

Drops-on-Drops Micro-film Formation by Stable Electrostatic Jets

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Abstract

Applying micro spray state of electrostatic inkjet to precision film coating was examined experimentally. High quality coating could be expected by drops-on-drops of super fine and mono-diameter droplets. At first, the most preferable jetting condition was determined through experiments for two types of coating liquid, one of which was dilute dispersion and the other was viscous solution. Then, with those parameters examined, the surface quality of the coated films was evaluated through several coating tests. Along increasing applied voltage, jetting mode was varied from Mode 1, dripping mode, to Mode 2, jetting mode. The basics of jetting mode variation was equivalent for both types of coating liquid, although a larger nozzle had to be used for the viscous solution to avoid clogging. The most favorable condition for coating was the stable cone-jet mode in Mode 2, where a well-oriented thread was jetted from the stable Taylor cone at the nozzle tip and broken up into mist during flight. Both types of quality coating, a submicron film with the dilute dispersion and a thick film, over 10 micrometers, with the viscous liquid could be demonstrated by piling up the single-digit-micron-size droplets.

Introduction

Since the first inkjet printer appeared in market more than 50 years ago [1][2], the inkjet technology has progressed tremendously in quality and print speed. Although the electrostatic inkjet technology has not applied to commercial printers, it is attractive in the industrial application because of its versatility in jetting forms; an individual droplet on demand [3], fine droplets in micro spray state [4], a thread for fabric [5]. Furthermore, it has the ability of jetting highly viscous liquid [6] and making (a) super fine, femtoliter-size, droplet(s) [3].

Herein, applying the micro spray state of electrostatic inkjet to precision film coating is proposed. Conventional spray methods are not suitable for precision coating owing to the problems such as over-spray, limitation in viscosity and range of thickness. The micro spray state of electrostatic inkjet is expected to overcome the problems by drops-on-drops concept, piling up super fine and charged droplets onto a substrate. Also, coating can be a good application for digital fabrication by inkjet because it can alleviate the deviation of delivery by dispersing droplets and their level-off.

In this report, two types of liquids were used; one of which was dilute dispersion to coat submicron film and the other was a viscous solution to coat thicker film, over 10 micrometer. At first, the most preferable jetting conditions for two different types of liquids were determined through experiments. Then, with those parameters examined, the surface quality of the coated films was evaluated through several coating experiments.

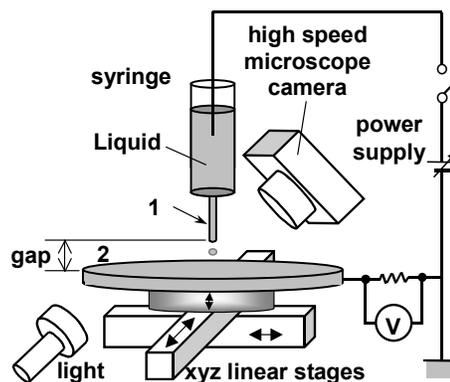


Figure 1 Experimental set-up of electrostatic inkjet (1: pin electrode=nozzle, 2: plate electrode).

Experimental Experimental set-up

An experimental set-up is illustrated in Figure 1. During applying the voltage up to 10 kV by a high voltage amplifier, the jetting state is observed with a high-speed camera. A nozzle, filled with liquid is assumed to be a pin electrode. The gap between the nozzle tip and the plate electrode can be controlled by a mechanical stage. A substrate on the plate electrode can be coated by traversing it in x-y direction under the jetting nozzle.

Liquids

The dilute dispersion consists of two solid components; poly(vinyl butyral) and an phthalocyanine-type pigment, and cyclohexanone as a solvent. The properties of this dispersion are listed in Table 1.

Two different viscous solutions were examined. The solid components of them consist of equal amount of polycarbonate and an arylamine-type low molecular component. These solid components were solved into two different solvents; cyclohexanone and mono-chlorobenzene. The properties of two solutions are listed in Table 2.

