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INK EVAPORATION ON SOFT SUBSTRATES FOR ADDITIVE MANUFACTURING OF STRETCHABLE ELECTRONIC DEVICES: EXPERIMENTAL STUDIES

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ABSTRACT: Additive manufacturing (AM) has emerged in various fields including prototyping, construction, biomedical science, and electronic fabrication. For manufacturing of electronics, several AM techniques have been developed, most notably droplet-based techniques such as inkjet and aerosol-jet printing. The progress in this field has been hindered due to the lack of appropriate materials, poor printing resolution, and lack of fundamental understanding on the deposition process of conductive materials. Typically for droplet-based printing, small droplets of a certain ink, i.e., micro- or nanoparticles suspended solvent, are ejected onto printed substrates. The ink droplets, after deposited on a substrate, evaporate leaving behind particles on the substrate. The evaporation process depends on various contributing parameters such as liquid properties, surface wettability, roughness, and stiffness. While this process has been extensively studied for rigid substrate, it has not been fully understood for soft substrates, which are relevant for fabrication of flexible and stretchable electronics. In this work, we study the effect of substrate’s elasticity on evaporation process of suspension droplets. Variation in the elasticity plays a crucial role as it directly influences the morphology of the substrate at the triple-phase contact line, thus resulting in different deposited patterns of particles on the substrate. By fine-tuning the substrate’s elasticity, we expect that the electrical properties of the printed patterns can be manipulated.

KEYWORDS: Ink evaporation, soft substrates, additive manufacturing, 3D printing, stretchable electronics

INTRODUCTION

AM is generally defined as a process to build 3D objects by means of joining materials layer-by-layer. It has created the new chapter of manufacturing industry with the possibility to transform digital information into invaluable-physical components [1]. For manufacturing of electronics, AM technology has emerged in electronic fabrication for more than a decade. Direct writing techniques are one of the AM technologies, which have several advantages as they can easily create a board range of patterns from simple flattened lines to complex three-dimensional (3D) patterns. Even though they possess different printing principle, most of them used ink as deposited materials due to the ease of fabrication, and the lower cost of the process, which make AM the rising topic in many applications [2,3].
As an example of the AM technology, inkjet printing can be a good example since its materials are often in the form of low viscosity suspension ink. Its printhead ejects a small droplet of ink out of the nozzle, and then the ink is dried through sintering process; which is a drying process of the ink, eliminating all solvents. Consequently, the deposited patterns are presented on the substrates [4]. However, the mechanism is not fully understanding, in particular on the soft substrates, because there are many phenomena are being involved.

The studies on the droplet evaporation on a rigid substrate, like silicon and glass, are the first group of the research work in this field [5-6]. Since polymeric and elastomeric substrates are widely used in many applications, especially in wearable and stretchable devices, investigations of the evaporation on these types of substrates were presented [7-9]. In fact, soft substrates differ from rigid substrates by their hardness [10]. As compared with the rigid substrate, a soft substrate is more elastic. Theoretically, a vertical force of surface tensions of the evaporating liquid can cause vertical deformation on the soft substrate and hence the evaporation process [7, 8, 11]. However, the studies on effects of these substrates on evaporation mechanisms and deposited patterns are not completely understood.

Printed electronic devices from an inkjet printer are typically produced as thin-film, ranging from nanometer to hundreds of micrometers. Since there are ultra-thin components, their properties (mechanical and electrical properties) largely depend on the deposited materials and deposited morphology. To control these properties, various knowledge on how the drying process affects the printed patterns should be studied. Particularly, a relationship between evaporation mode, time, and material’s properties.

Therefore, this work presents a dependence of ink evaporation on the elasticity of soft-rubbery substrates, Ecoflex. This substrate has been used in both industrial and research areas for additive manufacturing of electronics components. It is compatible with printed electronic application due to its high stretchability and good surface adhesion.

LITERATURE REVIEWS

Droplets evaporation on soft substrates

Deposition of ink via the inkjet printing, from the ink landing on the surface to the stain occurrence, involves the physics of ink spreading on the substrate’s surface and ink evaporation process. Considering a pure liquid drop on an ideal solid substrate (smooth and homogenous), three different phases- that are surface tensions of solid-liquid ($\sigma_{SL}$), liquid-vapor ($\sigma_{LV}$), and solid-vapor ($\sigma_{SV}$) –act on contact region as shown in Figure1. The relationship between these forces is explained by Young’s equation (1805) [12] as in an equation below.

