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Symmetric and uniform coalescence of ink-jetting printed polyfluorene ink drops by controlling the droplet spacing distance and ink surface tension/viscosity ratio

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ABSTRACT

The film quality is the core to produce long-life and efficient organic light emitting devices by ink-jetting printing technology which is deeply related to the ink droplet coalescence process, especially the coalescence bead morphology and thickness. However, the fluid flow from impacted drop to the previously deposited drops (drop to bead flow) usually leads to an asymmetry and heterogeneity of coalescence beads during droplets coalescence process in the substrate. Here we reduce the spreading speed of impacted drops to achieve a symmetric and homogeneous coalescence effect, by controlling the drops to deposit firstly and then coalescence. A uniform linear line morphology with a smooth straight edge and symmetric ends was obtained at drop distance $1.35 \leq y \leq 1.60$. Via adjusting the chloride benzene (CB)/cyclohexylbenzene (ChB) proportion of ink formula, when the γ/η value decreases to 4.73 m/s, the h_1/h_2 value is nearly 1.04, homogeneous bead obtained. Uniform and homogeneous bead was formed for 80/20 CB/ChB sample with a 4.73 m/s surface tension/viscosity ratio. The appropriate matching of the relationships of the spreading and coalescence speed of impacted drops plays a critical role for the final bead morphology during the droplet coalescence. The spreading and coalescence speed have a finite matching for the 80/20 CB/ChB sample with a 4.73 γ/η value, forming uniform beads.

1. Introduction

Ink-jetting technology is a high-efficient manufacturing method to fabricate components with applications for polymer electrics [1–3], displays [4], transducer [5–7], ceramic manufacture [8] and life and analytical science [9], which has drawn great interests of researchers. During the ink-jetting process, the ink droplets are deposited and coalesce on the substrate after being ejected from the ink nozzle. As for printing light-emitting pixels using ink-jet printing technology, the process of ink droplet coalescence is of great importance in resulting pixel patterns. A homogeneous and regular coalescence effect promotes better light brightness and homogeneity for light-emitting materials.

The previous researchers make more attempts to the coalescence of printed lines, which is related to contact angle [10–13], drop spacing [14,15] and so on. Davis first revealed that stable fluid lines with fixed contact lines can be formed if $\theta < \pi/2$. If $\theta > \pi/2$, the lines can be stable only at a perturbations of a wave number (k) larger than a critical value (k_C) [13]. Dan Soltman and Vivek Subramanian first investigated the influence of drop spacing on the printed line morphologies systematically [14]. They found that the line morphology ranges from stacked coins, bulging, uniform, scalloped lines to individual drops. The uniform lines can be formed in the range of drop spacing 0.89–1.52.

Wen-Kai Hsiao tried to investigate the transient dynamics of a newly landed drop and an existing bead in drop coalescence printing beads [11]. They verified the line stability mechanisms of Soltman and Subramanian experimentally and proposed that the drop to bead flow may be weakened by an increase in viscous dissipation in the thinner neck region or by a reduction in the driving pressure due to the smaller curvature variations between the deposited drops and the previously deposited liquid bead. What's more, they used a mixture of ethylene glycol and deionized

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water, the contact line motion of which being different from polymer solutions. They acquired stable and symmetrical tracks by increasing the inkjet printing frequency, but they didn't make a deeper discussion about the symmetry of forming beads. Further study of symmetric and homogeneity of forming bead with a finite contact angle is still relevant to achieve certain patterns in ink jetting printing.

Here in this paper, we mainly focus on the symmetry and homogeneity of the resulting coalescence beads. By printing a polyfluorene (PFO) solution CB/ChB as a mixed solute, we aimed to verify the influence of drop distance and surface tension/viscosity ratio on the lighting pixel coalescence morphologies. As a result, we acquire symmetric and homogeneous pixel bead using 10 mg/mL 10K PFO solution in an 80/20 CB/ChB mixed solvent at a drop spacing range of $1.35 \le y \le 1.60$. The proportion reduction difference of coalescence and spreading speed is a good explanation for the uniform and systemic pixel bead. These results throw new light on fabricating high quality luminous panels with uniform pixel patterns.

2. Experimental section

2.1. Materials

The polyfluorene (PFO, M_n = 100 KDa, PDI = 1.83) was synthetized by Prof. Wang's group [16–18]. Chloride benzene (CB) was purchased from Sigma-Aldrich Co. Ltd. Cyclohexylbenzene (ChB) was purchased from Sigma-Aldrich Co. Ltd. ITO glass (glass slide with indium-tin-oxide films) was purchased from Chinese South Glass Holding (CSC) Co. Ltd. The poly(styrene sulfonic acid)-doped poly(3,4-ethylenedioxythiophene) (PEDOT: PSS, Baytron PVP. AI4083) was purchased from H.C. Starck GmbH. All of the solvents were used without further purification.

