The Optimization of Conductive Inks for 3D Inkjet Printing

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Abstract

Commercially available nanoparticle precursor conductive inks are designed to prevent the blockage of the print-head nozzles by using low evaporation rate binder solvents. This low evaporation rate has the consequence of long drying times for those conductive inks which makes 3D printing of conductive routes a lengthy process.

In this paper we identify a number of solvents that have suitable properties to prevent nozzle blockage and allow for enhanced drying rates so that multiple conductive layers can be printed within a short time to form 3D conductive elements. To achieve this propylene glycol monomethyl ether acetate (PGMEA) was used as a solvent to form a 30 wt% silver conductive ink which, after sintering, reached a resistivity of 1.66 μΩ.m.

Introduction

Commercial nanoparticle precursor conductive inks are not designed for printing a large number of multiple layers because they take, relatively, long time to dry each layer, whilst this is acceptable for 2D printed electronic applications, for producing 3D components this is undesirable. These inks consist of conductive metal nanoparticles dispersed in solvents acting as binder liquids [1-3]. Solvents used within the inks have low vapor pressure indicating a low evaporation rate to prevent nozzle blockage during printing [4]. This low evaporation rate is the prime reason for the long drying time required for each printed layer and makes these inks unsuitable for printing large number of layers.

Although early reports used high vapor pressure solvents like toluene and hexane to allow for fast drying time of ink [3,5,6], recent reports used mixtures of low vapor pressure solvents to form stable inks and prevent blocking the print-head nozzles [7,8]. Commercial inks also use very low vapor pressure solvents like triethylene glycol monomethyl ether (TGME) and ethylene glycol as these inks are designed for 2D planer printing, and usually recommend 30 minutes drying time at 120 to 300 ºC [4,9,10].

Table 1 shows the properties of a list of solvents that are used and could potentially be used in formulating conductive inks.

Table 1: Properties of solvents used in commercial conductive inks and some potential solvents to allow for fast drying time.

Solvent	Boiling point (ºC)	Viscosity (mPa.s)	Vapor pressure (mmHg) at 20ºC
Toluene	110.6	0.6 [11,12]	29
TGME	122	6.25 [13,14]	0.01
PGMEA	146	1.1	2.8
3-pentanol	115.3	7	8.8

From the list in Table 1, PGMEA was chosen to formulate a high vapor pressure conductive ink due to its preferable environmental and safety over 3-pentanol.

The formulated ink was deposited and compared with a commercial ink from Advanced Nano Product (ANP, Product No. 40LT-15C) which uses TGME as the main solvent for their digital inkjet inks. The comparison includes the drying time and the resistivity of both inks as described in the results section.

Experimental Methods

Silver nanoparticles were purchased in a dry form and coated with a fatty acid to prevent particle agglomeration and stabilize the ink. The coated nanoparticles were suspended in PGMEA at 30 wt% load, as described in the ink formulation section, and the ink was deposited on glass slides to evaluate the drying time and the resistivity of the ink.

Materials

Silver nanoparticles (99.99% purity, 20nm in diameter) were purchased from US Research Nanomaterials Inc. in dry form. To stabilize the nanoparticles Sodium Oleate was used from Sigma Aldrich Co. as well as the high vapor pressure solvent PGMEA. Glass slides used as substrates were standard microscope glass slides from Cole-Parmer Instrument Co. Ltd.

Ink Formulation

Dry silver nanoparticles were suspended in 3 mM Sodium Oleate solution which has been reported to provide good stability of nanoparticle precursor inks [15]. The particles were mixed for 2 hours in a magnetic stirrer and sonicated for 1 hour.

The Sodium Oleate solution was prepared by mixing 9.13 mg of sodium oleate flakes into 10 mL of deionized water (DIW) and mixed until the solution became clear indicating to a complete dissolution.

The suspended nanoparticles in sodium oleate solution were then centrifuged for 1 hour using Hermle Z300 at 6000 rpm to separate the coated particles from the excessive DIW-sodium oleate solution. The nanoparticles were left to dry at room temperature and then loaded at 30 wt% into PGMEA solvent and sonicated for 2 hours. The ink stability using Sodium Oleate coated nanoparticles showed great improvement, prior to coating in Sodium Oleate the nanoparticles would sediment after a few hours when no coating was conducted as shown in Figure 1.