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta$$

This equation illuminates a mechanical equilibrium of three-phase contact lines (TLs) where all the forces of them are balanced. Besides, the surface tensions and the contact angle are then used to characterize the wetting and evaporating process of the sessile droplet [13].

After the TL is pinned and then evaporated, a drop that its contact angle decreases over time, but not its radius, is considered to evaporate in a constant contact radius (CCR) mode. While drop evaporation corresponds to a recession of only the TL, it refers to the evaporation in a constant contact angle (CCA) mode. In general, drop starts evaporating in the CCR mode and then convert to the CCA mode when the receding contact angle $\theta_r$ is achieved. The radius is becoming smaller, and the TL moves toward center of the drop. Furthermore, more complex evaporation mode exists
when these mentioned modes are in cooperate, especially at the end of the evaporation process where switching of these two modes is often found [14]

![Figure 1. A Schematic of liquid drops showing quantities in Young’s equation.](image)

Lopes and Bonaccurso [7-8] performed several tests showing that deformation of the Polydimethylsiloxane (PDMS) substrate caused by the interfacial and capillary forces affects the evaporation of sessile drops of pure water. The result showed that the deformation could control the evaporation. In particular, the elasticity directly alters vertical components of the forces acting on the TL and hence affecting the receding contact angle during the evaporation. The elasticity of the substrates results from their composition ratio and their dimensions (width, length, and thickness).

**EXPERIMENTAL METHODS**

**Substrate preparation**

A rubber Ecoflex (Smooth-on Inc., USA) which is widely used in the stretchable electronic and molding applications is selected. It is platinum-catalyzed silicone rubber which combines two commercial rubber solutions. Its main advantages are the ease of process and curing at room temperature with negligible shrinkage. The fully cured Ecoflex has an extreme stretchability and smooth surface.

Similar to the well-known PDMS, its elasticity can be adjusted by varying a mixing ratio. In this experiment, the mixing ratio of the commercial rubber A and B differ, for example, 30:70, 50:50, 70:30, and 80:20 by weight to produce substrates with various Young’s modulus. After the rubbers are blended, we coat a rubber thin-film by a spin coater (Spin150i table top spin coater, Spincoating, Netherlands) on a cleaned cover glass. All samples were left to cure at room temperature for at least 12 hours. The substrates are kept in a closed environment to prevent any contamination on the surface. The film thickness is measured by a laser scanning confocal microscope (Keyence vk-x200 series, Japan). To measure the substrate elasticity, a tensile testing machine (Universal testing systems, Instron 5569, Instron, MI, USA) with an attached 10N load cell is considered. The numbers of samples are three samples for each type of substrates to ensure data consistency.

**Ink preparation**

A drop of ink is a mixture of spherical polymer particles with a diameter of 1-5 μm (FMO-1.3 1-5μm, Cospheric, CA, USA) diluted in pure ethanol (99%). The suspension solution has a controlled concentration of 0.01 wt%. The drop with a volume of 0.5 μl is placed on the substrates by using a pipette (Research® Plus pipette (0.5-10μl), Eppendorf, Germany).

**Experimental setup**

The setup consists of a light source, an evaporating chamber, and a recording camera, as shown in Figure2. The light source helps to visualize images and increases the contrast of the sessile drops with their background. A high-speed camera (SA5, Photron Inc., Japan) is used to capture the evaporation of the droplet from side-view. Contact angle and contact radius of the sessile droplet are extracted from the image via ImageJ software with plug-in drop analysis. A closed chamber is a place where the evaporation occurred. All the lab experiments were done at ambient conditions with
constant humidity (%RH ≈ 66.2±4.3%), constant temperature (T ≈ 26.0±0.7 °C), and atmospheric pressure.

![Schematic of the experimental setup](image)

**Figure 2.** A schematic of the experimental setup.

**RESULTS AND DISCUSSIONS**

**Characterization of substrates**

Properties of samples A-D are presented in Table 1. We found that all elastomeric samples have a similar thickness, but the elasticity is different. Ranging from highest to lowest elasticity: sample D, C, A, and B, respectively. In the beginning, initial contact angle and initial contact radius are measured. All drops initially possess similar contact angle and contact radius, indicating an almost identical initial condition to all of them.

