Studies of suspension droplet evaporation on soft substrates for stretchable electronics applications

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**STUDIES OF SUSPENSION DROPLET
EVAPORATION ON SOFT SUBSTRATES
FOR STRETCHABLE ELECTRONICS
APPLICATIONS**

**SAENGCHAIRAT NITIPON
SCHOOL OF MECHANICAL AND
AEROSPACE ENGINEERING**

2019

**STUDIES OF SUSPENSION DROPLET
EVAPORATION ON SOFT SUBSTRATES FOR
STRETCHABLE ELECTRONICS
APPLICATIONS**

SAENGCHAIRAT NITIPON

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Saengchairat Nitipon

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Date

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Assoc. Prof. Tran Anh Tuan

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as Saengchairat, N., Tran, T., & Chua, C. K. (2017). A review: Additive manufacturing for active electronic components. *Virtual and Physical Prototyping*, 12(1), 31-46. DOI: 10.1080/17452759.2016.1253181

The contributions of the co-authors are as follows:

- A/Prof Tran provided the initial project direction and edited the manuscript drafts.
- I co-designed the study with A/Prof Tran. I also collected and critiqued the data
- I prepared the manuscript drafts. The manuscript was revised by A/Prof Tran and Prof Chua.

Chapter 4 is published as Goh, G. L., Saengchairat, N., Agarwala, S., Yeong, W. Y., & Tran, T. (2019). Sessile droplets containing carbon nanotubes: a study of evaporation dynamics and CNT alignment for printed electronics. *Nanoscale*. DOI: 10.1039/c9nr03261d

The contributions of the co-authors are as follows:

- A/Prof Yeong provided the initial project direction and edited the manuscript drafts.
- Mr. Goh prepared the samples, performed the sessile drops experiment, and conducted all the characterisation of the samples, including the optical microscopy, FESEM, Raman spectrometry, and images analysis for particle orientation/ arrangement.
- Mr. Goh wrote the drafts of the manuscript. The manuscript was revised together with Dr. Agarwala.

- I prepared the experimental setup for the droplet evaporation on heated substrates and assisted in the experiment.
- I also help to revise the draft of the manuscript.
- The manuscript was finally revised by A/Prof Yeong and A/Prof Tran.

.... 20/8/2019

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Abstract

Evaporation of sessile drops is a common phenomenon in various problems, but its fundamental understanding remains modestly unknown. Despite numerous reports of the factors affecting the evaporation processes, the effect of substrate elastic modulus has been seldom reported. This work aims to experimentally investigate the dependence of substrate elastic modulus or Young modulus on the evaporation dynamics of the sessile liquid drops containing the dispersed microparticles and the resulting deposition patterns. In this work, the evaporation dynamics of the sessile ethanol drops was experimentally investigated using thermographic approach. As a result, the substrate Young modulus can control the evaporation dynamics and the radius of deposition patterns. The temperature distribution across the liquid-vapour interface deviates larger on the substrate with higher Young modulus. Moreover, the evaporation dynamics of water droplets containing non-spherical particles such as carbon nanotubes were analysed as a function of substrate temperature and particle concentration. The evaporation dynamics and the resulting deposition patterns are comparable to that of the spherical microparticles. In addition, the conductive patterns were directly printed on the surface of substrates with varying Young modulus. The properties of the printed patterns dependent of the substrate Young modulus were measured. It was demonstrated that the substrate with lower Young modulus could prevent the formation of sintered particles due to the leaching of residual polymers, therefore, suppressing their electrical conductivity. To conclude, the substrate Young modulus can notably control the evaporation dynamics and the properties of printed patterns.

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a	radius of the particles (μm)
A	contact surface area of the droplet (mm^2)
B	bulk modulus (Pa)
c_0	vapor concentration at the droplet interface (kg m^{-3})
c_∞	vapor concentration far from the droplet (kg m^{-3})
c_s	saturated vapor concentration (kg m^{-3})
D	diffusion coefficient of the vapor ($\text{mm}^2 \text{s}^{-1}$)
D_p	average particle size (μm)
E	Young's modulus (Pa)
f_d	viscous force (N)
f_g	gravitational force (N)
F	force acting on a particular component (N)
g	gravitational acceleration (m s^{-2})
G	Shear modulus (Pa)
h	height of the droplet (mm)
h_{rim}	height of the substrate deformation (μm)
H	gas phase humidity (%)
J	evaporative flux ($\text{kg m}^{-2} \text{s}^{-1}$)
k_B	Boltzmann's constant (J K^{-1})
l	a distance from reference layers (mm)
L	characteristics length (m)
L_c	capillary length (m)
m	mass (kg)
$\dot{m}$	evaporative mass rate ($\text{kg m}^{-2} \text{hr}^{-1}$)
Q	volume flow rate (m^3/s)
P_A	Pressure at the surrounding air (Pa)
P_l	Pressure inside the drops (Pa)

r, R	contact radius of the spreading droplet (mm)
s	uniaxial stress (Pa)
S	spreading coefficient (J m^{-2} or N m^{-1})
t	time (s)
t_B	time for particles to diffuse its own radius (s)
t_D	diffusion time of the vapor (s)
t_f	Studied time of the material to flow (s)
t_F	evaporation time (s)
t_p	thickness of the printed patterns (μm)
t_u	time for particles to fall its own radius (s)
T	temperature ($^{\circ}\text{C}$)
T_s	substrate temperature ($^{\circ}\text{C}$)
u	velocity (mm/s)
u_s	velocity of the settling particles (mm/s)
U_r	receding speed of the contact line (mm s^{-1})
ν	kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)
ν, V	volume of the droplet (μl)
W	width of the printed deposition patterns (mm)
W_L	width of the printed line (μm)
$\dot{W}$	work rate (J s^{-1})

