Droplet Formation and Settlement of Phase-Change Ink in High Resolution Electrohydrodynamic (EHD) 3D Printing

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Abstract

This paper presents a modeling framework to model the droplet formation and settlement on substrate of phase-change ink in high resolution electrohydrodynamic (EHD) printing process, which can successfully produce sub 10- μm droplet footprints and 3D microstructure. We have used Finite Element Analysis (FEA) to develop the model for droplet formation and droplet settlement. Two important competitive forces in EHD printing, electrostatic force and surface tension force, are modeled by FEA. The droplet size is obtained by balancing the electrostatic force and surface tension of the pending droplets at the tip of the meniscus under different printing conditions. With the results from FEA analysis about the charge on a droplet and electrostatic field distribution, the droplets in-flight velocity and impact velocity on the substrate are derived numerically. With the derived impact velocity, the droplet spreading and settlement on the substrate is also modeled by FEA. The results from FEA models are compared with the experimental measured droplet dimensions at different process conditions to validate the developed model, which demonstrate very good agreement between the experimental results and model prediction. We have successfully applied EHD printing process for phase-change wax material, which is widely used in 3D printing or additive manufacturing for supporting and model material, to achieve high resolution sub 10- μm 3D structures.

Keywords: Electrohydrodynamic printing, FEA modeling, 3D printing, Phase-Change Ink

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1 Introduction

Additive manufacturing (Beaman 1997, Gibson 2009, Huttmacher 2004, Kruth 1998, Melchels 2011) is capable of rapid prototyping and small volume part production, which have been applied in many applications (e.g. aerospace, automotive, medic device, electric device). Traditional additive manufacturing including stereolithography, selective laser sintering, electron beam melting, 3D printing, and fused deposition modeling (Gibson 2009, Kruth 1998), have their best resolution no

better than 50 μ m. The limitations of traditional additive manufacturing processes are intrinsic and very difficult to be improved. For example, in laser or electron beam melting based processes, the fabrication resolution is limited by many factors, including beam spot size, thermal diffusion, and power size. For printing or extrusion based processes, the resolution is primarily limited by the size of the printing nozzle. Scaling down the nozzle size will require impractically high extrusion pressure for most liquid phase inks, since extrusion pressure scales up much faster when the nozzle diameter is decreased.

High-resolution additive manufacturing is important for many engineering applications. Bad part accuracy and surface finish significantly limit the application of current additive manufacturing processes in the production of high precision industrial parts. A high resolution 3D printing process with micron-scale accuracy and high quality surface finish can effectively reduce the time and cost in post-processing. High precision industrial parts need high precision micro-scale part with high surface finishing as to reduce the complexity of post-processing. In tissue engineering scaffolds, structure with micro-scale size similar with cells has many advanced functions to regulate cell responses to the scaffold (Tan 2002, Wang 2012). Given the resolution limitation of the existing additive processes, new printing methods need to be developed to meet the high-resolution requirements for additive manufacturing.

Electrohydrodynamic (EHD) printing (Mishra 2010, Park 2007, Poellmann 2011) is a high resolution printing approach, in which the ink is subjected to electrostatic field to form a Taylor-cone and produce a fine jet or droplet from the cone. Since the produced jet/droplet diameter is significantly smaller than the nozzle size, EHD printing can overcome the resolution limitation from the nozzle size in traditional 3D printing. Currently, most of the EHD printing applications focus on the 2D pattern with only some initial investigation in 3D structure fabrication (Wei 2013, Wei 2014). Drop-on-demand EHD printing with using phase change ink would provide a promising process for micro-scale 3D structure fabrication. To achieve reliable process control and planning, it is very important to understand the mechanism of the EHD printing process and developing a reliable process model. However, it is still very challenging to predict the droplet formation (Collins 2008, Collins 2013) and droplet size for EHD printing at different process conditions. Computational modeling can provide promising result on droplet formation in electrospray (Collins 2008, Collins 2013, López-Herrera 2011, Forbes 2010), but due to the complex coupled physics (electrostatic force, fluid dynamics, and singularity from droplet pinch-off) of EHD printing, so far, there is no commercially available numerical solver that can be successfully applied to EHD drop-on-demand printing. Some groups (Collins 2008, Collins 2013, López-Herrera 2011, Forbes 2010) have developed their own solver to study some sub-set problem in EHD printing process with lots of computational load. Few of them have constructed a highly simplified model just to provide the insight of this process from engineering perspective (Han 2014, Kim 2010, Lee 2013, Wei 2014).