Table 1 Properties of dilute dispersion (4.1wt%, 26.0°C).

conductivity, S/m	viscosity, mPa.s	surface tension, mN/m
1.15×10^{-6}	4.5	36.28

Table 2 Properties of viscous solutions (15.0wt%, 20.0°C).
CHN:Cyclohexanone, MCB:Mono-chlorobenzene

solvent	conductivity, S/m	viscosity, mPa.s	surface tension, mN/m
CHN	1.55×10^{-6}	172.0	35.74
MCB	$<10^{-7}$	137.0	-

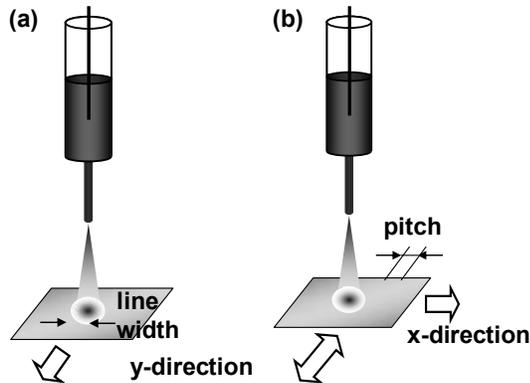


Figure 2 Coating procedure. (a) Line coating; scan a plate substrate in only y-direction. (b) 2D coating; scan a plate in both x and y-direction. Coated area was 20x20 mm². Scan pitches in x-direction were 200-1000 μ m.

Coating procedure

Several coating experiments were tried by jetting droplets onto a traversing aluminum plate as shown in Figure 2. Line coating was done by scanning a plate in only y-direction, whereas 2D coating, by scanning a plate reciprocally in x-direction while offsetting a certain pitch in y-direction at both ends of x-direction. The film qualities, thickness, its profile and surface roughness were measured with mechanical or laser profilometers.

Results

Jetting mode

With the less viscous liquid, along increasing the applied voltage, the forms of jets varied from dripping (Mode 1) to jetting (Mode 2) through transition mode, a mixture of them, as shown in Figure 3 [4][7]. The onset voltage of mode change was shifted to higher voltage with wider nozzle, although the forms of jets were basically equivalent within the same mode. In the Mode 2, the tip of liquid formed well-known Taylor cone [8]. The Mode 2 could be further divided into two states; Mode2-1 at lower voltage in which a single thread was ejected from the tip of Taylor cone and Mode2-2 at higher voltage in which multi-threads were jetted. Because the sites of multi-threads were unstable, it is clear that the single thread or cone-jet mode is better for coating application.

Figure 4 confirms the jet mode of the two different viscous solutions described in Table 2. The basic phenomena of the mode change were equivalent, although a larger nozzle had to be used for the viscous solution to avoid clogging. As the matter for coating application, spray-state hardly appeared with the MCB-base viscous solution. Drozin [9] and Hayati [10] indicated that it depended on the conductivity of liquid whether the jetted liquid became spray-state. The conductivity of the MCB-base viscous solution might be too low to form spray. The CHN-base solution was used for following experiments.

Effect of the range of jetting mode of the dilute dispersion was determined from the jetting form as shown in Figure 5. The range of stable cone-jet mode (Mode 2-1) is relatively wide and enlarged slightly as the gap is increased.

Figure 6 shows the effect of nozzle diameter on jetting mode with the CHN-base viscous solution. The cone-jet region is narrow, although it is widened slightly as the nozzle outer diameter is enlarged.