Dimensionless numbers

Bd	Bond number
De	Deborah number
Ma	Marangoni number
Pe	Peclet number
Ra	Rayleigh number
Re	Reynolds number

Greek letters

θ	contact angle of the spreading droplet (degree)
θ_a	advancing contact angle (degree)
θ_r	receding contact angle (degree)
α	thermal diffusivity ($\text{mm}^2 \text{s}^{-1}$)
β	thermal expansion coefficient ($1/^\circ\text{C}$)
ε	emissivity of an object
ϵ	tensile strain
ρ	density (kg m^{-3})
ρ_e	electrical resistivity ($\mu\Omega\text{m}$)
τ	shear stress (Pa)
τ_Y	Yield stress (Pa)
η	apparent viscosity ($\text{Pa}\cdot\text{s}$)
μ	dynamic viscosity ($\text{Pa}\cdot\text{s}$)
μ_f	friction
ν	Poisson's ratio
γ	shear strain
$\dot{\gamma}$	shear rate or strain rate (1 s^{-1})
σ	surface tension (J m^{-2} or N m^{-1})
λ	material relaxation time (s)
ξ	length of the base of the deformed substrate (μm)
φ	Ink's concentration (wt.%)

Subscripts

0	initial or at equilibrium
A	droplet's apex
cap	capillary force
CL	contact line
def	deformation
LV	liquid-vapour

SL	solid-liquid
SV	solid-vapour
m	mean value
L	liquid
V	vapour
x	x-axis
y	y-axis
z	z-axis

Chapter 1. Introduction

1.1 Background

Additive manufacturing (AM) technologies have emerged in electronic fabrication for more than a decade. Examples of the AM technologies are direct writing techniques, including inkjet printing and extrusion-based printing, which are advantageous compared to conventional microfabricating techniques. They can easily create a broad range of patterns from simple flat lines to complex three-dimensional (3D) patterns. Most of such AM technologies use liquid-based inks as deposited materials due to the ease of fabrication and lower cost

As an example of the AM technology, inkjet printing can be a good example because of capability in printing with variations of materials, reducing time-consuming, and lower cost. Its materials are often in the form of low viscosity dispersed ink. Typically, inkjet printing works as follows: its printhead ejects small droplets of ink to the substrate. Subsequently, the dispersed ink is dried, and dispersed particles are sintered [2]. The physics behind the inkjet printing of electronics largely relate to the spreading and evaporation of the droplet. After a liquid droplet containing particles evaporates, a pattern is always presented. The patterns can be controlled digitally to create a wide range of designs. The deposition patterns are also known as the coffee-ring effect. The formation of the coffee-ring effect has been intensively studied [3-7]. It is clear that the coffee ring is influenced by pinning of the droplet's contact line [3-5] and recirculation flows inside the droplet [6].

The problem of droplet wetting on flat substrates was initially studied in the early 1800s by Thomas Young [8] and Pierre-Simon Laplace [9]. They first

examined the wetting of a droplet on the surface, a role of the contact angle, and interaction of the liquid and solid. The wetting mechanism is challenging due to its physical complexity, but it has promising potentials for numerous industrial applications.

The studies of the droplet evaporation on a rigid substrate, e.g., silicon and glass, are the first group of the research work in this field [10-12]. Some studies investigated the evaporation dynamics of dispersed droplets on the rigid substrates [13-15]. It has been found that several factors affect the evaporation process. For instance, particle concentration can control the evaporation time [16, 17]. The droplet is pinned to the substrate throughout the evaporation under heated substrates [17]. Moreover, the surface hydrophobicity can determine the droplet geometry during the evaporation [18]. Since polymeric and elastomeric substrates are widely used in many applications, especially in wearable and stretchable devices, investigations of the evaporation dynamics of the droplet on the soft substrates were conducted [19-21].

Soft substrates differ from rigid substrates by their stiffness [22, 23]. As opposed to the rigid substrate, a soft substrate can be deformed. Theoretically, a vertical force of surface tensions of the evaporating liquid can influence vertical deformation on the soft substrates [19, 20, 24]. In particular, the substrate elastic modulus can control the elevated height and hence the evaporation process. However, it has not completely understood how the substrate elastic modulus or Young modulus will influence the evaporation dynamics of the sessile droplet. Therefore, it is of great interest to investigate the dependence of the substrate Young modulus on the evaporation dynamics of the droplet containing dispersed particles and the resulting deposition patterns. Such fundamental knowledge can

be used to control the properties of the printed electronic components on the soft and elastic substrates via AM technologies.