In this work, we have applied EHD printing for phase-change ink (wax) for micro-scale 3D printing of sub-10 micron structures. The droplet formation, size, droplet impact and settlement on the substrate in EHD printing is modeled by Finite Element Analysis (FEA) with respect to different process conditions. The model for the overall printing process is divided into two sub-models. First, FEA is used to develop the model for droplet formation and in-flight speed before impact substrate. Two important forces in EHD printing, electrostatic force and surface tension force, are modeled by FEA. The droplet size is obtained by balancing these two competing forces on the pending droplets at the meniscus tip for different printing conditions. After calculating the overall charge on a droplet and electrostatic field distribution between the nozzle and substrate from FEA analysis, the droplets in-flight velocity and impact velocity on the substrate are derived numerically. Then, using the derived impact velocity, the droplet spreading and settlement on the substrate is modeled by ANSYS Fluent. The results from FEA models are compared with the experimental measured droplet dimensions to validate the developed model, which demonstrate very good agreement between the experimental results and model prediction. We have successfully applied EHD printing process for phase-change

wax material, which is widely used in 3D printing or additive manufacturing for supporting and model material, to achieve high resolution sub 10- μm 3D structures.

2 Electrohydrodynamic Printing System and Process

The material used in this EHD printing process is wax (as a phase-change ink) with a melting point of $\sim 55^\circ\text{C}$, which will be solidified quickly once it is printed onto the substrate. Our printing system consists four parts: a three-axis (XYZ) precision stage, a thermal control system, a high voltage supply, and a pneumatic dispensing system, which are shown in figure 1. The motion stage is installed on a vibration isolated table. Three linear stages are configured in XYZ directions and are used to move the printing head to the programmed locations. A high-resolution camera is used to monitor and record the printing process. The pneumatic dispensing system

Figure 1: Schematic of the EHD printing system.

provides backpressure to the nozzle for control the liquid material flow rate. The syringe temperature is set to 110°C for melting wax and reduces wax surface tension and viscosity. The nozzle with 50 μm orifice and 150 outer-diameter is used in the EHD printing processes. The gap between nozzle and the substrate is chose about 130 μm , which gives the best performance for the printing processes. A function generator (Agilent 33220A) was used to generate the voltage command, which was then amplified by a voltage amplifier (Trek 610A) to be used for EHD-jet printing. The printed patterns and 3D structures are characterized by using optical microscope and SEM.

In EHD-jet printing, a large voltage is applied between the nozzle tip and substrate, which causes mobile ions in the printed ink (melted wax in this study) to gather near the surface at the nozzle tip. The electrostatic force deforms the meniscus at the nozzle end into a conical shape (i.e., Taylor cone). With large enough electric field, the electrostatic force from surface charge repulsion at the cone apex exceeds the surface tension of the meniscus, and a droplet or a jet of ink is printed from the Taylor cone onto the grounded substrate. The fluid properties of the printing material, along with the process conditions, mostly the applied voltage determines the plotting results.

In our experiment, for melted wax in EHD printing, as we gradually increased the voltage, a meniscus and Taylor cone was gradually forming at the tip of the nozzle (Figure 2(a)). When the applied voltage is large enough (around 700v to 750v), micro droplets were ejected from the Taylor cone and printed onto the substrate. When the voltage is too large, satellite droplets are printed, indicating unstable printing condition. From Figure 2, clearly

increasing the voltage will decrease droplet size from 17 μm to 8 μm and increase ejection/printing frequency from 5Hz to 19Hz, which can be easily explained by the mechanism of EHD printing. A

Figure 2: (a) Pulsating mode of EHD printing of wax. (b) Droplet size and printing frequency at positive voltages (Droplet sizes from top to bottom: 17 μm , 14 μm , 11 μm , 8 μm)

higher voltage or electrical field strength will increase surface charge density at the Taylor cone. As a result, droplets with smaller volume can obtain large enough electrostatic force to overcome surface tension to be ejected from the cone tip. The high electric field also increases the charge migration rate. As a result, it takes less time to accumulate enough charge at the apex to initiate ejection, which increases the printing frequency.

