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Influence of Solvents on Characteristics of Inkjet Printing Conductive Ink Based on Nano Silver Particles

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Abstract: Solvents are used in ink as diluents to control the rheological properties of the ink such as viscosity, surface tension, contact angle, flow and leveling properties and evaporation rate. The solvents are used to keep the ink in liquid form when applied to the printing plate or cylinder from cartridge until transferred onto the substrate surface to be printed. In this study, silver nanoparticles were synthesized by reduction of silver nitrate in ethylene glycol under ultrasonic wave. The silver nanoparticles-based ink was prepared by dispersing silver nanoparticles in the mixture of different organic solvents. The inks were characterized by using Ultraviolet-visible spectrophotometry (UV-Vis), particle size analyzer (DLS), surface tension and contact angle measurement. The surface of the printed silver layers was observed by 3D optical profilometry microscope. Modification of the solvent led to changes in the surface tension and the contact angle of the ink. This affected the printing process, the evaporation rate of solvent and the presence of coffee ring effect. The role of the solvents was examined to prevent this effect. The main purpose of this study was to prevent coffee ring effect of the silver nanoparticles ink and to improve the quality of printed patterns in inkjet printing process.

Key words: Silver nanoparticles, solvents, coffee ring effect, rheological properties.

1. Introduction

Metallic nanoparticles-based ink has been attracting researchers due to its high conductivity and potential applications in a variety of device manufacturing processes such as displays [1], RFID antennas [3], sensors [4, 5], photovoltaics [6], transistors and other electronic devices [7-9]. However, many applications of inkjet printing for industrial production have no appropriate ink, only a limited number of ink are usable. In addition, the cost of production is expensive because of their low productivity and high material costs. Among the conductive metallic nanoparticles, silver is a suitable material for ink fabrication with high conductivity. Silver nanoparticles (AgNPs) are more stable than copper nanoparticles and cheaper than gold nanoparticles. In order to obtain a well silver conductive ink, the components of the ink need to be well controlled. Typically, the ink includes four basic components: pigments, resins, solvents and additives. In the mentioned components, the solvent plays an important role in transporting the particles from the cartridge to

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the print head. At this point, the solvent must separate from the component of the ink to dry the pattern and adhere to the surface. The ink formula depends on the types of substrate which are printed on and the printing method with different printing conditions. The inkjet printing process using Dimatix Materials Printer (DMP) requires a solvent that evaporates slowly. The viscosity and surface tension of the solvent greatly influences the transport of a droplet from nozzles to the substrate. These parameters directly affect the evaporation rate, the appearance of convection flow and Marangoni flow forming the coffee ring effect [11-13].

This report presents the fabrication process of AgNPs and the AgNPs -based ink using a variety of solvents to disperse the AgNPs. Some investigations were performed to study the effect of solvents on the properties of the ink. These results are presented and discussed.

2. Materials and Methods

2.1. Materials

The chemicals were used as follows: Silver nitrate ($AgNO_3$, 99.8% Spain), Poly (acrylic acid) (PAA, Mw 1800 g.mol-1) from Sigma-Aldrich. Ethylene glycol (EG) from China for fabrication. The organic solvents (Sigma-Aldrich Co.) such as ethylene glycol (EG), ethanolamine (EA, 99%), ethanol (EtOH, 99%), 2-methoxyethanol (2-ME, 99%). All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ.

2.2. Preparation of silver nanoparticles

In order to prepare the silver nanoparticles, the following procedure was used. The AgNPs solution was synthesized by ultrasonic vibration bar (250 W, Sonic ruptor 250 Ultrasonic Homogenizer) in the presence of poly (acrylic acid) (PAA) as a surfactant and ethanolamine (EA) as a reducing agent. Firstly, the amount of 4 g PAA and 24 g EA were dissolved in 26 ml of ethylene glycol (EG). While stirring vigorously, silver nitrate was added to the mixture. Then, the solution was stirred under ultrasound for 10 minutes. At the beginning of the reaction, the light yellow solution turned orange yellow, indicating the formation of the silver nuclei, and finally the yellowish black solution was achieved, which indicated the high density of the particles in the solution which could be used to prepare silver conductive ink.