1.2 Applications

Extensive studies of the spreading and evaporation of the droplet containing dispersed particles on the soft substrates can be applied to numerous applications.

Depositions via additive manufacturing such as screen-printing [25], inkjet printing [26], aerosol-jet printing [27]; technical applications like spray cooling [28], crop spraying [29], combustion, heat exchange, diffusion in polymer films [30], microfluidic and lab-on-chip applications [31-33], as well as practical application in nature such as spreading of pesticides on leaves [34], drop of blood spreading and drying for medical investigation [35], and thermoregulation of human skin [36] are some of highly attractive applications of the droplet evaporation in various industries. For instance, the properties of the printed patterns via AM techniques are determined by the evaporation of the ink on the surfaces. Moreover, the qualities of the coating in crop spraying largely depend on the droplet spreading. The bloodstains in some criminals are investigated using the fundamental knowledge of liquid spreading and evaporation.

1.3 Motivation

Inkjet printing is widely used to fabricate electronic components and devices [37, 38]. It mainly involves the ejection of small droplets of ink and a drying process. However, the evaporation mechanism is not fully understood, in particular the droplet evaporation on the soft substrates, due to numerous involving phenomena. I think that we know how to control the evaporation process, it might help to enhance the performances of the printed devices.

To enhance the properties of the printed device, various knowledge must be involved, including how the drying process affects the printed patterns should be studied. Particularly, a relationship between evaporation mode, time, and material's properties. Moreover, the deposited materials (i.e., dispersions and solvents), substrate's properties (i.e., roughness and surface energy), and deposition rate, also play an essential role in the drying process. In AM, electronic components are typically produced as thin-film, ranging from nanometre to hundreds of micrometres. Since there are ultra-thin components, their properties (mechanical and electrical properties) largely depend on the deposited patterns.

Most of the research work in this field focus on the device's performance based on the properties of the materials, which also has a tremendous impact on its properties. However, the mechanism of how materials are being deposited on the substrate is also useful. The control of the evaporation process can lead to higher performances of printed devices.

Therefore, the understanding of the droplet evaporation mechanism on soft substrates will help to unlock many more functional devices with the desired

range of properties and hence enable many applications, especially wearable, flexible and stretchable electronic applications.

1.4 Research objectives

- To characterize the effect of substrate's elastic modulus on the evaporation dynamics of dispersed droplets.
- To determine the effect of the substrate's elastic modulus on the performance characteristics of deposition patterns.
- To determine the evaporation dynamics of the droplet containing the non-spherical particles under the influenced of substrate temperature and particles concentration.

1.5 Scope of works

- Experimental investigations of the dependences of the substrate's elastic modulus on the evaporation dynamics of a sessile dispersed droplet.
- Experimental examinations of the droplet evaporation dynamics on soft-elastic substrates using the thermographic approach.
- Characterization of the mechanical and electrical properties of the deposition patterns on soft substrates.
- Experimental analysis of the deposition patterns of the non-spherical particles under the influences of the substrate temperature and particle concentration.

- This work focuses on the effect of elasticity from soft solid substrates but not the effect from liquid surfaces.

1.6 Organization of the thesis

The outline is summarized here. Chapter two will cover literature reviews, including relevant printing techniques, a theoretical explanation of sessile drop evaporation, the suspension droplet evaporation on the soft substrates, properties of soft solid substrates, and some relevant works. The literature reviews will give an insight from the fabrication of printed electronic components via AM techniques to the physics of printing, especially the evaporation of the droplet/ ink on substrates. Chapter three presents the thermographic investigation of the drying droplet on soft-elastic substrates. The thermography of the evaporating droplet shows temperature profile across the liquid surfaces, which helps to determine the evaporation mechanism. In chapter four, the dependence of substrate temperature and particles concentration of a nanofluid on the evaporation dynamics of sessile droplets containing non-spherical particles will be investigated. The effect of substrate's elastic modulus on the characteristic performances of deposition patterns is presented in chapter five. The experimental result and characterization will be discussed. In conclusion, summaries of this work are included in chapter six.

Chapter 2: Literature reviews

2.1 Introduction

In this chapter, relevant literature reviews will be included: printing techniques that are often used to produce the electronic components, particularly droplet-based printing. Then, the physics behind this printing technique which consists of wetting and evaporation of the sessile droplet are addressed. The evaporation of the sessile droplet is mainly focused because it theoretically effects the deposition patterns. Besides, the liquid properties on soft solid substrates can alter the evaporation process. In microscopic scale, the deposited pattern on the substrate and its properties depend largely on its evaporation mechanism. The study on the droplet evaporation will provide better understanding of the phenomena which can lead to the fabrication of the higher device performances. Their properties and the impact on the droplet evaporation will be reviewed. Current works on the evaporation of suspension droplets on the soft substrates will be presented.

2.2 Printing techniques for electronics

There are many deposition techniques to fabricate electronic devices. For instance, the deposition via gas-phase methods, such as chemical vapor deposition (CVD) [39, 40], physical vapor deposition (PVD) [41], sputtering [42, 43], and electro-spinning [44] have been reported. To lower the manufacturing cost, many economic processes are being used, such as drop casting [45], spin coating [46], and additive manufacturing [25, 47]. Additive manufacturing has

gained much attention to the world of manufacturing of the electronic components.

