

Title: **Inkjet deposition of complex mixtures to textiles**

Project Number: C05-GT07

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Project Goal: The goal of the research is to develop fundamental understanding of the process of deposition of complex mixtures by the inkjet method. Specific objectives of the project are to: i) identify the effects of the solid-laden ink properties on drop formation in drop-on-demand (DOD) inkjet systems, ii) prescribe regions of reliable jetting behavior in DOD inkjet systems, iii) develop a model for prediction of the solid-laden ink properties on drop impaction and spread on rough and heterogeneous surfaces, including textile surfaces.

Abstract

In order to better understand the drop formation and post-impaction dynamics of pigment ink, various numbers of drop-on-demand inkjet drops were deposited on textiles, and the formation process was visualized using a high speed camera. A capillary rheometer has been designed, constructed and used to measure shear viscosity for shear rate ranging from 10^3 to 2×10^5 s^{-1} .

Introduction

Inkjet printing is already established as a useful technology to the textile industry. Not only is it important in textile printing, but also has potential for creating high-value textiles such as e-textiles. Broad utilization of this flexible method faces a number of barriers, springing from the requirement that "inks" in a growing number of textile applications contain solid particles which may serve as colorant or binder, but may also be ceramic or metallic particles in other applications. Based on prior study, we have identified and begun the process of surmounting technical hurdles in the technology, which come in two forms. The first is in the dynamics of drop formation and drop impaction of solids-laden inks. The second is the role of the surface morphology and surface chemistry encountered in textile materials. The proposed study will utilize this foundation to guide characterization of these processes at the very small-scale and high speed typical of application, and develop a model incorporating the material properties for deposition of complex mixtures by the inkjet method.

The NTC has funded research (C99-G08 and C02-GT07) by this team in imaging of drop formation and impingement. Under this funding, an experimental facility has been developed for imaging of drop formation and impingement for drops from 50-micron diameter up to the millimeter scale. Significant progress (Furbank et al. 2001, 2002, 2004a, and 2004b) has been made in understanding the effects of particles on drop formation in drip and continuous jetting of millimeter sized drops, laying a foundation for badly needed study of drop-on-demand (DOD) drop formation. Work has been initiated in DOD drop formation; however, much is left to be done to understand the effects of solid-laden ink properties on drop formation in DOD inkjet systems. Drop impaction studies have been conducted under this NTC funding. Also, the wetting behavior and the effects of chemical heterogeneous surfaces have been studied by one of the investigators (Leopoldes et al. 2003). The previous NTC research (Park et al. 2001, 2002, 2003a, and 2003b) was for pure-liquid, millimeter-sized drops impacting smooth surfaces as well as a rough, textile-like surface. It provided the needed background for ongoing research of the effect of particles on

the impaction process for millimeter-sized drops. The research has resulted in what are believed to be the first-ever refereed publications on the effects of particles on drop formation (Furbank et al. 2004) and impaction (Ok et al. 2004), and thus the team study is at the leading edge of understanding of key issues in the process. This work to date provides a basis for the recently initiated research investigating the effects of particles on the impaction process for application-scale, O(50 micron)-sized drops (see Figure 1). Since the dimensions are extremely small (50 micron drops, containing micron scale particles) and deformation times are short (~100 microseconds), research on micron-sized drops is difficult; however, the advanced experimental facility developed under this funding makes this study possible.

Understanding of the dynamics of DOD drop formation and micro-drop impaction on surfaces is important in the control of inkjet deposition. Since the dimensions are extremely small (50 micron drops, containing micron scale particles) and deformation times are short (~100 microseconds), research on micron drops is difficult; however, the advanced experimental facility developed under this funding makes this study possible. In our previous work, inkjet drop formation and impaction were investigated using a pure liquid. The results are given in detail in Dong et al. (2006a, 2006b, 2006c, 2007). We also investigated the effects of printing fabric structure, finishing and ink on line image quality (Park et al., 2006). Over the last year, work has been conducted to better understand impaction and post-impaction dynamics of pigmented inks jetted onto textile substrates and the role of particles in these processes. The drop impaction and spreading processes were visualized using a high speed camera (Wang et al. 2007; Wang 2008).