2.3. Preparation of silver conductive ink

Ethanol (150 ml), a poor solvent for the PAA capping agent, was added to the prepared silver nanoparticles solution for raising particle precipitation. Then, the coagulated particles were centrifuged at

10,000 rpm for 15 minutes to collect the particles. The concentrated particles were re-dispersed in different organic solvents by sonicating for 30 minutes by indirect ultrasonic vibration bar at room temperature.

2.4. Inkjet printing equipment

Dimatix Materials Printer (DMP 2831) was used for printing on glass substrates with a printhead containing 16 nozzles (a mean diameter of nozzle was 21.5 μm). The main features of the printer included a piezoelectric "drop-on-demand" inkjet cartridge, non-contact liquid coating, precise X-Y-Z motion stage controller, integrated camera which observed a droplet of the ink. The printhead could dispense the droplet of 10 pl. Therefore, a pattern would be printed with high resolution. Each nozzle was controlled by a piezoelectric mechanism. Therefore, the material was coated onto the substrate at a desired position and without being affected by the signals from the adjacent nozzle. In addition, this printer allowed to adjust the drop spacing as low as 5 μm.

2.5. Characterization

The silver conductive ink solutions were analyzed by UV-Vis absorption spectroscopy with a double-beam spectrophotometer (Cary 100, Varian, Australia) in the wavelength range from 190 to 1,100 nm. The rheological properties of the ink including surface tension and contact angle were measured by dynamic contact angle system (CAM 101/KSV Instruments, Finland). The mean diameter of the particle size and the size distribution were characterized by Particle size analyzer (DLS, Horiba LB550, Japan). The texture of the silver tracks were investigated with 3D optical profilometry microscope (S neox, Sensofar, Spain).

3. Results and Discussion

The silver nanoparticles ink (10 wt% of the solids) in water and ethanol were prepared. Then, 10 μl of each ink was dropped on a glass slide and heated at 100 ℃ for 15 minutes to observe the evaporation of the solvent. The surface image of the samples and the UV-Vis spectra were shown in Figure 1. The surface plasmon resonance (SPR) peaks were observed at 403 and 523 nm, 408 and 483 nm for water and ethanol, respectively. These spectra showed the instability of the ink because of two regions, the small particles size (short wavelength region) and the large particles size (long wavelength region) that easily led AgNPs to aggregate [14].

Table 1 The basic parameters of different organic solvents [16]

Solvent	Chemical formula	M (g/mol)	D (g/cm^3)	T_b (℃)	ε	n_D	η (mPa.s)	γ (mN/m)
EtOH	C_2H_6O	46.07	0.7893	78.4	25.3	1.3611	1.2	22.1
EG	$C_2H_6O_2$	62.07	1.1132	197.3	37.7	1.4306	16.1	48.0
2-ME	$C_3H_8O_2$	76.09	0.9650	124.0	16.9	1.4020	1.7	31.8
EA	C_2H_7NO	61.08	1.0117	170.4	37.7	1.4539	16.2	48.3
H_2O	H_2O	18.02	1.0000	100.0	80.4	1.3333	1.0	72.8

The basic parameters of different organic solvents are shown in Table 1. Ethanol (with a lower boiling point) often evaporates faster, causing the crevice on the substrate surface. In contrast, the AgNPs spreaded more evenly in the substrate when using water as seen in Figure 1. Next, AgNPs ink (5 wt% of solids) in different solvents were prepared and indicated in Table 2. The samples named from PAA1 to PAA5 were dispersed and the samples from PAA6 toPAA9 was dispersed in water-ethylene glycol binary mixture. When increasing the concentration of ethanol, AgNPs tended to be agglomerated because ethanol is a poor solvent for washing the PAA. The increase in ethanol also reduced the surface tension of the solution. The reason is that water has a high surface tension because it is strongly attracted to itself. However, if ethanol is added, instead of water interacting only with other water molecules, it now interacts (less strongly) with ethanol, and the surface tension of the mixture is lower [16].