These techniques are classified into two groups: contact printing and non-contact/ direct writing techniques. Both have their own advantages and disadvantages which are suitable for the fabrication of different electronic components. The comparison of the two types of printing techniques is present in Table 2.1.

The contact printing techniques deliver the ink, which becomes a deposited pattern, onto the substrates via the impression cylinder. The cylinder carrying ink on its surface is then in contact with the substrates, delivering the ink from its own surface to the surface of the substrates. The example of contact printing is flexographic printing, gravure printing, offset lithography, and screen-printing.

Flexographic printing is a commonly used technique in labelling and packaging [48] and has recently been adapted to print electronic components [49, 50]. In this method, ink is transferred from an ink bath to a designated substrate by an anilox roller. Subsequently, a printing plate transfers controlled amounts of ink from the anilox roller to the substrate by adjusting the pressure between the printing plate and an impression cylinder. This method is suitable for a variety of substrates, ranging from metal to paper. For gravure printing, the printing mechanism consists of two steps. In the first step, the gravure cylinder collects inks from the ink fountain. The amount of transferred ink is controlled by the volumes of gravure cells. In the second step, the substrate is placed between the gravure cylinder and the impression cylinder. When the gravure cylinder rotates,

ink from the cells is transferred to the substrate by the pressure imposed by the impression cylinder. The advantage of gravure printing is the high throughput, which is suitable for mass production [51] and the capability of printing a broad range of ink film thickness in a single print unit [52]. Lastly, one of the contact printing processes that has been used with printed electronics is the screen-printing. This technique is generally used in printed circuit boards, packages, and large posters [25]. It plays a vital role in electronic device fabrication, especially photovoltaic cells fabrication [53-55]. Screen-printing is often used because of the capability of low-cost mass production with a repeatedly accurate printing of large patterns for electronic components [56]. Nevertheless, several parameters, for example, printing condition, ink properties, and screen condition, must be well controlled. Post-processing, such as heat treatment, might be required depending on ink composition and ink and substrate interaction [57]

Within this decade, the direct writing techniques are becoming more popular due to their high resolution (line width $<10\ \mu\text{m}$) and low amount of materials (nanolitre or picolitre) required. Moreover, the printer's price is affordable for small businesses. The examples of the direct writing techniques are droplet-based printing and extrusion-based printing, including inkjet printing, aerosol jet printing, and organic vapor-jet printing (OVJC). More details about the inkjet and aerosol-jet printing will be discussed in the next section. In fact, the nozzle is not in contact with the substrate during the printing. The ink droplet or stream of ink is ejected from the nozzle, which is located above the substrate, and landed on the specific target. They are usually applied with advanced functional electronic components such as sensors [58, 59], Organic thin-film transistors (OTFTs) [60, 61], Organic light-emitting diodes (OLEDs) [62]. The

deposited ink consequently dries on the substrates from the pressure difference between the ink and the ambient pressure and the effect of the given temperature, producing the stain on the surface. Thus, the different patterns can alter the electrical and optical properties of the printed devices.

Table 2.1. Comparison of printing techniques [25, 27, 63-73].

Printing techniques	Ink viscosity (cP)	Minimum line width (μm)	Layer thickness (μm)	Speed (m/min)	Advantages	Disadvantages	Example
Contact printing	~50-5,000	10-100	~0.8-10, up to 100	~100-1,000	<ul style="list-style-type: none"> - Outstanding for high-speed mass production - High aspect ratio of printed object - Possible to print thick layer (~100 μm) - Variety of ink can be printed on any substrate. - Capable of repeatable printing of electronic patterns 	<ul style="list-style-type: none"> - Practically, all of the ink on the plate/ roller is not transferred to the substrate. - The resolution is limited - An organic solvent that might cause swelling of the roller is normally used. - Inks are only high viscous or paste-like materials. - High initial cost and complex setup 	<ul style="list-style-type: none"> - Flexographic printing - Gravure printing - Offset printing - screen-printing
Non-contact printing / direct writing	<20	10-50	<2	~15, up to 100	<ul style="list-style-type: none"> - Contactless digital printing method - Possible to print on various types of substrates, from rigid to flexible - Capable of printing on non-planar surfaces and 3D surfaces/ structures - High-resolution printing technique with accurate alignment system - Wide ranges of deposited materials 	<ul style="list-style-type: none"> - Nozzle clogging is usually occurred. - Formation of coffee stain pattern (Coffee-ring effect) prevents the depositing uniformity. - Lower throughput comparing with the conventional printing methods - Constrain in rheological properties of ink formulation - Additional supporting systems 	<ul style="list-style-type: none"> - Inkjet printing - Aerosol-jet printing - Organic vapor-jet printing (OVJP) - Laser-induced forward transfer - Extrusion-based printing

2.3 Droplet-based printing for electronics

Among those printing techniques, droplet-based printing techniques, such as inkjet and aerosol-jet printing, are often found in both research and industrial sectors. These techniques place the individual ink drop-by-drop or continuously on the surface, creating functional patterns. The ability of direct writing and minimum material wastage are the main advantages because electronic devices always require high precision process with the least wastage of noble material. In this topic, we will discuss two printing techniques: inkjet and aerosol-jet printing. A detailed comparison of these methods is presented in Table 2.2.