3 EHD Printing of 3D Microstructures

We have successfully fabricated high aspect of ratio micro-scale 3D structures using EHD printing process with phase-changed ink. The 3D micro-structures were drop-on-demand printed layer by layer, following the programmed sequence. Due to the micro-scale size of the droplets, the ejected melted wax droplets solidify quickly after printed onto the substrate, thus enables layered manufacturing of 3D structures, as shown in Figure 3. Complex continuous 3D structures can be printed by coordinating the ejection speed and plotting speed to achieve the required overlap between the neighboring droplets. With proper overlap between droplets, continuous features can be fabricated with very smooth edge. Repeating the printing sequences layer by layer, 3D structures can be printed directly with good surface finish. Figure 3 (a) and (b) demonstrate the 3D structures of a circular tube. The height of those structures is about 40 μm to 60 μm , with a wall thickness of $\sim 6 \mu\text{m}$. This printing resolution is one or two magnitude better than the capability of traditional 3D printing. High aspects of ratio pillars are directly printed with a diameter similar to the each single droplet diameter. Droplet will printed on top of the previous droplet once the nozzle is fixed at a certain location. Figure 3(c) (d) shows an EHD printed pillar. The diameter of pillars are $\sim 15 \mu\text{m}$, and the maximum height of those pillars can reach to $\sim 100 \mu\text{m}$, which will give an aspect of ratio of ~ 7 .

Currently the structure height of our EHD 3D printing configuration is limited by the distance between nozzle and substrate. In our printing system, the ground electrode is located under the substrate. When the printed structures are close to the nozzle, the electric field is distorted, which cause unstable printing with uncontrollable printing speed and droplet diameter. However, this height

Figure 3: Micro-structures printed from EHD printing process.(a,b) circular tube with thin walls. (c) Close view of a single pillar. (d) Micro-pillar array matrix.

limitation can be solved by using new printing head design that integrate ground electrode into the printing head.

4 Modeling of Electrohydrodynamic Printing Process

Modeling the EHD-jet printing process is essential for process control. It is valuable to predict the droplet dimension at different system configurations and process conditions for planning the printing sequences. Due to highly complex and coupled physics of the EHD printing process, it is extremely difficult to obtain the analytical solution to describe the EHD printing behaviors. In this paper, instead of studying the complex coupled electrical and fluidic behavior together, we separated the printing process into two stages and developed their models individually. The first stage is droplet formation and in-flight to substrate under electrostatic force, in which two important forces (electrostatic force, and surface tension force) in EHD printing are modeled by FEA using ANSYS APDL. The second stage is the droplet impact and settlement on the substrate, which is modeled by ANSYS Fluent.

Figure 4: Schematic configuration for FEA modeling of the electrostatic force on the droplets. b) Electrical field distribution around the nozzle tip during droplet ejection.

4.1 Modeling for Droplet Formation and In-Flight Velocity

To model the droplet formation, we assumed a hemispherical meniscus forms at the end of the nozzle tip, and the diameter of the hemispherical meniscus is same to the diameter of the nozzle tip. The scheme for FEA model is shown in Figure 4 (a). The EHD printing process depends on two competing forces, the electrostatic Coulombic force, and surface tension force. When the electrostatic Coulombic force exceeds the surface tension force, a droplet is ejected from the meniscus. In FEA analysis, we study a state that the pending droplet at the meniscus apex has a hemisphere shape. In this state, the droplet with the fixed diameter has the largest surface tension force, and will be ejected from the meniscus if the electrostatic force acting on the droplet surface is larger than the surface tension force.

