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Effects of fluid properties and laser fluence on jet formation during laser direct writing of glycerol solution

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Laser-induced forward transfer (LIFT), a direct-write technique to deposit materials, has been widely studied to print various structures in microelectronics1 and tissue engineering2–6 using different electronic and biological materials. For example, by printing various kinds of living cells and biomolecules to mimic natural tissues, this bottom-up biofabrication approach has demonstrated its practical potential in numerous biomedical applications.7–9

Compared with other direct-write technologies such as orifice-based inkjet printing,10 which has inherent limitations such as nozzle clogging, LIFT and its variations have advantages in direct-writing viscous materials6 including its potential as an orifice-free printing technique. Biomaterial and biological patterns, ranging from biocompatible polymers, for example, polyethylene glycol (PEG) to complex living microorganisms, for example, eukaryotic cells9 also have been successfully deposited.11,12

The minimum feature size for LIFT is of great interest for microfabrication, and it is closely related to the jet and droplet formation process.13 Ideally, monodispersed droplets are desired during LIFT. As such, it is important to understand and further model the jet and droplet formation process and the droplet landing/spreading process under different LIFT operating conditions when different electronic or biological materials are used. This will allow better control of the resulting printing quality and feature resolution. The objective of this study is to understand the effects of fluid properties and laser fluence on the jet formation process during laser-assisted direct writing of glycerol solutions. The glycerol solution has been tested because of its relevance to biomedical applications.13

II. BACKGROUND

Jet/droplet formation is an important step during fluid jet-based direct writing or printing, which determines the pattern uniformity and spatial accuracy. During orifice-based direct writing, fluid jets are first ejected from an orifice and then broken into droplets with, or without, satellite droplets.14,15 The droplets that are generated combine to form various structures in a controllable manner. During laser-assisted orifice-free direct writing such as LIFT, the material transfer and deposition can be due to either ejected droplets16 or the contact between formed long, thin jet and the receiving substrate17 depending on the direct writing height and the material properties.

The jet formation mechanism in laser-assisted direct writing has been studied using time-resolved imaging analysis.18–21 Depending on the applied laser fluence, three distinct working regimes have been identified: sub-threshold (no material deposition), jetting (having well-defined jet formation), and plume (generating atomized droplets).13,16,19,22 The well-defined jet formation regime is generally desired for better direct writing. During this process, a bubble is first generated by absorbing the energy of the incident laser pulse, then a needlelike jet is formed as the bubble expands, and finally a long, thin jet is formed. In addition, some phenomena may accompany the formation of the well-defined jet; for example, the formation of a counter jet inside the ribbon coating,19 a bulgy structure due to the possible lateral collapse of jet,21 or droplets after jet breakup.23

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Jet morphology has been characterized in terms of the bubble size, \(^{23}\) jet diameter, \(^{19,21}\) and jet breakup. \(^{21,23}\) Specifically, the effects of laser fluence on the jet morphology and jet velocity have been studied, \(^{16,19,21,24}\) and the jet and plume velocities were found to increase with the laser fluence. \(^{16,19}\) In addition, the jet formation process has been evaluated under various operating conditions such as the sacrificial layer thickness, \(^{25}\) ribbon coating thickness, \(^{25}\) direct writing height, \(^{18,26}\) and laser beam dimensions. \(^{23,27}\)

However, the investigation about the effects of fluid properties as well as the combined effects of laser fluence and fluid properties on the jet formation process is still largely elusive. In this study, time resolved imaging analysis has been applied to investigate the individual and combined effects of fluid properties and laser fluence on the jet formation process to have a comprehensive understanding of the LIFT technology.