Experimental

Inks

CAB-O-JET® 200 (Cabot Corp.) is used to prepare carbon-black pigmented water-based inkjet inks. The pH and surface tension of the purchased inkjet ink preparation are 7.5 and 70.4 dynes/cm, respectively. The surface of the pigment is modified by covalently grafting $-\text{SO}_3\text{Na}^-$ group so that it can stabilize in water without adding any surfactants, dispersion aids or polymers. This ink preparation has about 20% w/w pigment (10.3 vol%, with pigment density of 1.95 g/ml), 0.2% w/w foaming agent, about 79.8% w/w water and a concentration of sodium of 4952 ppm/solids (4952 parts per million of carbon black). The particle size distribution (PSD) of the carbon black pigment is shown in Figure 1, and the mean particle size is 130 nm. Based on this ink preparation, various amounts of water and glycerin are added to adjust the apparent shear viscosity and particle volume fraction of the inkjet ink samples. Properties of three inkjet ink samples used in the study are given in Table I. Although the volume fraction of pigment varies significantly (0, 5.7 and 15.0 vol%), the low shear rate viscosity, surface tension, and density of the three samples are similar. The shear viscosity and surface tension were measured by using Brookfield Part No. LVDVI+ Couette viscometer at shear rate of 26.2 s^{-1} and KRUSS Bubble Pressure Tensiometer BP2 with a capillary diameter of 1.110 mm.

Table I: Three Inkjet Inks Used for Studying DOD Drop Formation

Ink	Pigment, vol%	Glycerin, vol%	Distilled water, vol%	Low shear-rate viscosity, cP	Surface tension (20 °C), mN/m	Density, g/ml
1	0	48.4	51.6	6.4	67.8	1.14
2	5.7	35.5	58.8	6.4	69.5	1.19
3	15.0	0	85.0	6.3	71.0	1.24

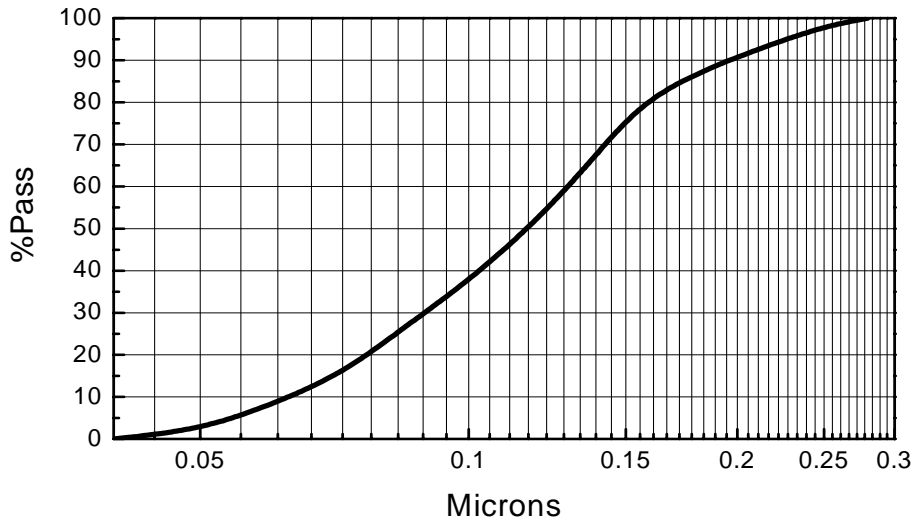


Figure 1. Particle size distribution (PSD) of CAB-O-JET® 200 ink preparation (measured by Leeds & Northrup Microtrac® UPA150 Particle Analyzer. Information provided by CABOT, Inc.)