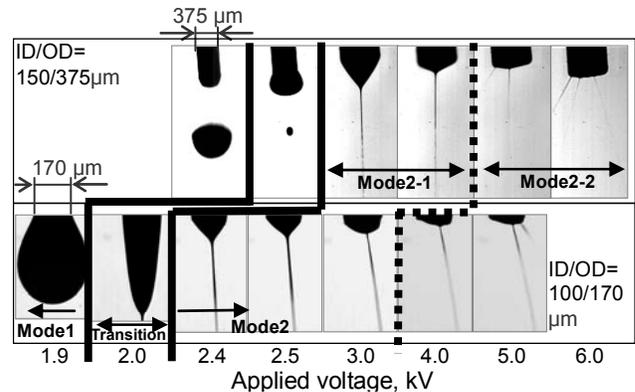
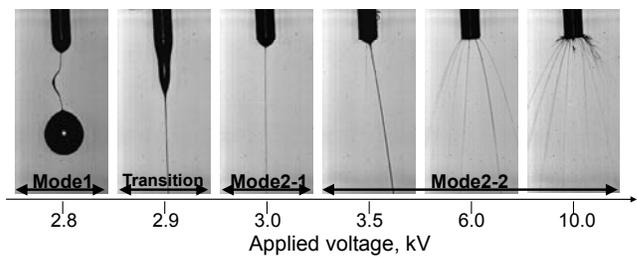
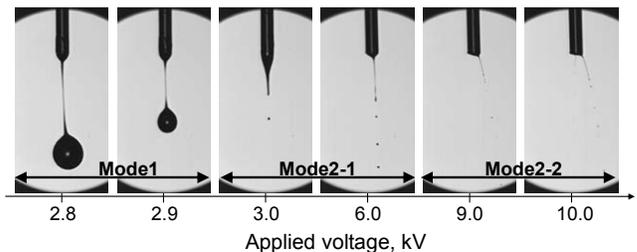


Figure 3 Forms of jet with dilute dispersion by applying voltage with three different nozzles. Gap = 10 mm. Shutter speed = 1/13500 s.



(a) CHN-base viscous solution, Mode 2 is from 2.9 kV.



(b) MCB-base viscous solution, Mode 2 is from 3.0 kV.

Figure 4 Forms of jets with two different viscous liquids. Gap=15 mm. Nozzle diameter = 320/450 μ m.

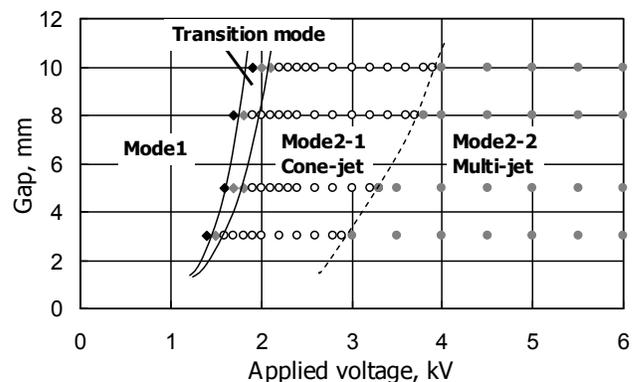


Figure 5 Effect of gap on jetting mode of dilute dispersion with I.D./O.D. = 100/170 μ m nozzle. Mode 1 and Mode 2 are divided by a solid line. Mode 2 is further divided into 2 regions by broken lines; Mode2-1 and Mode2-2.

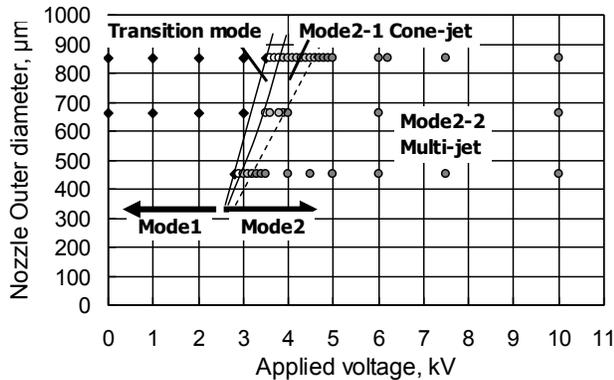


Figure 6 Effect of nozzle diameter on jetting mode with CHN-base viscous liquid. Gap=15 mm.

Drop size and distribution

Figure 7 and 8 show the distribution of droplet-sizes estimated from sprayed dots on a photo quality inkjet paper in Mode 2 of dilute dispersion and CHN-base viscous solution, respectively. The size tends to be smaller and mono-dispersed according to the increment of applied voltage. For the dilute dispersion, 3.5 kV was the best condition for coating. The mode-diameter was small as 3 μm (the volume which is about 14 femtoliter). For the viscous solution, though 4.8 kV seems to be the best mode, but the jet was multi-threads state. 3.2kV was selected for coating experiment for the viscous solution.