2.3.1 Inkjet printing

Inkjet printing has recently been adopted to fabricate prototypes for electronic circuits [74]. This technique is now considered to be only suitable for printing low volumes of simple circuit boards. It generally consists of two main components: an ejecting system and a control system. The main principle is to generate, dispense small droplets, and deposit materials contained within the working ink onto a substrate. Inkjet printing has two main operating modes: drop-on-demand (DOD), which is typically used in graphics and planar pattern printing with droplet size as small as 20–50 μm , and continuous inkjet printing, which is mostly used in marking and coding applications with drop size around 100 μm [26]. DOD inkjet printing relies mainly on the thermal and piezoelectric mechanisms to generate droplets (Figure 2.1a-c). In thermal DOD printing, the printing mechanism involves pressure generated by the bubble. On applying power through the heater which is located inside the fluid chamber, the ink is heated to form a bubble. The rapid expansion of the bubble causes the pressure

pulse to conduct ink ejection. In the piezoelectric DOD printing mechanism, the pressure pulse is generated directly by the mechanism of the piezoelectric transducer. On applying current through the piezoelectric transducer, fluid shape and volume change. Then, the pressure pulse is produced [75]. While others involve the pressure to eject the droplets, electrostatic inkjet uses electrostatic force to push the droplets out. The force is generated when applying a high voltage between conductive ink and a plate electrode [76]. For printing of electronics, the piezoelectric technology has higher potential in printing both passive and active electronic components compared to the thermal technology because it has a higher printability and provides less damages to the deposited materials. Piezoelectric DOD printing is uncomplicated to adjust the actuation pulse to control the droplet's size and velocity. The fluid with high vapor pressure under the room condition is not suitable for thermal DOD printing due to a large amount of bubble formation [77, 78]. However, there are a few roadblocks. For example, first, the main problem in using this technique is printhead blockage due to air bubble and large particle formation. Thus, pre-processing steps, for example, ink filtration, need to be done carefully. Second, several parameters, such as ink and substrate properties, and printing condition: initial set-up and interaction between the nozzle and the substrate, might be involved in order to accomplish a high-quality printed pattern. Third, post-processes, such as sintering and UV-curing, are needed. Conductivity depends on sintering because sintering influences the microstructure of the metallic materials [74]. However, the heat sintering process is not suitable for low melting point substrates, for example, paper and plastic, because the substrate can be deformed or damaged.

UV-curing is especially used to create a high-density polymer-dielectric layer in order to prevent short circuit.

2.3.2 Aerosol-jet printing

The aerosol-jet printing technology is one of the most recent technologies that is commercially available in the printed electronic industry. The term ‘aerosol’ refers to the suspension of fine liquid droplets in a gas and is generated in this printing system to carry ink droplets to substrates (Figure 2.2). This technique is capable of handling a wide variety of materials to print patterns at high resolutions (line width $<10\text{ }\mu\text{m}$, layer thickness of $0.1\text{--}2\text{ }\mu\text{m}$) (Aerosol Jet[®] 300 Series Systems, Optomec, USA). Due to these advantages, many researches have been using this technique to fabricate electronic components that require fine details and high precision such as capacitors, sensors, antennas, silicon solar cells, and flexible thin-film transistors [27, 79, 80]. Nonetheless, a main challenge for the wider adoption and development of this technique is the high cost of the system.

Figure 2.1. Schematic drawing of (a) thermal inkjet, (b) electrostatic inkjet, and (c) piezoelectric inkjet printing [47].

Figure 2.2. Schematic drawing of aerosol-jet printing techniques [47]

Table 2.2. Comparison of droplet-based printing: inkjet and aerosol-jet printing techniques [25, 27, 63-73].

Printing techniques	Ink viscosity (cP)	Minimum line width (μm)	Layer thickness (μm)	Speed (m/min)	Advantages	Disadvantages
Inkjet	<20	30-50	<1	15-500	<ul style="list-style-type: none"> - Contactless digital printing method - Low possibilities of cross-contamination - Possible to print on various types of substrates, from rigid to flexible - 3D coating with non-contact processing - Lower wastes of costly materials - Possible to print with multi-materials and multilayer pattern 	<ul style="list-style-type: none"> - Nozzle clogging usually occurs. - Sometimes, spread-out dots can be found. - Constrain in rheological properties of ink formulation - Formation of coffee stain pattern (Coffee-ring effect) prevents the depositing uniformity. - Unable to printing on non-planar surfaces - Lower throughput comparing with the conventional printing methods
Aerosol-Jet	1-5 (UA) 1-100 (PA) *	>10	0.1-2	Up to 12	<ul style="list-style-type: none"> - Contactless digital printing method - Possible to print on any types of the substrate, from rigid to flexible - Capable of printing on non-planar surfaces and 3D surfaces/ structures - High-resolution printing technique with accurate alignment system - Elimination of nozzle clogging issue - Several options of deposited materials - Decrease the possibilities of cross-contamination - Possible to print with multi-materials and multilayer 	<ul style="list-style-type: none"> - Additional supplying systems are required, e.g., sheath gas and cooling system. - Lower throughput comparing with the conventional printing methods

* UA = Ultrasonic Atomizer, PA = Pneumatic Atomizer

2.4 Electronic components printed on soft surfaces

Current fabrication techniques and advances in materials enable many more applications in soft electronics that are not possible with planar, rigid circuits [81]. Soft electronic components that are flexible and stretchable while maintaining their performances are intensively studied. The performance characteristics of soft electronics depend largely on the selected materials, the underlying substrates, and the compatibility between them.