Results

Final ink distribution on inkjet paper and textiles - Figure 2 shows a SEM picture of a 43- μm single DOD drop (41.6 picoliter, no satellite, Ink 2) deposited on inkjet paper and on cotton fabric. The circles in the middle of the pictures indicate the size of the DOD drop. The ink distributions on inkjet paper resembled an irregular circle with diameter approximately doubled that of the impacting drop. The ink distribution for the cotton fiber is not circular. The cotton fiber size is about $20 \pm 10 \mu\text{m}$ and the yarn size is about $200 \mu\text{m}$. Consequently, the size of the DOD drop is about the size of 2 to 3 fibers, including the gap between neighboring fibers, and the yarn size is about 4.7 times bigger than the ink drop. The distribution of the pigment on the surface of the fibers indicates the direction of spreading process. The impacting ink drops spread further along the fiber direction than in the transverse direction. The fibers acted as a barrier for transverse spreading. This observation agrees well with the phenomena discussed below for the cases of multi-drop impaction on fabrics.

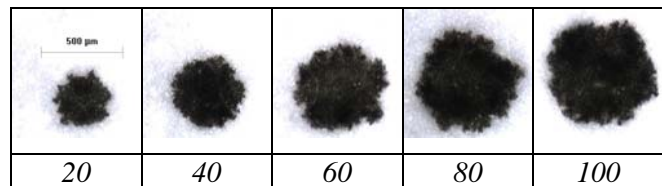
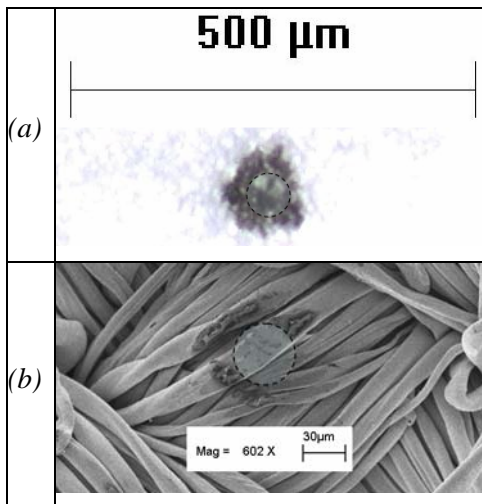


Figure 3. Varied amount of ink deposited on high quality inkjet paper. The number of drops deposited is shown below the image.

Figure 2 (left). (a) Optical microscope picture and (b) SEM picture of a single DOD drop of 43- μm diameter deposited on high quality inkjet paper (top) and cotton fabric (bottom). The dashed circles represent the size of a single drop.

Final ink distribution was studied varying the amount of Ink 3 deposited on cotton fabric and inkjet paper. The printing distance between the nozzle and the substrate was 0.3 cm so that primary drops and satellites were deposited on the same position. Figure 4 shows the dried patterns of 20, 60, 100 drops (approximately 1.1, 3.3, 5.5 nanoliters, including satellites) deposited on the cotton fabric. The jetting frequency was 1 kHz.

The final ink distributions on inkjet paper resembled irregular circles, with their size increasing as the number of drops increased. The final ink distribution on the cotton fabric was greatly affected by the fabric structure, that is, the yarn direction and intersections. The ink tended to stay on one yarn as drops accumulated until excess ink moved to neighboring yarns. As the number of drops increased, the change in the ink distribution on the cotton fabric was mainly the increasing distance over which the ink spread along the yarns.