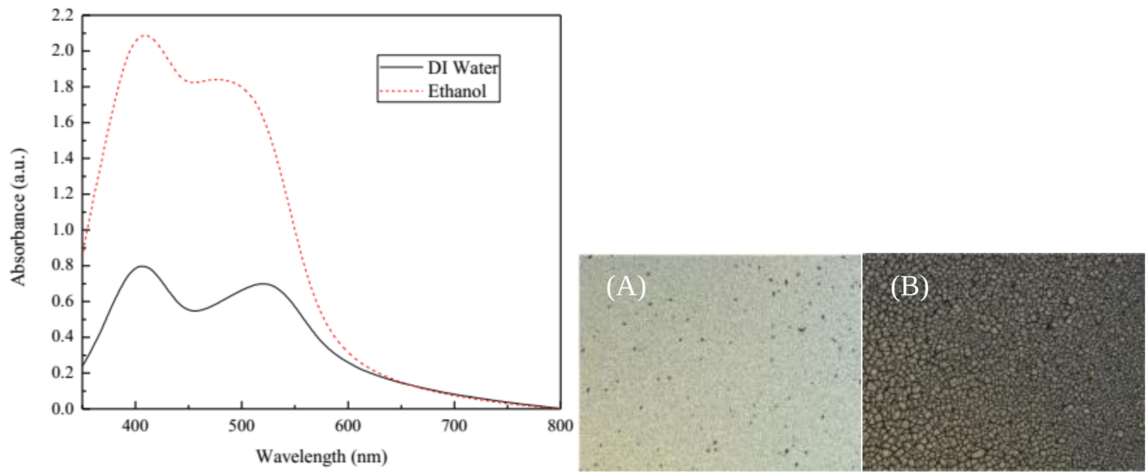


Fig. 1 The UV-Vis spectra and surface image of the ink with silver nanoparticles re-dispersed in DI water (A), ethanol (B).

Table 2 The parameters of the ink with 2 wt% of the solids as silver in the different solvents

Sample	EtOH (ml)	EG (ml)	H_2O (ml)	Mean size (nm)	Contact Angle (°)	Surface Tension (mN/m)	UV-Vis λ_{max} (nm)	Aggregation
PAA1			1	48.0	15.47	52.49	414	No
PAA2	0.1		1	38.0	19.79	38.84	408	No
PAA3	0.2		1	46.0	17.57	32.73	403	No
PAA4	0.5		1	…	…	…	…	Yes
PAA5	1		1	…	…	…	…	Yes
PAA6		0.1	1	37.3	30.79	43.09	408	No
PAA7		0.2	1	49.3	27.40	43.46	406	No
PAA8		0.5	1	43.0	45.16	45.75	402	No
PAA9		1	1	55.3	47.87	44.10	400	Little
PAA10	0.5	1	1	50.6	32.37	29.83	401	No
PAA11	1	1	1	34.0	19.94	27.84	400	No

In UV-Vis spectra (Figure 2), when increasing the concentration of ethanol, the lower the absorption intensity and the SPR peak also gradually shifts towards the short wavelength as well as becomes narrower. The absorption intensity decreased, indicating a decrease in the particle density. According to Mie theory, the lower the surface plasmon resonance wavelength, the smaller particle size [14, 15]. The increase in ethanol coagulated the particles and led them agglomerated and then sank to the bottom of the solution. The smaller and more homogeneous AgNPs presented. The similar results with the series named PAA6 to PAA9 and the series named PAA10 and PAA11 (Figure 2). The absorption intensity, surface tension and contact angle decreased.