Coating experiments

At first, line coatings were examined with the dilute dispersion. Figure 9 (a) and (b) are the profile of the line coatings with the identical conditions, described in the caption of Figure 9, except the scanning speed; 0.575 mm/s for the profile in Figure 9 (a) and 0.375 mm/s for the profile in Figure 9 (b). The film of in Figure 9 (a) was found to be rough, although it looked flat. As times of drops-on-drops were more for the film in Figure 9 (b) than that in Figure 9 (a), the film quality of Figure 9 (b) was flat and smooth. The film thickness was 0.6 μm and its surface roughness, Ra was equal to 0.007 μm.

Next, 2D coatings were demonstrated with the same liquid as above. In Figure 10, the images of coated films with four different conditions are revealed. The scan speed and the pitch were determined as the color of these films looked equivalent. The quality of these films looked fine and smooth. Figure 11 shows the surface roughness of the film in Figure 10 (b). The surface roughness seems to be large but it is the matter of range. The surface roughness, Ra was 0.08μm.

Lastly, 2D coatings of thicker layer were demonstrated with the CHN-base viscous solution. Figure 12 (a) and (b) show the examples of coating films, whose coating conditions are described in the caption of Figure 12. The film thicknesses were 3.71μm by scanning once and 7.17μm by scanning over a film twice. As there were no visible scanning traces on those films, the possibility of precision thick film coating was demonstrated. But further study is indispensable to meet industrial needs such as in manufacturing cost as well as quality.

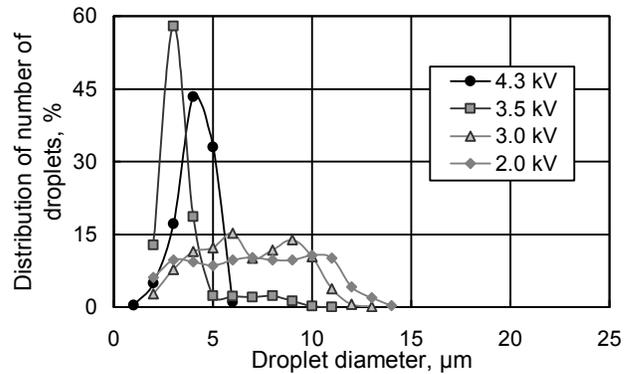


Figure 7 Droplet size distributions of dilute dispersion in jetting Mode 2. Gap=10 mm. Nozzle I.D./O.D.=100/170 μm.

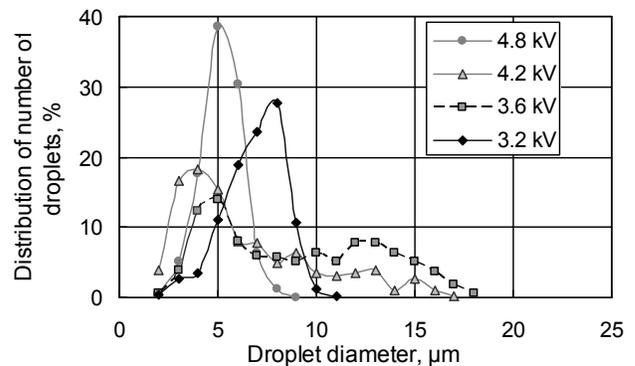
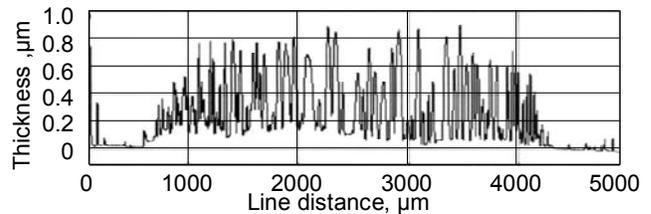
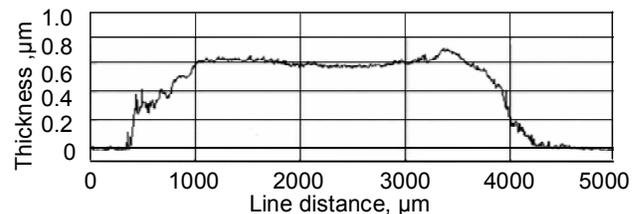


Figure 8 Droplet size distributions of CHN-base viscous solution. Gap=15 mm. Nozzle diameter=320/450 μm.