In this section, we highlight some stretchable devices that show superior performances in different fields.

Stretchable and foldable integrated circuits

Rigid electronic devices almost reach their performance limit. Therefore, people are looking forward to high-performance, foldable, and stretchable devices. Recent advances in materials and fabrication techniques show that high-performance integrated circuits (ICs) with reversibly foldable and stretchable capability can be produced [82]. These ICs will play an important role in biomedical devices [83-85].

Figure 2.3. Optical images of wavy Si-CMOS inverters on Polydimethylsiloxane (PDMS) under an applied strain along x and y directions [82].

Epidermal electronic system (EES)

A bio-integrated electronic device that is shown in Figure 2.4 is called epidermal electronic system (EES). It measures electrophysiological signals from inner organs, muscle tissues, blood vessels, etc. The EES is aimed to overcome traditional point-contact electrodes. The electrodes attach comfortably to the skin via van der Waals forces, similar to a temporary tattoo. It requires no adhesions or conductive gels; therefore, the EES can function for a longer time. Furthermore, the elastic substrates provide better mechanical supports, comparable to conformal tissues and skin. Their microstructure of electrodes can withstand a large strain without fractures [86]. The EES can be used tremendously for wearable health monitoring devices [87, 88].

Figure 2.4. The integrated EES on skin when it is (a) undeformed, (b) compressed, and (c) stretched [86].

Stretchable light-emitting diodes (LEDs)

The stretchable LEDs are made from ultrathin LEDs and interconnectors in a mesh layout, which are bonded onto Polydimethylsiloxane (PDMS) substrates. They can be wrapped onto curvilinear structures without any damage or loss in operating performances. They can be stretched up to 30-50% elongation

before malfunction [1, 89]. The stretchable LED devices can be useful in applications of optogenetics [90] and light-based therapies and diagnostics [81].

Figure 2.5. Stretchable LED display devices: (a) Stretchable LEDs display devices with microscale LEDs on mesh designs [1], and (b) Organic LEDs with stretchable interconnectors [89].

Stretchable antennas

Antennas are commonly used in radiofrequency (RF) applications. They transmit and receive signals wirelessly. Kubo *et al.* [91] presented a stretchable antenna that is made from a liquid metal enclosed in microfluidic PDMS channels. This antenna shows new characteristics; for example, it can be bent, twisted, and stretched up to 50% of its original length. After being stretched more than 100 times, its radiation efficiency remains almost constant. The stretchable antennas can be integrated with non-planar devices such as wearable electronics devices [92, 93] and body area network [94, 95].

Figure 2.6. The stretchable microfluidic radiofrequency devices. (a) The dependences of resonance frequencies on a stretch ratio [91]. (b) A stretchable RF radiation sensor [96].

Interestingly, PDMS has often been selected as the stretchable substrate due to its stretchability. Apart from its stretchability, PDMS is also transparent, chemically inert to solvents, thermally stable, biocompatible, gases permeable, simple to process, and low cost [97-100]. Therefore, PDMS is widely used in many applications.

2.5 Suspension droplets

A suspension is a heterogeneous mixture of solvents and solid particles. The particles must be sufficiently large for sedimentation. They are usually larger than $1\ \mu\text{m}$ in diameter. Importantly, they do not dissolve, but only get suspended in the medium. The suspension can be distinguished from colloid by the particle's size in which the particle whose dimension as small as 1-1000 nm is called colloid [101]. However, whether it is suspension or colloid, its properties are determined mainly by the nature of the liquid's interface [102].

In this topic, the properties of the suspension will be discussed. In fluid mechanics, liquid's properties such as viscosity and surface tension are often used to describe the behaviours of the liquid. Relevant variables related to those liquid properties, such as stress, strain, shear rate, and viscosity, will be introduced in the following section.

Shear stress (τ) is defined as the magnitude of the force F acting on a unit area A of the material as presented in equation 2.1. The unit of the stress is Newton per unit area (N m^{-2}) or Pascal (Pa).

$$\tau = \frac{F}{A} \quad (2.1)$$

When the stress is applied, deformation of the material is seen. The deformation refers to as the shear strain (γ). The strain is particularly a ratio of displacement of a layer (δl) proportionally to its distance from a reference layer (l). The dimensionless strain can be written by:

$$\gamma = \frac{\delta l}{l} \quad (2.2)$$

The shear rate ($\dot{\gamma}$) or strain rate is a change of strain with unit time t as shown in equation 2.3. It has a unit of the reciprocal second (1 s^{-1}).

$$\dot{\gamma} = \frac{\delta \gamma}{\delta t} \quad (2.3)$$

Substituting the strain from equation 2.2 into equation 2.3, the shear rate becomes

$$\dot{\gamma} = \frac{\delta}{\delta t} \left(\frac{\delta l}{l} \right) = \frac{v}{l}, \quad (2.4)$$

where v is a velocity of a moving fluid and a distance $\delta l = v \delta t$.