III. EXPERIMENTAL SETUP AND MATERIALS

Matrix-assisted pulsed-laser evaporation direct-write (MAPLE DW), a type of modified LIFT technique, is of interest in the study of jet formation during laser-assisted direct writing. In this study, glycerol-water solution is transferred using MAPLE DW. As shown in Fig. 1, the ultraviolet laser pulse is focused perpendicularly through the backside of a ribbon that consists of an optically transparent quartz disk with a coated thin film, known as the ribbon coating. The ribbon coating is locally heated and sublimed by the incident laser pulse, generating a small vapor pocket/bubble at the interface between the ribbon coating and the quartz support. Because of rapid localized heating, the resulting bubble expands rapidly. The expansion of the bubble then helps eject the coating material beneath away from the ribbon onto the receiving substrate. \(^{13}\)

The MAPLE DW setup herein included an ArF excimer laser (Coherent ExciStar, 193 nm, 12 ns full-width half-maximum) with a laser spot size of 150 \(\mu\)m in diameter and a repetition rate of 2 Hz. A quartz optical flat disk (Edmund optics, Barrington, NJ) with 85% transmittance for 193 nm wavelength beams was used to make the ribbon, which was attached to a specially designed fixture. The levels of applied laser energy were 0.15, 0.20, 0.25, and 0.30 mJ, and the actual laser fluence during direct writing was determined based on the averaged measurements using a FieldMax laser power/energy meter (Coherent, Santa Clara, CA). The measured laser fluence level varied slightly every time under the same operating conditions due to the laser output instability. The laser fluences measured after 15% loss due to the quartz disk were 717 \(\pm\) 45, 957 \(\pm\) 35, 1183 \(\pm\) 67, and 1433 \(\pm\) 77 mJ/cm\(^2\).

The jet formation process and jet velocity were monitored and estimated using the JetXpert imaging system (ImageXpert Inc., Nashua, NH). The light strobe was triggered by the control pulse from the laser, and a single image frame was acquired for each laser pulse using an integration time of 2 \(\mu\)s. The system was set up at the grazing incidence with respect to the coating surface without the receiving substrate in the camera scope. Fifty laser pulses were emitted each time for a given laser fluence and glycerol concentration combination. The jet formation process was captured by the imaging system one frame per second, triggered by the output control signal of the laser, and a single image frame was acquired for each laser pulse as in other studies. \(^{19,21,23,28}\)

The jet velocity was estimated based on the spatial position difference of jet front of two sequential imaging frames of the jetting process.

Glycerol (Acros Organics, Fair Lawn, NJ, 99% pure) and de-ionized water were used to make the glycerol-water solution with different glycerol concentrations (v/v): 15%, 25%, 35%, 50%, 65%, 75%, 85%, and 99%. The matrix was prepared at a thickness of 100 \(\mu\)m by blade coating 15 \(\mu\)l glycerol-water solution onto a 1.5 cm (length) \(\times\) 1 cm (width) \(\times\) 100 \(\mu\)m (depth) plastic frame on the quartz disk.

IV. EFFECTS OF FLUID PROPERTIES ON JET FORMATION

Time-resolved imaging analysis was performed in this study to obtain a better understanding of the material transfer process during MAPLE DW. Several events occur during a typical MAPLE DW process: bubble formation, jet formation/breakup, and jet/droplet landing. During the direct-write process, the energy of the incident laser pulse is absorbed by the glycerol solution-based ribbon coating, producing a high pressure and high temperature bubble that forms and further expands within the coating due to sublimation. \(^{13,29}\) Well-defined jets only form under certain operating conditions for
a given glycerol solution. In particular, the jet formation process can be classified into four different scenarios depending on the laser fluence and the glycerol concentration: splashing (Fig. 2), jetting with bulgy shape (Figs. 3(a) and 3(b)), well-defined jetting (Figs. 3(c) and 3(d)), and no material transferred (Fig. 3(e)) as the glycerol concentration varied from 15% to 99% under a laser fluence of 717 ± 45 mJ/cm².

The background of these figures is composed of two different regions: the top portion corresponds to the ribbon and its coating and the lower part the free space or ambient environment. There were some reflections of jetting phenomena on the ribbon, which acted as a mirror during imaging. The phenomena observed herein when the concentration changed are consistent with others reported or discussed when operating conditions varied during laser direct writing.