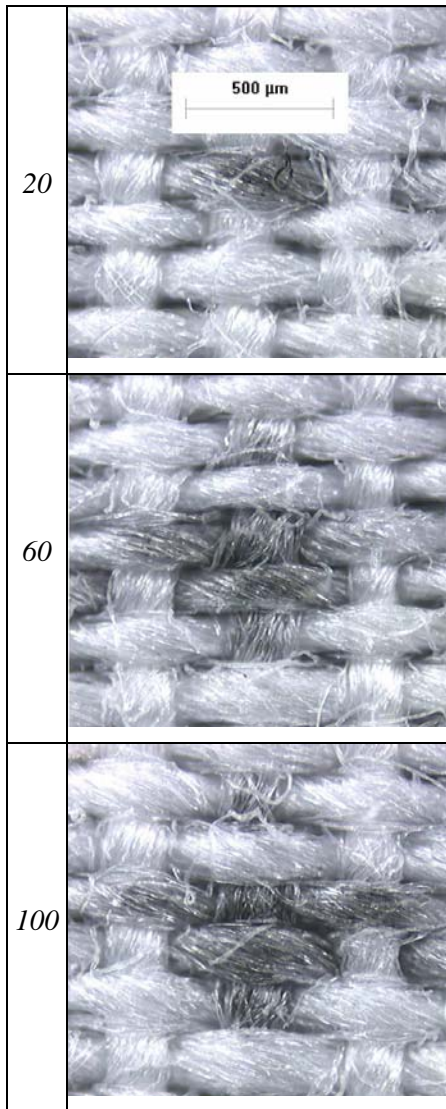


Figure 4. Varied amount of DOD drops deposited on the cotton fabric. The number of drops deposited is shown next to the image.

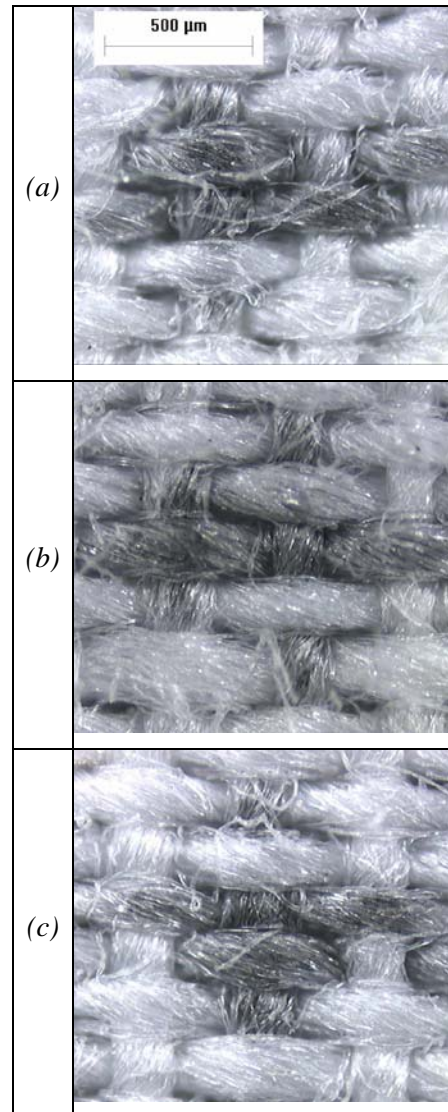


Figure 5. Three random chosen cases of 100 drops (including satellites) depositing on cotton fabric.

Figure 5 shows three randomly chosen pictures of 100 drops deposited onto the cotton fabric after drying. The distribution of ink depended on the impaction location on the fabric, and the patterns on the three fabrics were different. While the patterns were different, in all three cases, the movement of liquid was along yarns. Sometimes when yarns intersected, some of the ink moving along the yarn changed directions and moved along the intersecting yarn.

Shear Viscosity and Surface Tension - The viscosity of the samples measured using the capillary viscometer is shown in Figure 6. Although the three samples have almost the same shear viscosity (~ 6.4 cP) at low shear rates, at shear rate of $2 \times 10^5 \text{ s}^{-1}$, the shear viscosities of inks 2 and 3 are about 3.5 and 5.7 cP, respectively. The shear-thinning behavior observed for both inks 2 and 3 is attributed to the structure breakdown of agglomerates in the inkjet ink samples due to strong hydrodynamic motion.