2.2. Inkjet printing of PFO film pixels

The polyfluorene (PFO) solution was prepared using CB/ChB mixed solvents with a 10 mg/mL concentration of polyfluorene. The ChB content was varied as follows, 0%, 10%, 15%, 20% and 30%. All the solutions were placed for 24 h after heating for 10 min to ensure a totally dissolution.

The ITO glasses were etched for 90 s using a plasma etching machine. Then the ITO glasses were spin coated with PEDOT solution for 40 s with a 3000 rad/s spin speed. The roughness of ITO substrate modified by PEDOT is 0.8651 nm, which shows a flat surface, indicating that the roughness of PEDOT has no influence on the spreading and coalescence process. Before inkjet printing, these glasses substrate were dried for half an hour at 130 °C in the drying oven.

The inkjet printer was equipped with a drop on demand (DOD) piezoelectric inkjet nozzle (Microdrop Technique Co., Germany) with a 55 μm orifice and a computer controlled X - Y axis station panel. The distance was maintained as 1 mm from the nozzle to the substrate at 25 °C during inkjet printing. By controlling the speed of X - Y axis station panel and appropriate ink jetting printing frequency we can acquire various drop distances.

To make sure the printer unblocked, all the inks should be filtered before being printed. After being installed on the printer, the ink solution was filled into the inkjet nozzle using a pump. After pressing the “start” buttons the ink droplet was appeared in the observation window with a piezo-electric crystal driven. The drop ejecting process should be maintained for 10 min after a single and stable droplet is acquired by controlling the printing voltage and pulse length. The ITO glass substrate was absorbed onto the X - Y axis station panel through a vacuum. The solution was inkjet printed with a 125 Hz printing frequency at various printing speed. Each condition was printed four rows, four drops as a group to form a bead without heating the substrate. The nozzle was cleaned four times using chloride benzene before printing a new ink.

2.3. Characterization

The roughness of PEDOT was characterized using a SPI3800 N AFM (Seiko Instruments Inc., Japan) with a Si tip with a spring constant of 2 N m^{-1}.

The surface tension of PFO solution was acquired from the liquid drop shape analyzer (DSA10 from KRUSS Gmbh Germany) using a pendent drop method. During measure, a whole droplet was extruded manually to ensure a correct measurement. The advancing, static contact and receding angles of the ink drop on the substrate were also characterized using DSA drop shape analyzer.

The viscosity was measured by LVDV-III+ Programmable Control Rheometer from Brookfield Ltd., America at room temperature. We used the average of eight test results to characterize it.

The PFO film profile was observed by axio optical imager from Zeiss Ltd., Germany. The morphology of pixels was characterized by the Zeiss Polarizing microscope in the normal and fluorescent light mode.

The thicknesses of films were characterized using a Veeco Dektak 6 M Stylus Profilometer.

3. Results and discussion

3.1. The morphology of coalescence bead at different drop distance

The ink we used for inkjet printing in this section was 10K PFO dissolved in 80/20 CB/ChB mixed solvent with a concentration of 10 mg/mL. Four ink droplets were inkjet-printed on the substrate drop by drop separately. We firstly investigated the effect of drop distance on the final drop coalescence morphology.

The actual distance of two drops (center to center) can be expressed as Δx. To eliminate the influence of individual drop radius on the coalescence effect, a dimensionless drop distance y was put forward, defined as

$$y = \Delta x / R_0 \quad (1)$$

R_0 is a free spreading radius in the same substrate [11,14,19].

The effect of drop distance y on the coalescence result is shown in Fig. 1. Drop distance y = 0.9, 1.3, 1.5, 1.7, 2.0, 2.3 and 2.5 were chosen. Three different drop coalescence morphologies were observed with decreasing y value, i.e., individual drops, scalloped lines and linear lines. When the drop distance $y \ge 2.2$ (more than twice of a drop radius), the drops keep isolate. When $1.7 \le y \le 2.0$, the drops began to contact and coalescence, leading to a distinct scalloped line morphology. When the drop distance continues to decrease, linear line morphology is observed. However at the drop spacing section $y \le 1.30$, the resulting coalescence drop presents a state of asymmetric ends, i.e., one end is bigger than the opposite end. From the above results, it can be concluded that an appropriate drop distance is necessary to obtained linear line morphology without asymmetric end.

In order to get the appropriate drop distance for linear line morphology without the asymmetric end, we define two heights of two ends, i.e., the distance between two tangency points of linear line morphology with asymmetric end, the higher one as h_1 and the shorter one as h_2 as shown in Fig. 2a. Fig. 2b illustrates h_1/h_2 vs the drop spacing y. There is a linear relationship between h_1/h_2 and drop spacing y.