5) as well as a comparison of the microscope images(figure1) and surface data(table 2) suggest that high absorption rate is the dominant factor explaining the excellent line definition of substrates 1-4. For this group of papers, substrate 3 exhibits worse definition and lower absorption rate than the rest, which is consistent with this assumption.

The weak line definition of substrate 8 and 9 is arguably dominated by excessive surface roughness. Capillary forces drive ink along the surface pore channels and fibres associated with these papers, an effect known as feathering[11] (see figure 3).

However, it can be speculated that a limited amount of surface roughness may actually be beneficial for print definition under certain conditions, if local surface perturbations act as physical barriers restricting nanoparticle movement. The very smooth surface would then partly explain why the polyimide film has the least defined lines, although the dominating factor is the lack of absorption. It has been shown that a thin coating layer on a smooth plastic film can improve print definition considerably, with an associated increase in surface roughness [12].

As expected, definition differences between the two inks are most noticable for the least absorbing substrates (6, 7 and 10), for all of which the non-polar ink show worse definition. This can be understood from a surface energy/surface tension perspective; the non-polar ink has a lower surface tension and therefore larger spreading on the same substrate.

The main reason for the low definition on substrate 5 is probably of chemical nature, in that it may be understood as an effect of dissolvation and diffusion. With the polar dispersion, the polymer coating layer partly dissolves and silver nanoparticles diffuse in the dissolved layer. The better definition seen here for the non-polar ink should be expected if the non-polar solvent does not dissolve the coating layer.

Regarding the multivariate analysis, the groups of papers appearing in the score plot correspond well with the groups of similar coating that was found in the porosity/material analysis (table 1). It is therefore indicated that the model work well for coating classification within this set of papers. The model shows high values of model fit and predictive ability and should therefore be effective for analysis of correlation structure inside the model range.

Conclusions

When examining structure definition with inkjetted silver nanoparticle suspensions, all paper substrates compared very favourably with the polyimide film(the non-absorbing substrate). It is speculated that, for low absorption rate surfaces in particular, surface roughness may in fact be beneficial due to pinning of the nanoparticle ink, limiting excessive spreading.

With the low absorption rate surfaces, clear differences in the structure definition were seen for the different inks (with polar as compared to non-polar dispersion), suggesting that surface energy considerations and chemical interactions also come into play. For the high absorption rate surfaces however, this ink dependence was significantly reduced.

Performing a multivariate analysis on the complete data matrix indeed suggests that high absorption rate and porosity are strongly correlated with low line width and raggedness and can be regarded as the dominating factors for good print definition. Apparent surface energy and surface roughness had less clear correlations with print definition within this data set.

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