Using the configuration in Figure 4, with FEA analysis, we can calculate the electrostatic force acting on the half-ejected droplet surface at different process conditions, such as voltage, droplet diameter, and the nozzle/meniscus diameter, as shown in Figure 5. The electrostatic force F_e , can be expressed by an empirical equation using power law fitting as $F_e = c V^{k1} D_d^{k2} D_N^{k3}$ in which F_e is a

Figure 5: a) Intersection of electrostatic force and surface tension force on the droplet give the resulting droplets diameter at different voltages. b) Result of droplets in-flight dimension from FEA (blue line) and experimentally measured (red data points)

function of voltage V , droplet diameter D_d , and the nozzle/meniscus diameter D_N . By changing one parameter and keep other parameter constant at a time, we can calculate the value for c , k_1 , k_2 , and k_3 from FEA analysis, which provide the relationship between the electrostatic force and the process parameters. For the tip used in this study, the final equation is $F_e = 3.46e-6 V^{2.0} D_d^{1.702} D_N^{-1.078}$.

In the EHD printing when the electrostatic force is larger than surface tension force, the sum of force will make droplet detach from the meniscus. The equation for surface tension force is $F_s = \sigma \pi D_d$ Where σ is surface tension coefficient of melting wax (mN/m). By connecting two equation together, we can get that $F_s = \sigma \pi D_d = F_e = c V^{k_1} D_d^{k_2} D_N^{k_3}$, and resulting droplet diameter D_d as

$$D_d = \left(\frac{c V^{k_1} D_N^{k_3}}{\pi \sigma} \right)^{\frac{1}{1-k_2}}. \quad \text{The solution for the resulting droplets diameter can be solved graphically as in}$$

Figure 5(a). When the line of the surface tension force intersects with the curve of the electrostatic force for a certain nozzle tip with applied voltages, the electrical static force is large enough to overcome the surface tension to produce a droplet with certain diameter. Using this method, for each voltage applied to the nozzle, we can estimate the corresponding droplet diameter in EHD printing at a specific process conditions.

Due to the phase-change ink (wax) used in EHD printing, we can directly measure the volume of printed wax droplets on the substrate, and validate the FEA model with experimental results. The droplets diameter predicted by the FEA model and the experimental results are plotted in Figure 5(b). The FEA results are in good agreement with the measured droplet dimensions with the maximum prediction error less than 10%. The difference between FEA model and the experimental results may come from factors that include the measurement error of the nozzle diameter, the difference in the surface tension for different tips due to the temperature variation.

Droplet in-flight velocity, especially the droplet impact velocity is critical to study droplet impact/settlement on the substrate. In this study, an analytical model is developed to obtain the impact velocity of the droplets using the results from FEA analysis. The schematic of the droplet in-flight model are shown in Figure 6 (a). Two different forces are applied on the in-flight droplet, electrostatic force and viscous drag force. Electrostatic force accelerates the droplet velocity, and viscous drag force decelerates the velocity. The expression of electrostatic force is $F_{es} = Eq$, and the expression for drag force is $F_d = 1/2 \rho v^2 A C_d$, where ρ is air density, C_d is drag coefficient, and v is the droplet velocity and A is droplet cross-section area. The electrostatic field strength along the axial direction of the nozzle can be obtained from FEA analysis. An example of electrostatic field strength along the center axis is shown in Figure 6(b). The electrostatic field strength relies on the voltage difference between the nozzle and the substrate, which is largest around the nozzle tip and gradually decreases when the

Figure 6: a) FEA model of droplet in-flight between tip and substrate. b) Electrostatic field distribution along center axis. c) The amount of charge of droplet under different voltages. d) Droplet velocity under different voltage and different flight time e) Droplet impact velocity with different printing voltages.

droplet moves to the substrate. The charge of the droplet is obtained from the charge accumulating on the ejecting hemisphere droplet, and is uniformly distributed on the droplets surface. Figure 6(c) shows the charge of each droplet at different process conditions. Then we can calculate the droplet in-flight velocity using the electrostatic force and drag force. In our calculation, the gravity force of the droplet is extremely smaller (six-order of magnitude smaller) than other two force, thus the gravity effect can be neglected. After integrating the acceleration along z-axis, the velocity of the droplets can be derived as the function of time and travel distance. Figure 6 (d) shows that the velocity of droplet in-flight under different voltages and different flight time. When droplet finally impact on the substrate, it will get the largest velocity, which is the impact velocity and this velocities are shown in Figure 6(e).