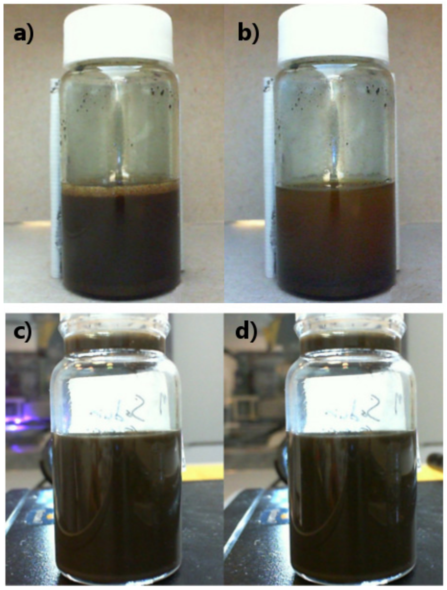

Figure 1. Silver nanoparticles suspended in PGMEA, a) without Sodium Oleate coating just after sonication, b) without Sodium Oleate after 4 hours, c) with Sodium Oleate coating just after sonication, d) with Sodium Oleate coating after 24 hours.

Results

To evaluate the ink in this study, which was designed to produce a fast drying conductive ink, two sets of experiments were conducted. One was to compare the evaporation rate of a commercial ink with the ink formulated in this study. The other set of experiments was to measure the resistivity of the developed ink and the commercial ink by measuring the cross sectional area and the resistance of a sintered 20 mm long track as described in this section.

Evaporation Rate

A droplet of each ink between 1 and 2.5 nL was deposited on a microscope slide at ambient conditions and onto a hot plate at 50 ºC. A reference commercial ink (ANP) was deposited to compare against the PGMEA ink developed in this study. Time-lapse photography was used to take pictures of 1 fps for each of the droplets as shown in Figure 2 at room temperature.

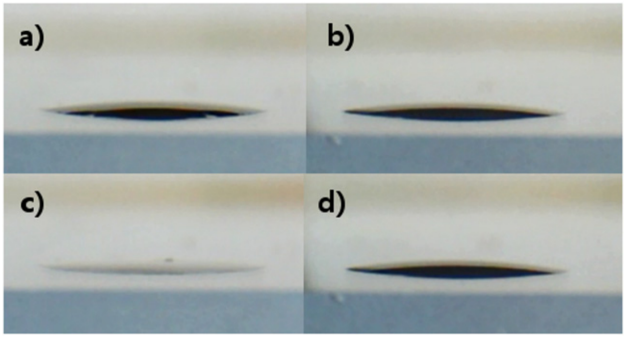

Figure 2. a) PGMEA ink taken after 1 second of depositing the droplet, b) ANP ink taken after 1 second of depositing the droplet, c) PGMEA ink after 300 seconds, d) ANP ink after 300s.

The rate of volume change of the droplets was analyzed as shown in Figure 3 and Figure 4 at room temperature and at 50 ºC, respectively.

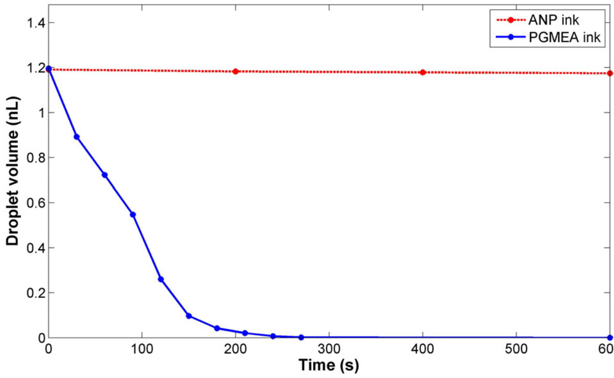

Figure 3. The volume of ink droplets as it changes with time at room temperature.

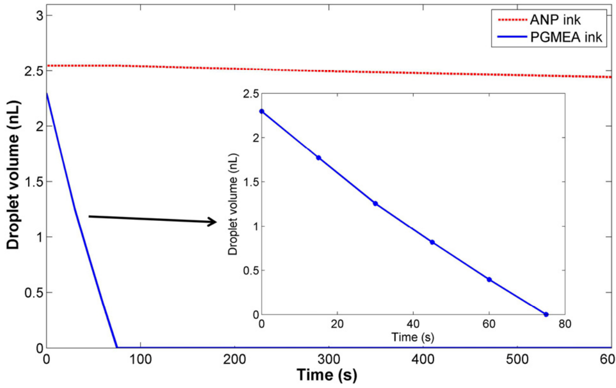

Figure 4. The volume of ink droplets as it changes with time at 50 ºC.

The volume of the PGMEA droplet after drying is assumed based on the area of the dry silver spot and its thickness which was measured using a surface profilometer.

The ANP ink is recommended to be sintered for 30 minutes at least 130 ºC which explains the long time required to dry it. The short time required to dry the PGMEA ink is very suitable to allow for drying each layer of ink as it is printed so multiple layers can be built, however sintering of the nanoparticles would still be required at elevated temperature after printing the entire structure to develop suitable conductivity.