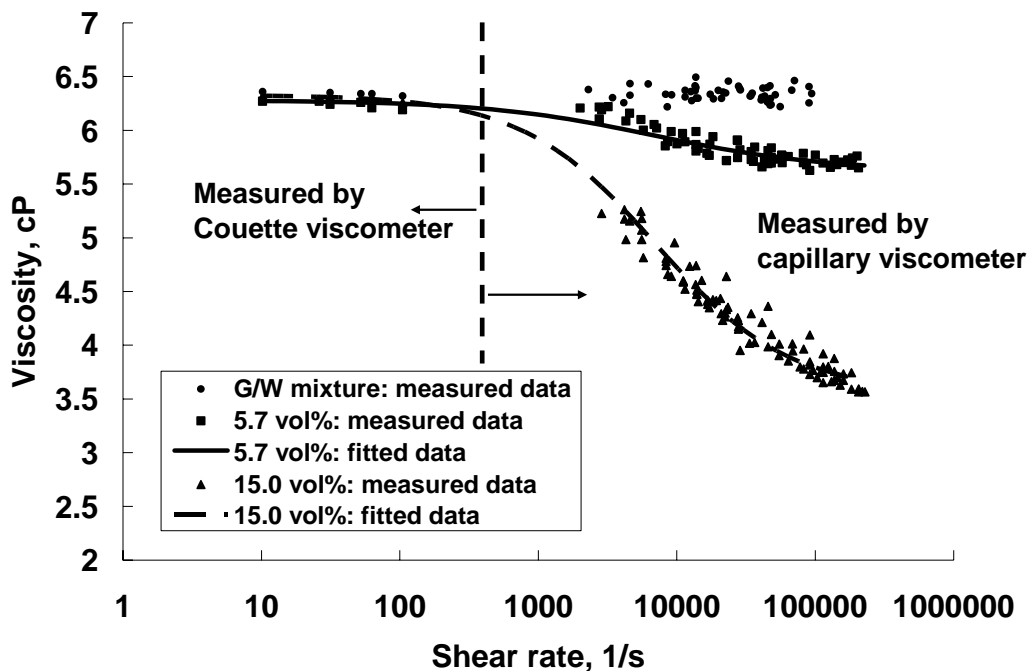


Figure 6. Shear viscosity measurement of inkjet ink samples as a function of shear rates at temperature of 22°C. Fitting curves are obtained with a generalized Cross equation. The fitting parameters, A and m , are 0.00204 and 0.699 for the ink sample with 5.7 vol% of pigment and 0.000346 and 0.900 for the ink sample with 15.0 vol% of pigment, respectively.

The results shown in Figure 6 reveal that surface-modified-carbon-black pigmented water-based inkjet inks exhibit a Newtonian behavior at low enough shear rates, a pseudo-plastic one in the middle shear rate range, and a second Newtonian plateau at very high shear rates. The transition from Newtonian to non-Newtonian behavior is associated with volume fraction of particles. At low shear rates, the shear viscosity for Inks 1, 2, and 3 is 6.4 cP, but as the shear rate reaches $2 \times 10^5 \text{ s}^{-1}$, the shear viscosity of Ink 3 drops to about 3.52 cP while the shear viscosity of Ink 1 change insignificantly. Our experimental results at other volume concentration inks also showed similar trend.

As the carbon black pigment particle used in this study is surface modified by covalently grafting functional groups on the surface of the pigment, the nature of the dispersion mechanism is electrostatic

and no polymeric dispersant or surfactant is used. For that reason, it is expected that for all three samples, dynamic surface tension will be similar to the static surface tension; however, an instrument for measuring dynamic surface tensions at high deformation rates was not available.

DOD Drop Formation - We have studied drop formation of a pure liquid using the imaging system, and based on the experimental results, have developed a fundamental understanding of the dynamics of DOD drop formation for pure liquids (Dong et al., 2006a, 2006b, 2006c, 2007). In this section, our discussion is focused on DOD drop formation of carbon black pigmented colloidal suspension (see Table 1).