Newton's law of viscosity proves that the apparent viscosity (η) is the ratio of the shear stress to the shear rate as presented in equation 2.5 below.

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (2.5)$$

The viscosity is a material characteristic which provides the relation between the shear stress applied to a liquid and a rate of deformation of the liquid. The viscosity is also called absolute viscosity or dynamic viscosity and has a unit of Pascal seconds (Pa s) or N·s m⁻² [103]. A material whose viscosity follows Newton's law of viscosity is called *Newtonian*. Otherwise, it is *non-Newtonian*.

Newtonian fluids are those fluids whose viscosity is independent of the shear rate. Examples of Newtonian fluids are water, air, oils, solvents (i.e., ethanol and acetone), and very dilute dispersions. However, the viscosity is not a constant value as it can be easily affected by various conditions such as temperature, pressure, and flow pattern. Newtonian liquids decrease in their viscosity exponentially when the temperature increases [102].

The non-Newtonian suspensions have a high-volume fraction and do not follow Newton's law. The viscosity of non-Newtonian fluids depends on not only temperature and pressure but also the shear rate [103]. Their fluid mechanics is characterized by the rheology of liquid which relates to the deformation and flow of the liquids [102].

The liquid where its viscosity decreases with increasing shear strain rate is considered as shear-thinning liquid. It is sometimes called pseudoplastic liquid. Shear thinning liquids include blood, yogurt, toothpaste, mud, etc. The shear thinning behaviour can be due to an additive. On the other hand, some non-Newtonian liquids are shear thickening (or dilatant). Their viscosity increases

with shear strain rate. Examples of shear thickening fluids are starch-based liquids and cornflower-based liquids. Furthermore, other behaviour of non-Newtonian liquids is thixotropic; the viscosity is time-dependent; it decreases over time when the shear stress is applied. Rheopectic liquids exhibit the opposite behaviour in which their viscosity increases with time after the shear stress is being applied. Another non-Newtonian liquid is Bingham fluid. It behaves like a solid when subjected to low shear stress, but it flows like Newtonian fluids when the shear stress exceeds some threshold level so-called yield stress (τ_Y). Some materials, such as gels, ice-cream, margarine, lubricating greases are Bingham fluids [102, 103]. Variation of the shear stress and viscosity with the shear rate for Newtonian and non-Newtonian fluids is shown in Figure 2.7.

Figure 2.7. (a) shear stress and (b) viscosity as affected by shear strain rate for both Newtonian and non-Newtonian fluids [103].

Kinematic viscosity (ν) is a ratio of the absolute viscosity μ over the fluid density ρ as shown in equation 2.6. It is often used in a case where the gravitational force is a driving force in the system. The unit for kinematic viscosity is unit area per second ($\text{m}^2 \text{s}^{-1}$) and Stoke (St) [102].

$$v = \frac{\mu}{\rho} \quad (2.6)$$

At the surface of a liquid where liquid molecules are in contact with surrounding vapor molecules, it is called the liquid-vapor interface. Liquid molecules constantly cross this interface until they reach an equilibrium. The interface can be considered as a membrane in tension, and this leads to an identification of a liquid property called surface tension (σ). Surface tension is defined as an interfacial force per unit length and has a unit of Newton per meter (N m^{-1}). The surface tension of a pure liquid decreases linearly when the liquid temperature increases. Moreover, the surface tension is reduced by contaminations, e.g., detergents and impurities [103, 104].

The shape of a water drop can be described by a concept of surface tension, as shown in Figure 2.8. Assuming a spherical drop of water has a radius of R , the circular surface segment has its radius of r which subtends the angle ϕ at the drop center. The pressure difference between the drop interior (P_I) and the surrounding (P_A) is $\Delta P = P_I - P_A$. Therefore, at static equilibrium, the segment can be described as:

$$2\pi r \sigma \sin \phi - \pi r^2 \Delta P = 0 \quad (2.7)$$

Considering $\sin \phi = r/R$, equation 2.7 becomes

$$\Delta P = \frac{2\sigma}{R} \quad (2.8)$$

From equation 2.8, the internal pressure increases with the decrease in the drop size. For a tiny drop, the internal pressure becomes so large that the effect of gravity is negligible, and its shape becomes spherical.

Liquids wet solid substrates. The liquid subsequently adheres to the substrates. The attraction between liquid molecules and the substrate surface is quantified by an angle, called the contact angle (θ). Liquids with $\theta < 90$ degrees is wetting; otherwise, they are non-wetting. On the other hand, the shape of the liquid sitting on the surface is determined by the surface tension and contact angle [103].

Figure 2.8. Forces are acting on a liquid droplet [103].