A. Typical jetting regimes

As aforementioned, four different jetting regimes have been observed in direct writing of glycerol solutions. Under the laser fluence of 717 ± 45 mJ/cm², splashing happened with the 15%, 25%, and 35% glycerol-water solutions as shown in Fig. 2. Fig. 4 further illustrates a time-resolved study of jet formation of 15% glycerol solution under laser fluence of 1433 ± 77 mJ/cm². The following discussion regarding the jetting regimes is based on the 717 ± 45 mJ/cm² laser fluence condition.

It can be seen that well-defined jets were difficult to form using the less viscous 15%, 25%, and 35% solutions.
under these investigated conditions. For the 15% and 25% solutions, splashing dominated the process, and burst of bubbles were visible at the ribbon coating. Since the 35% solution has a higher viscosity and a higher viscous damping force, it had a mixed appearance: splashing with bulgy shapes.

When the concentration was 50% or 65%, a jet formed but with a bulgy shape (Figs. 3(c) and 3(d)). Upon the expansion of laser-induced bubble, a protrusion first generated and elongated to form a long jet. Then bulge(s) formed around the forming main jet and further elongated out as little subjets. Finally, the main jet broke up with some residual protrusion materials remained and retracted to be part of the ribbon coating. The bulge appeared later when the concentration increased. The bulgy shape was most pronounced using the 50% glycerol solution, but not so observable with glycerol solutions having concentration lower than 50% or higher than 65%.

Well-defined jets were formed using the 75% and 85% solutions as shown in Figs. 3(c) and 3(d). Such a jet lasted longer when the concentration was higher. There was no material transferred using the 99% solution, and part of the ribbon coating protruded out but finally recoiled back without any fluid jetting. The recoiling process was slower for such a highly viscous solution, and the entire process lasted more than 100 µs.

As seen from Fig. 3, the temporally averaged jet velocity decreased as 122.2, 118.1, 93.4, 83.0, and 77.4 m/s when the glycerol concentration increased as 50%, 65%, 75%, 85%, and 99%, correspondingly. Intuitively, the jet formation process mainly is the result of two competing effects: the inertia effect to form and elongate the jet and the viscous damping effect to slow down the forming jet and dissipate the jetting energy. As such, the higher the viscosity, the lower the jet velocity.

B. Jetting regime as functions of fluid properties and laser fluence

Jetting during MAPLE DW is the result of the formation of laser-induced vapor/plasma bubble inside the ribbon coating. As the absorbed laser energy raises the solution temperature in the laser focal volume above the boiling temperature, the heated fluidic coating material undergoes a metastable superheated state. Any slight perturbation in coating density may lead to the initiation of vapor nuclei in the superheated liquid, known as homogeneous nucleation; once vapor bubbles reach a critical size, their further growth is spontaneous and the superheated volume may explode, leading to phase explosion, a form of rapid evaporation. When the internal bubble pressure reaches a balance with that due to the ambient pressure and the surface tension, the bubble has its largest size. As the bubble continues to grow, the internal bubble pressure becomes lower than that due to the ambient environment and surface tension. Then it shrinks and eventually collapses.

In this study, it is considered that the laser pulse-induced phase explosion contributes most to the generation of sublimation pressure, which ruptures the coating material beneath to form a jet or jets. It should be pointed out that laser pulse-induced thermoelastic stress might also contribute to the jet formation in addition to phase explosion. The aforementioned scenario is also applicable to the sacrificial layer-assisted LIFT process, during which the bubble is induced by the expansion of a vapor or plasma resulting from the ablation of sacrificial film.