In Figure 7, the ejection and stretching of the three inks are compared for two different driving voltages. At surface tension of 69 ± 2 mN/m, the first breakup occurred between 28-30 μ s after ejection, which is about the same as for Newtonian fluid with similar surface tension. The ejection process was very similar for the three inks.

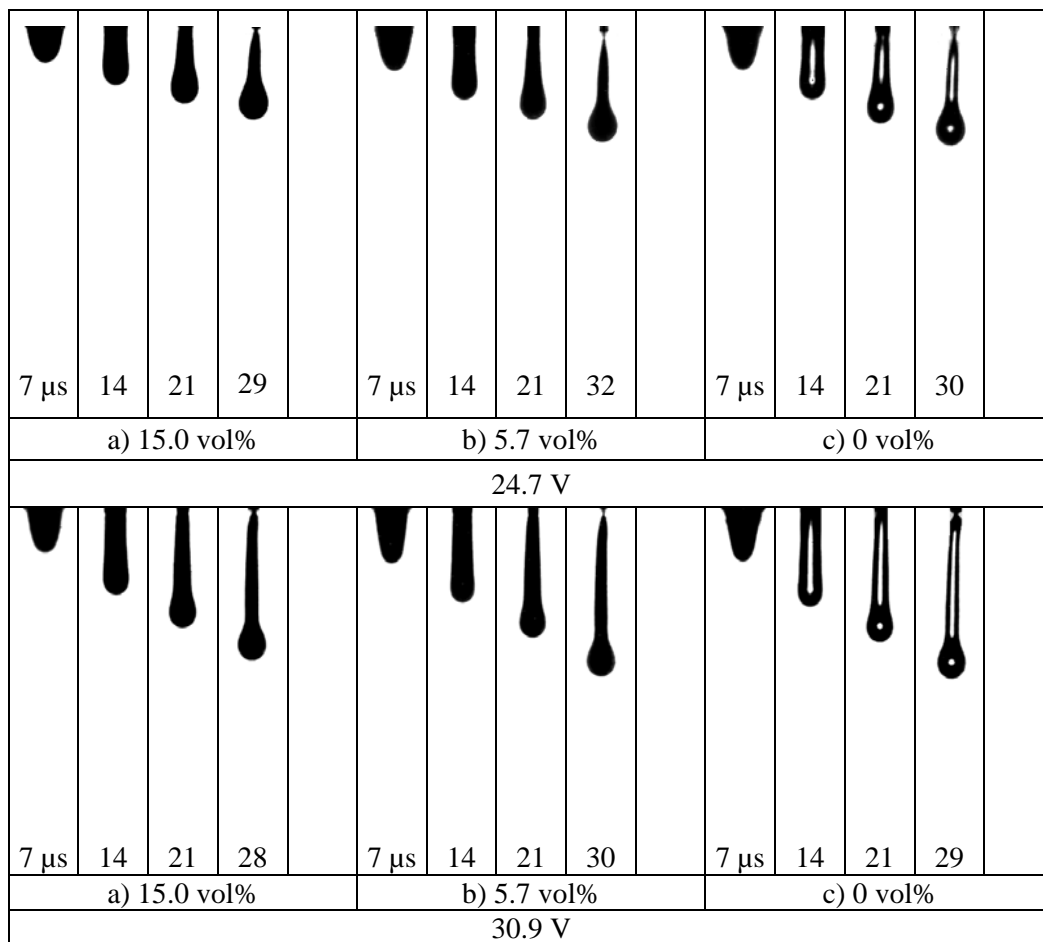
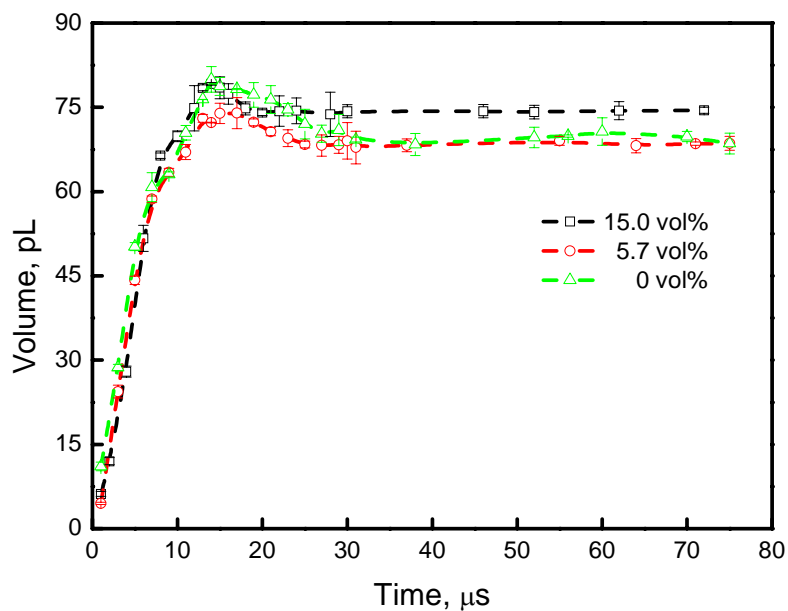
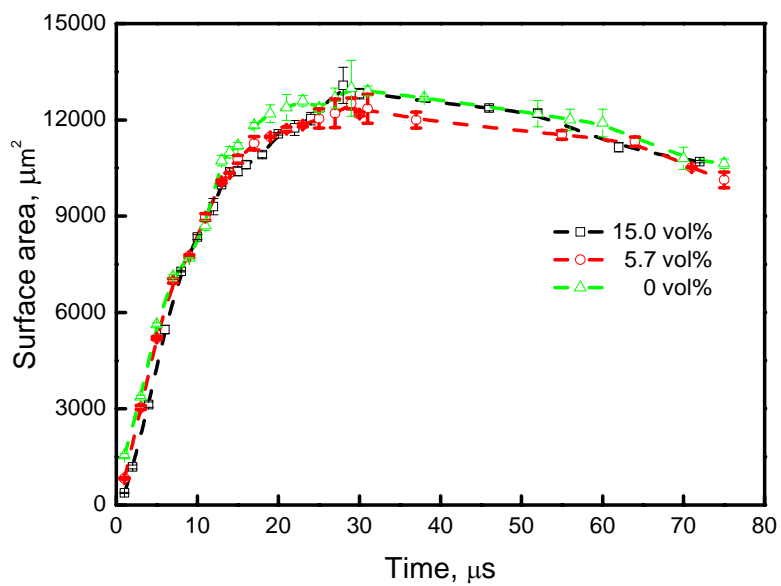