The suitable ink used for Dimatix printer required the surface tension of 28-33 mN/m and the viscosity of 10-12 cP. In Figure 3, when increasing the solids of AgNPs, the surface tension decreased (in 1:1 water-EG by volume). Another approach to adjust the AgNPs-based ink formula was to adjust firstly the surface tension of the water with the different solvents and then examined the surface tension reduction by the dispersed AgNPs concentration. However, the higher increased, the more saturated in the solvent mixture led the AgNPs to aggregate. The maximum dispersion of the AgNPs solid was 15 wt% in 1:1 water-ethylene glycol binary mixture.

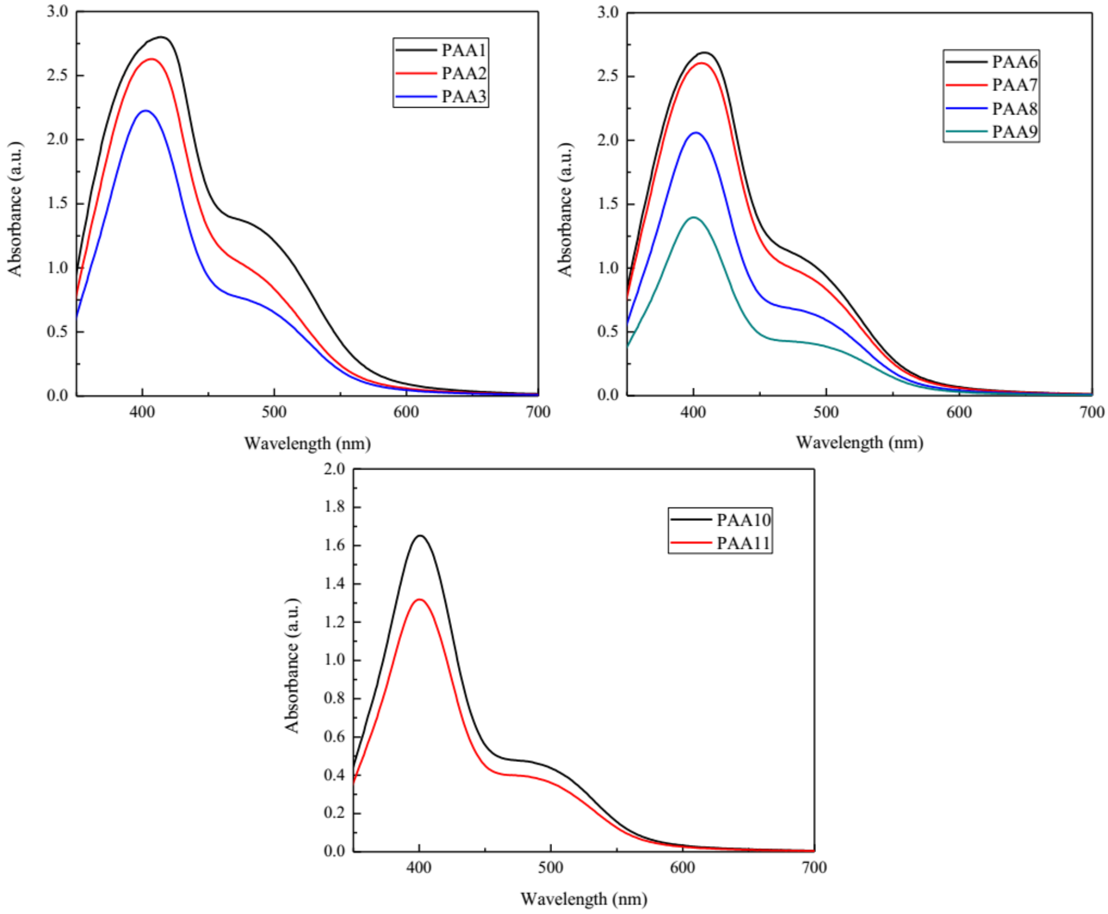


Fig. 2 The UV-Vis spectra of the PAA1- PAA3 samples (A), PAA6-PAA9 samples (B) and PAA10-PAA11 samples (C).