**Table 1.** The properties of sample A-D.

<table>
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<tr>
<th>Samples (A%: B%)</th>
<th>A (30: 70)</th>
<th>B (50: 50)</th>
<th>C (70: 30)</th>
<th>D (80: 20)</th>
<th>Glass</th>
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<td>Thickness (μm)</td>
<td>53.67±0.57</td>
<td>54.3±1.52</td>
<td>59.67±1.52</td>
<td>59.33±3.05</td>
<td>-</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>0.073±0.009</td>
<td>0.055±0.008</td>
<td>0.078±0.006</td>
<td>0.113±0.015</td>
<td>-</td>
</tr>
<tr>
<td>Initial contact radius $R_0$ (mm)</td>
<td>0.99±0.05</td>
<td>1.18±0.04</td>
<td>1.07±0.08</td>
<td>0.97±0.07</td>
<td>1.47±0.13</td>
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<tr>
<td>Initial contact angle $\theta_0$ (°)</td>
<td>32.53±1.24</td>
<td>26.72±0.98</td>
<td>31.73±0.17</td>
<td>30.80±0.24</td>
<td>14.57±2.6</td>
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**Droplet evaporation**

During the evaporation, the sessile drops evaporate as a function of time. Therefore, we recorded all the samples respected to time. A first frame where $t=0$ is set from a frame 5 seconds after the drop wets the surface. Reasons are to exclude the effect of the wetting process. The droplet evaporation of the sample A-D is presented in Figure 3.

We found that the evaporation of the droplet on sample A-C has a similar trend, and the dynamic contact radius shows similar values. Due to the similar Young’s modulus value of sample A-C, the results overlap. However, for sample D, the dynamic contact angle differs from the rest. During first 70 seconds, all dynamic contact angle is almost the same. After 70 seconds, the value of the dynamic contact angles decreases faster than those of sample A-C. The droplet is fully dried at 180 seconds, roughly 40 seconds earlier than the rest.
Figure 3. (Top) Side-viewed snapshots of the sessile drop evaporating on the elastomeric substrate at room temperature. (left) The plots represent the dynamic contact angle of the sessile droplet on different substrate’s elasticity. (right) The plots represent the dynamic of normalized contact radius as an influence of different substrate’s elasticity.

The effects of the substrate’s elasticity seem not to influence the contact radius. The normalized contact radius gradually decreases during the evaporation. The surface tension at the solid-liquid interface might be identical among sample A-D so that the receding radius has the same trend dynamically. The evaporation on glass surface occurs quicker than that on the rubber substrate, approximately 90-130 second faster. The initial contact angle of the glass is lower almost by half of that of the rubber substrate. This can be explained by a surface hydrophobicity of the substrate. Particularly, the rubber surface is hydrophobic, while the glass surface is hydrophilic. The hydrophilic surface allows the droplet to spread more as compared with the hydrophobic surface. Moreover, the initial contact radius on the glass is larger than that of the rubber almost 50%. The elasticity of the substrate might have slightly impact on these two parameters, but the impact from the surface hydrophobicity is much more significant. The droplet on the glass has more surface to volume ratio, so the evaporation occurs faster than the case of the rubber. As a result, the drop on the glass evaporates more quickly, and the single drop typically separates into smaller droplets during the evaporation.

Deposited patterns

The plot presented a dependence of substrate Young’s modulus on a deposited radius of the particles is shown in Figure4. As a result, all samples tend to obtain similar results on the deposit’s radius. An average radius is ~150 μm. Since the substrate’s elasticity has no significantly different, the influence of the evaporation and the deposits are similar. Therefore, the same range of deposited radius is shown. However, for sample D, which has the highest modulus among all samples, the average deposited radius is ~364 μm. In fact, Droplet evaporation on sample D has earlier pinning mode, so it causes the deposition at the TL differently from that of other samples. Particles deposition may start after 70 seconds, while the deposition of other samples begins after 120 seconds when pinning occurs. This may cause the bigger deposited radius for sample D.
CONCLUSIONS

This work shows a macroscopic view of the suspension droplet evaporating on the smooth-rubber substrate with different elasticities. The dynamic contact angle of sample D differs from the rest. However, the substrate elasticity of sample A-C has no significant difference, so the results from these samples show almost similar results. The Ecoflex substrate shows a narrow range of elasticity with presented mixing ratio. However, the broader range of substrate’s elasticity might be needed to extend the study.

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