Figure 7. Comparisons of ejection and stretching of three inkjet ink samples (A double-peak waveform was used with voltage amplitude of 24.7 and 30.9 V and frequency of 10 kHz).



(a)



(b)

Figure 8. Volume and surface area of ejected liquid vs. time (The double peak waveform was used for three samples with voltage amplitudes of 30.9 V and frequency of 10 kHz. Marker “+” indicates the time of liquid separation from the nozzle exit. The error bar stands for one standard deviation).

In Figure 8, the volume and surface area of ejected liquid versus time are shown for the three inks. The curves for the three inks are very similar. These plots can be used to estimate the magnitude of shear rate versus time during the emergence of liquid ligament out from the inkjet nozzle before the liquid volume reached its maximum value. The shear rate is estimated using

$$\bar{\dot{\gamma}} \sim O\left(\frac{\bar{V}}{R_{noz}}\right) \sim O\left(\frac{S}{A_{noz} R_{noz}}\right) \quad (1)$$

where $\bar{\dot{\gamma}}$ is the scale of shear rate, \bar{V} is the averaged speed of liquid ligament being jetted out from the inkjet nozzle, S is the volumetric flow rate, A_{noz} is the cross-section area of the inkjet nozzle, and R_{noz} is the radius of the inkjet nozzle.