The effect of glycerol concentration is summarized in Fig. 5, and some images are chosen to illustrate the different regimes under a laser fluence of 717 ± 45 mJ/cm². For the highest concentration solution (99%), the bubble pressure is not high enough to overcome the effect due to the ambient pressure and the surface tension, so no material is transferred. For the 85% and 75% solutions, a well-defined jet forms. The expanding bubble collapses outwards the coating instead of shrinking or collapsing inwards the coating. For the 65% and 50% solutions, a jet may form but with bulge(s) around it. As the laser-induced bubble expands, a high-pressure area forms between the bubble and the free surface. The formation of bulges is attributed to the collision of the liquid flows around the ablation spot and/or the breakup of the main bubble when vapor bubble collapses inwards and/or bursts outwards the coating. This phenomenon is analogous to the evolution of cavitation bubble during ablation in liquid. For the 35%, 25% and 15% solutions, splashing and bubble bursting clearly reveal the effect of highly pressurized bubble, which bursts outwards the coating and even may atomize the coating being transferred.

The effect of laser fluence on the jet formation has also been studied herein, and similar phenomena have been observed as previously reported. Fig. 6 shows some
representative jetting regimes during MAPLE DW using a 65% glycerol solution. Four jet formation regimes were also observed: no material transferred, well-defined jetting, jetting with bulgy shape, and splashing as the applied laser fluence increased. The laser fluence determines the jet kinetic energy, and higher laser fluences result in a higher jet/droplet velocity.\textsuperscript{16,19,28} The glycerol concentration affects the viscous dissipation energy and the capillary force. When the jet kinetic energy is higher than that due to viscous dissipation, a jet forms; when the surface tension effect dominates and leads to the Rayleigh instability, the jet breaks up, forming flying droplet(s).

Under laser fluences lower than of $717 \pm 45 \text{ mJ/cm}^2$ such as $478 \pm 45 \text{ mJ/cm}^2$, no material was transferred, and the bubble pressure did not exceed the pressure due to the surface tension of ribbon coating and the ambient environment. This is a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5}
\caption{Jetting regimes during MAPLE DW with different glycerol concentrations (laser fluence = $717 \pm 45 \text{ mJ/cm}^2$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6}
\caption{Jetting regimes during MAPLE DW under different laser fluences (65% glycerol solution).}
\end{figure}
similar scenario as shown in Fig. 3(e). Under a laser fluence of 717 ± 45 mJ/cm², well-defined jet formed as shown in Figs. 3(c) and 3(d). Under laser fluences of 957 ± 35 and 1183 ± 67 mJ/cm², the forming jet turned bulgy and curved as seen in Figs. 3(a) and 3(b). The higher the laser fluence, the more the coating material being transferred, resulting in a larger but less stable jet. When the applied laser fluence was even higher such as 1433 ± 77 mJ/cm², splashing occurred instead of a jet, similar to those shown in Fig. 2. It should be noted that the laser fluence level for different jetting regimes varies as the coating solution changes.

In summary, jetting dynamics is a function of fluid properties such as the glycerol concentration and operating conditions such as the laser fluence. If the laser fluence is too low and/or the glycerol concentration is too high, it is less likely for a bubble to totally form and/or grow before it diminishes.30 There is no enough kinetic energy provided by the expanding bubble. Even when a jet can be formed, it retracts back after the bubble diminishes. If the laser fluence is too high and/or the glycerol concentration is too low, it is also difficult to form a well-developed jet since dramatic bubble expansion may lead to a bulgy shape7 and even splashing.13,21,30 Only under some selected conditions of glycerol concentration and laser fluence as aforementioned, can a well-defined jet form.