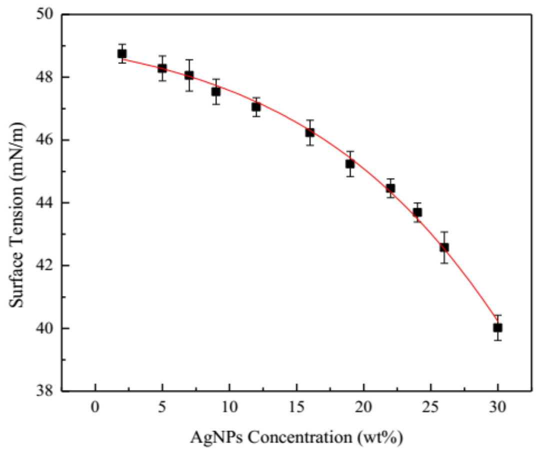
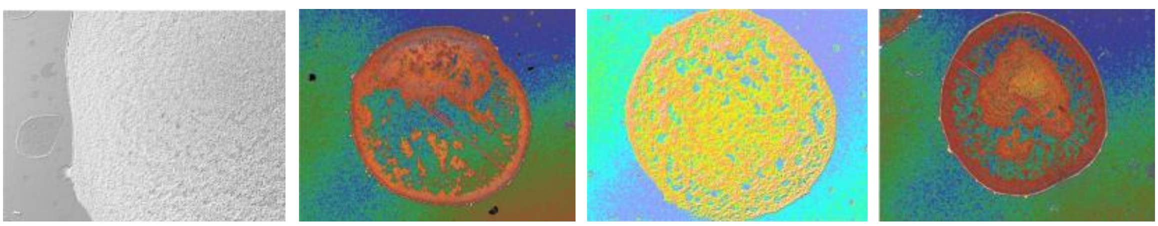


Fig. 3 The decrease in the surface tension with varying AgNPs concentrations in water-ethylene glycol binary mixture.

Figure 4 indicates the 3D optical microscope image of the printed patterns by using the ink with 15% wt of the solids as silver in different solvents (Table 3). Then, the cover glasses with printed silver pattern were heated at 100oC for 1 hour. The cause of coffee ring effect was the appearance of two flows in the interior liquid: the convection flow and the Marangoni flow. When the liquid evaporated, the evaporation rate at the outer edge was higher, thereby producing a convective flow containing the AgNPs directed to the edge to compensate for the loss of the solvent, leading to the phenomenon of the coffee ring. There are several ways to overcome this effect: Mixing some solvents with a low evaporation temperature and a high evaporation temperature to balance these two flows. On the other hand, the concentration of the dispersed AgNPs was increased in the solvent mixture. According to the ref. [10-12], the suitable AgNPs concentration to fabricate the silver conductive ink was about 20 wt%.

Table 3 The parameters of the ink with 15 wt% of the solids as silver in the different solvents

Sample	H_2O (ml)	EG (ml)	2-ME (ml)	EA (ml)	Mean size (nm)	Contact Angle (^{o})	Surface Tension (mN/m)	UV-Vis λ_{max} (nm)	Aggregation
PAA14	1	1			95.6	15.25	42.22	417	No
PAA15	1		1		140.3	34.87	33.74	400	Little
PAA16	1			1	71.3	25.17	45.42	403	Little
PAA17	10	10	10		162.3	32.25	33.80	417	Little



(a) PAA14 (b) PAA1 (c) PAA16 (d) PAA17

Fig. 4 The 3D optical microscope images of the 15 wt% AgNPs ink with different solvents.

4. Conclusion

In this paper, different kinds of the solvents were investigated for the production of silver conductive ink in order to examine the effect of the solvents on the rheological properties of the ink, such as the surface tension, contact angle, particle size. As the results obtained, the components of the fabricated conductive ink included two major solvents which were water and ethylene glycol. In order to adjust the suitable surface tension for the Dimatix inkjet printer, other solvents, humectants and additives were added to the ink formula. Further research needs to be performed to well disperse AgNPs to achieve the homogeneous solution without aggregation. The conductive ink products could be printed by the Dimatix inkjet printer and other inkjet printers.

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