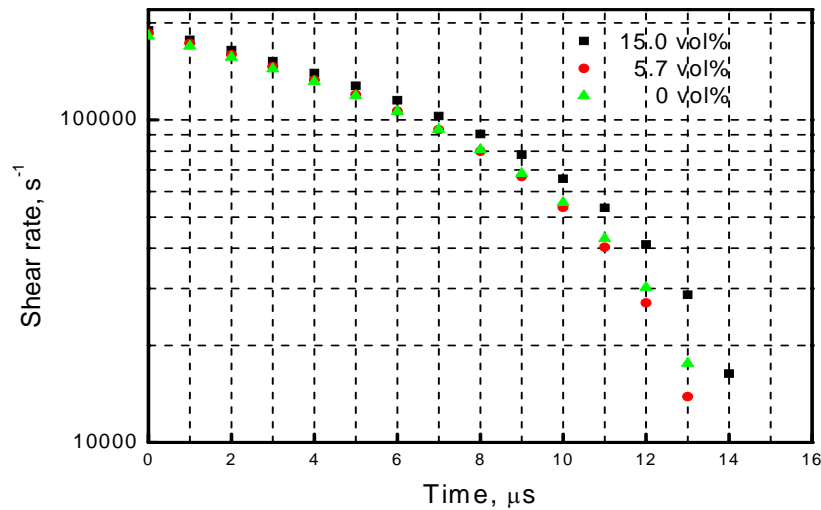


Figure 9. Estimated shear rate vs. time (based on Eq. 1 and the data shown in Figure 8(a) for three samples tested in Table 1 with voltage amplitudes of 30.9 V and frequency of 10 kHz).

Also, based on the data shown in Figure 8(b), the average rate of surface dilatational deformation, $\dot{\lambda}_{exp}$, can be estimated by using

$$\dot{\lambda}_{exp} \sim O\left(\frac{\Delta A}{A_{max}} \frac{1}{\Delta t}\right) \quad (2)$$

where A_{max} is the maximum surface area that the liquid ligament reached during the ejection process and is determined by using the peak values shown in Figure 8(b); ΔA is the difference between the maximum surface area and the minimum surface area A_{min} ; and Δt is the time taken for the surface area to reach to the maximum value. In our case, two difference values of A_{min} are used for calculating $\dot{\lambda}_{exp}$: one is the cross-section area of the inkjet nozzle or approximately the surface area of the nozzle meniscus before the ejection process, and the other is the surface area of a drop with liquid volume equivalent to the volume of the liquid ligament with the maximum surface area. Based on the first case, the estimated values for

$\dot{\lambda}_{\text{exp}}$ with voltage amplitudes of 24.7, 27.8, 30.9, and 36.5 V are about 25000, 28300, 29700, and 28500 s^{-1} , respectively; and based on the second case, estimated values are 6000, 10300, 12500, and 12100 s^{-1} , respectively.

DOD drop formation involves a very high shearing field with a similar scale of shearing rate to those experienced in the capillary viscometer where the inks demonstrated shear thinning behavior. However, DOD drop formation for all three inks was very similar, indicating that shear thinning behavior may not occur during drop formation. There are two major differences in DOD drop formation process and flow through a capillary. The time scale for the shearing in the DOD inkjet nozzle is much shorter than that in the capillary viscometer. Also the DOD ejection process is a transient process while the flow through the capillary is steady state. Although the inks used in our experiments apparently do not exhibit shear thinning behavior during DOD drop formation, other complex fluids may behave differently. Thus observation of drop behavior at the nozzle exit is necessary to determine if these liquids behave differently from Newtonian liquids with similar low shear viscosity and surface tension.

Web Site URL Address for C05-GT07: <http://www.tfe.gatech.edu/faculty/carr/ntcproject.htm>

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