Ink resistivity

To measure the resistivity of the PGMEA ink and compare it to the ANP ink, a track of each ink was deposited on a microscope glass and was left to sinter at 200 ºC for 30 minutes. Each track was 1 mm wide, 20 mm long and 3 µm thick on average measured using Taylor Hobson profilometer.

The resistance of the tracks was measured at the furthest points of each track using a Hameg LCR high precision meter. At the furthest points of the tracks a pad of conductive paste was deposited to prevent scratching of the deposited silver tracks during resistance measurements. The resistance of that paste was also measured and was negligible when compared to the resistance of the tracks.

When the tracks geometry and resistance was analyzed the resistivity of each ink was measured as summarized in Table 2.

Table 2: Resistivity measurement parameters.

Ink	Cross sectional area (m^2)	Length (mm)	Resistance (Ω)	Resistivity (μΩ.m)
ANP	4.5×10^{-9}	20	2.9	0.65
PGMEA	3.9×10^{-9}	20	8.4	1.66

We noticed that the resistivity of the ANP ink was much higher than what the ink datasheet shows (50-90 nΩ.m) [4]. This can be due to inaccuracy of the cross sectional area measurements which requires further study.

Studying the resistivity of each ink, we noticed that the PGMEA ink had higher resistivity which could be due to the presence of the Sodium Oleate coating. Early experiments of this study used Poly(Vinyl Pyrrolidone) (PVP) as a dispersant coating showed lower resistance at lower temperatures. However due to instability of the ink Sodium Oleate was used instead of PVP which improved the stability of the ink but increased the resistivity and the temperature required to sinter the nanoparticles.

Ink stability

Prior to conducting any printing the ink showed good stability after being stored for a few days. During the printing using a Dimatix DMP2800 the PGMEA ink was generally stable where some nozzles required cleaning cycles to ensure the stability of the print-head. The droplet ejection was stable as shown in Figure 5 at room temperature using 27 V at the piezoelectric nozzles and using double peak printing waveform.

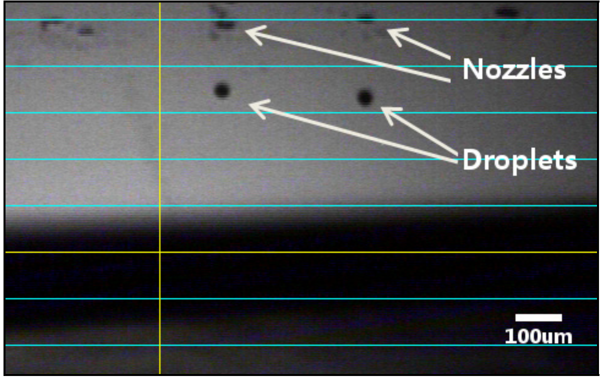

Figure 5.Conductive PGMEA ink being jetted from 21 μm diameter nozzles of the Dimatix DMP2800 print-head.

The stability of the ANP ink was unprecedented when compared to the PGMEA ink and other inks that the research group had used. The ANP ink was chosen in this study due to its very stable properties, however these properties are in contradiction to the main purpose of this study was to formulate an ink with close properties but fast drying for 3D printed applications.

Conclusion

A fast drying conductive ink was developed in order to allow for a feasible 3D inkjet printing of conductive tracks. The ink used propylene glycol monomethyl ether acetate (PGMEA) as the main solvent due to its relatively high vapor pressure when compared to the solvents used in commercial conductive inks. Sodium Oleate (at 3 mM concentration) was used to stabilize the ink and disperse the silver nanoparticles well within the PGMEA solvent.

The drying rate of the conductive inks was measured where PGMEA ink showed much shorter drying rate (8 pL/s) compared to the commercial ANP ink (20 fL/s) at room temperature.

The resistivity of the inks was also measured showing very comparable results where the ANP ink and the PGMEA ink had a resistivity of 0.65 μΩ.m and 1.66 μΩ.m, respectively.

Further study of the stability of the developed PGMEA ink during printing is still required, and the choice of dispersant should be revised to improve the resistivity of the sintered ink.

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Ehab Saleh received his BEng in Digital Electronics and Communications from the University of Brighton and his PhD in Optoelectronics from the University of Southampton working on direct write technologies for jetting metal and glass nanoparticles. Since then he has worked in the 3D Printing Research Group at the University of Nottingham. His current work has focused on the development of various jetting related conductive inks and processes. Ehab is currently an editor in the Additive Manufacturing journal and a member of IET.