4.2 Modeling for Droplet Settlement on Substrate

It is important but very difficultly to study the droplet impact and settlement on substrate surface theretically. Understanding this process will help us to predict the final droplet footprint on the substrate and the resulting shape for 3D fabrication. The ejected droplets only travel several micro-seconds before reaching the substrate. In the model, we use Ansys Fluent to study the droplet interaction with the substrate mechanically (by impact) and thermally (solidification). Droplet impact and solidification can be divided into four typical stages: droplet in-flight before impact, initial droplet impact, droplet spreading, and droplet solidification, as shown in Figure 7. The initial stage in the model is that the droplet has reached the maximum inflight speed and ready to impact the substrate,

Figure 7: a) In-flight droplet before impact the substrate. b) Initial impact of the droplet on substrate. c) Droplet spreading on substrate surface. d) Droplet settlement and solidification. e) Experimentally measured droplet cross section on substrate. (Unit of x and y coordinates is μm, and measurement is shown as red line).

which is shown in Figure 7(a); and the final state in the model is that droplet have completely solidify, which is shown in figure 7(d). The critical parameter in this process is the solidification time. If simulation time is shorter than the solidification time, the FEA results cannot get correctly. It is very difficult to precise calculate droplet solidification after impact to the substrate, but we can use

$$\text{equation } \tau_s \approx \frac{2a^2k}{3\alpha k_t} \left(\ln \left(\frac{T_0 - T_a}{T_f - T_a} \right) + \left(1 + \frac{k_t}{2k} \right) \frac{L}{c(T_f - T_a)} \right)$$

where a is the droplet radius, α is the thermal

diffusivity, k is the thermal conductivity, T_0 is the melting droplet temperature, T_a is substrate temperature, T_f is fusion temperature, c is the melts specific heat and L is the latent heat of fusion, to

Figure 8: Comparison between droplets height (a) and diameter (b) from FEA (lines) and experimentally measured results (data points) at different process conditions.

roximately estimate its solidification time (Gao 1994), which is about 12 μs . In the FEA simulation, we have set the total simulation time at least two times larger than the estimate solidification time, to ensure that the droplets have completely solidified and stabilized. For each droplet ejected at different conditions, droplet impact velocity is obtained from the previous model, as shown in the figure 6(e). Figure 8 shows the modeling result at the four stages of droplet settlement and an experimentally measured droplet cross-section using Atomic force microscopy (AFM). Figure 8 shows the droplet dimension on the substrate obtained from the model and experimental measurements. There is a good agreement between the model and experiments, which means the model we have developed can describe the solidification and stabilizing process very well, and this model can be used to estimate droplet settlement under other different conditions.

5 Conclusion

In this work, we have studied and modeled the EHD printing process using a phase-change material (i.e. wax) for micro-scale additive manufacturing, which can print sub-10 μm 3D microstructures. We built process models for modeling droplet formation, impact and settlement in the printing process by FEA to predict droplet size in different process conditions. To model the droplet formation, we focused on the two competitive forces, surface tension force and electrostatic force. By balancing those two forces at droplet pinching from the Taylor cone, the droplet in-flight diameter can be derived. Droplet impact velocity can be calculated numerically by counting the effect from the electrostatic field when the droplet travels to the substrate. Then this velocity is used to model the droplet settlement on the substrate. We have measured the volume and droplet footprint under different printing conditions, and compared them with the model prediction, which have a good match between them. We have also demonstrated the capability of using phase-change ink (wax) to print 3D structures by using EHD printing approach. This printing method gives high resolution and high aspect ratio 3D structures with sub-10 μm resolution.

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