C. Jettability in laser printing

The droplet formation process on the printing quality has been of great research interest during drop-wise manufacturing, especially in terms of the printability37 and the droplet formability15,38 during orifice-based inkjetting. Of different non-dimensional numbers used to quantify the process dynamics during the jet and/or droplet formation process, the Ohnesorge number (Oh) provides a convenient way of capturing the relative magnitudes of inertial, viscous, and capillary effects for such free-surface fluid mechanics problems.30 Generally, the Ohnesorge number can be determined as follows:

$$\text{Oh} = \frac{\mu}{\sqrt{\rho \sigma l}}$$  \hspace{1cm} (1)

where \(\mu\), \(\rho\), and \(\sigma\) are the fluid viscosity, density, and surface tension, and \(l\) is the characteristic length which is taken as the laser spot diameter (150 \(\mu\)m in this study). As seen from Eq. (1), the Ohnesorge number only depends on the thermophysical properties (viscosity, density, and surface tension) of fluid and the laser spot size.

As discussed, a good jet only forms under certain combinations of fluid properties and operating conditions. For given operating conditions such as the laser fluence in this study, a new non-dimensional \(J\) number, defined as the inverse of the Ohnesorge number, is proposed to evaluate the jettability during laser printing

$$J = \frac{1}{\text{Oh}}$$ \hspace{1cm} (2)

It is noted that the inverse of the Ohnesorge number has also been proposed as a non-dimensional \(Z\) number to quantify the fluid printability during inkjetting under a certain excitation voltage, and the printability was evaluated based on the single droplet formability, minimum stand-off distance, positional accuracy, and maximum allowable jetting frequency.37 Alternatively, \(J\) can be also interpreted as the ratio between the viscous diffusion time scale \(t_v\) and the Rayleigh time scale \(t_r\), which are defined, respectively, as follows:

$$J = \frac{t_v}{t_r}$$ \hspace{1cm} (3)

where \(t_v = \frac{\rho l^2}{\mu}\) and \(t_r = \left(\frac{\mu}{\sigma}\right)^{1/2}\). Figure 7 illustrates the relationships among \(J\), the viscous diffusion and Rayleigh (capillary) time scales, and the glycerol concentration under a laser fluence of 717 ± 45 mJ/cm². As the glycerol concentration increases, the viscosity increases significantly while there are negligible variations with the density and surface tension,13 resulting in a decreasing \(J\). Due to the same reason, the viscous diffusion time scale increases significantly while the Rayleigh time scale almost stays the same as the glycerol concentration decreases. As seen from Fig. 7, no materials are transferred if the Rayleigh time is longer than the viscous diffusion time scale. Once the viscous diffusion time scale is longer than the Rayleigh time scale with a 85% glycerol solution, good jet forms; if the glycerol concentration further decreases, splashing may happen. The \(J\) values for 15%, 25%, 35%, 50%, 65%, 75%, 85%, and 99% solutions are 70.46, 48.54, 32.07, 14.61, 5.87, 2.49, 0.86, and 0.13, respectively, and the \(J\) value decreases almost exponentially with the glycerol concentration. It is observed that a good jet forms at 0.86 ≤ \(J\) ≤ 2.49 (corresponding from 75% to 85%) in this study under the laser fluence of 717 ± 45 mJ/cm².

It should be noted that the jettability range varies as the laser fluence changes, which means the change of external forcing dynamics such as the jet velocity. Fig. 8 illustrates different jetting regimes (no materials transferred, good jet forming, and splashing/bulgy) delineated using dashed lines based on the experimental observations in this study as the laser fluence varies. Fig. 8(a) is based on the jettability number, \(J\), while Fig. 8(a) is based on the glycerol concentration. The
can be formed, it retracts back after the bubble diminishes. If the laser fluence is too high and/or the glycerol concentration is too low, it is also difficult to form a well-developed jet since dramatic bubble expansion may lead to a bulgy shape and even splashing. Only under some selected conditions of glycerol concentration and laser fluence, can a well-defined jet form. When a jetting fluid is given, its jettability \((J)\) can be characterized as the inverse of Ohnesorge number. It is observed that a good jet forms at \(0.86 \leq J \leq 2.49\) in this study under the laser fluence of \(717 \pm 45 \text{ mJ/cm}^2\). To better appreciate the jettability, a phase diagram is expected by considering the contributions from both the material properties and the operating conditions in future studies.

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