(a)



(b)

Figure 9 Cross section of line coatings. Gap=10 mm. Nozzle I.D./O.D.=100/170 μm. (a)Applied voltages 3.5kV, Scan speed 575 μm/s in., (b)Applied voltages 3.5kV, Scan speed 375 μm/s /s.

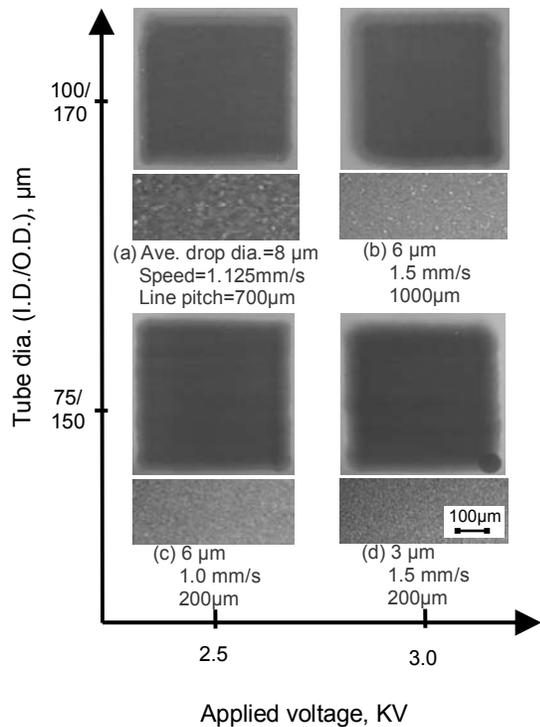


Figure 10 2D coating results. Gap=10 mm. Average drop diameter, stage speed and line pitch are described under each coating sample.

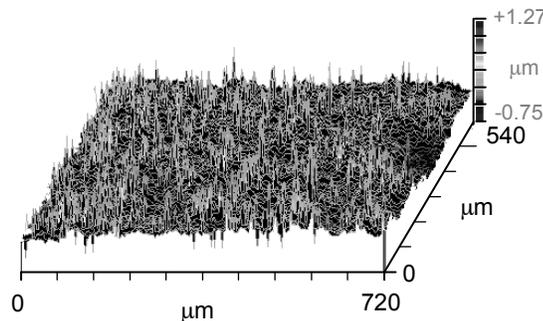


Figure 11 Surface profile of 2D coating. Applied voltage= 3.0kV. Gap=10 mm. Nozzle I.D./O.D.=100/170 μm.

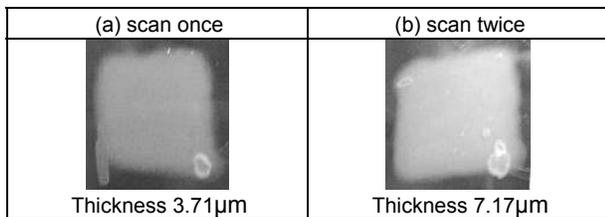


Figure 12 Examples of coated film with CHN-base viscous solution, (20 mm × 20 mm). Applied voltage=3.2 kV, Nozzle diameter=320/450 μm, Gap=15 mm, Stage speed=2.0 mm/s, Scan pitch=0.5 mm.

Concluding remarks

Ability of jetting fine droplets and viscous liquids and applying the spray state to coating by electrostatic inkjet were examined experimentally with two types of coating liquids. It was found that,

- ✓ cone-jet mode was preferable for stable jets,
- ✓ submicron quality coating was possible by drops-on-drops concept and
- ✓ possibility of relatively thick film coating was demonstrated by accumulating the viscous droplets.

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Author Biography

Kazuyuki Tada started his professional career as an engineer in 1990 following completion of a M.S. degree. Since then he has been working in a manufacturing engineering division. From 1997 to 1999 he had a chance to study coating science and technology in University of Minnesota where he received another M.S. degree. During the stay in Minnesota, he participated in Nip14 at the first time as an audience in Toronto, CANADA and returned to Nip24/DF2008 last year to make a presentation. Currently he enjoys double statuses of his career, a professional engineer and a doctoral-course student in Waseda University.