2.6 Deposition mechanism

The processes involved from the ink being ejected to the formation of drying patterns rely on the physics of droplet spreading and evaporation. In this topic, we will discuss both the phenomena, especially the evaporation of the droplets, which has a significant impact on the printed pattern formation.

2.6.1 Wetting mechanism

The deposition of the ink involves the physics of ink spreading on the surface of the substrate and ink evaporation process. The original work of the

liquid wetting on the surface is done in 1805 by Thomas Young [105]. He found the relationship of the contact angle θ as a result from the balancing of the forces acting on the liquid droplet. These forces consequently relate to the phase difference, so the surface tensions are considered: surface tension of the wetting liquid (σ_{LV}), the surface tension of the solid surface (σ_{SV}), and the solid-liquid interfacial tension (σ_{SL}). Young's equation is given as:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV}\cos\theta \quad (2.9)$$

This equation illuminates the mechanical equilibrium of the contact line where all the forces of the three-phase contact line are balanced. The unit of the surface tension is an energy per unit area (J m^{-2}), but it can be considered as the force per unit length (N m^{-1}). The surface tension and the contact angle are then used to characterize the wetting properties of the droplet deposited on the solid substrates.

The spreading of the drops is the consequence of Young' equation. However, in the case of the rough surface, the wetting dynamic also relies on the surface roughness and how the droplet is placed on the surface, instead of the surface energy of the interfaces. Thus, we will only discuss the wetting on the smooth surface in which the effect of the surface roughness is negligible.

The wetting of the drops on the solid substrate can be categorized into three groups: The widely studied cases include those when the drops are present on the surface. It is called the *partial wetting state* (Figure 2.9a). The contact angle which is influenced by the three surface tensions can be altered when some thermodynamic variables (i.e., temperature and pressure) are added. If the contact angle becomes zero degree when the fluid uniformly covers the solid surface, this

wetting denotes as a *complete wetting state* (Figure 2.9b). On the other hand, by changing the temperature, the contact angle reaches 180° . The drop consequently does not wet the surface and hence remains separated by a film of vapor. It is called *complete drying state* (Figure 2.9c).

The partial state becomes the complete wetting state when thermodynamic effects such as the temperature changes so-called the wetting transition. The distinction between different states determines by the spreading coefficient S , which refers to the surface free energy difference between the partial and complete wetting:

$$S = \sigma_{SV} - (\sigma_{SL} + \sigma_{LV}) \quad (2.10)$$

In case of partial wetting, the coefficient always has negative value because the solid-vapor tension is lower than the summation of the solid-liquid and liquid-vapor tensions. The spreading coefficient is zero when there is a complete wetting state in which the sum of the three tensions is at equilibrium. Consequently, the positive spreading coefficient can be determined in some of the non-equilibrium situations, such as the complete drying state [106].

Figure 2.9. Wetting of the drop on the solid substrates: (a) partial wetting state, (b) complete wetting state, and (c) complete drying state.

If the drop of the pure fluid is placed on a smooth solid surface, the drop will spread by the hydrodynamic flow until it reaches the equilibrium contact angle. Moreover, in the case of complete wetting, the drop will keep spreading until it obtains the thickness restricted by its own volume and possibly by the van der Waals forces. The dynamic of the droplets has received much attention over a fast few decades. However, the wetting problems are complicated due to the unknown form of the droplet during the wetting. Assuming the perfect drop is wet on the flat surface, and the effects of the anchoring of the contact line are negligible, the drop spreads on the surface and its radius increases with increasing time.

In fact, the spreading occurs slowly. The spreading coefficient is not as same as the driving force toward the wetting. The driving forces are only a weak capillary pressure within the drop. This pressure is described as the liquid-vapor surface tension multiplied by the curvature of that interface. Another reason for the slow wetting is the hydrodynamic singularity at the contact line, where the viscous stresses diverge [107].

Industrial applications, for example, painting and coating, need to have an efficient spreading of the aqueous solutions rather than the pure liquid. To enhance spreading, surfactants are added into the droplet to reduce the liquid-vapor interfacial tension and hence increase the spreading coefficient. However, the studies of the spreading of the aqueous solutions are less explored. The influence of the surfactants on two other surface tensions remains unclear. Therefore, the effect of the surfactants on the spreading behaviour requires more studies [108].

2.6.2 Evaporation mechanism of a sessile droplet

Diffusion

The evaporation is a phase change transition from a liquid to a vapor [109, 110]. Evaporation happens simultaneously when the vapor partial pressure in the surrounding gas is lower than the saturation pressure. This phenomenon is called diffusive evaporation, and it cannot be stopped unless the saturation conditions are reached. Evaporation can be described as a transfer of molecules from one to another state (molecular scale), and as a mass flux crossing the liquid/ vapor interface (macroscopic scale).

An evaporation rate of the sessile droplet is induced by three mechanisms: the phase transition at the liquid-vapor interface. Vapor molecules move away from the liquid surface to the surrounding. This second mechanism can be induced by purely diffusive [3, 5, 111], or a combination of diffusive and free convection [112]. The third mechanism is an evaporative cooling and heat transfer to the liquid-air interface [110, 113, 114].

In this topic, the droplet evaporation is considered a process which is controlled by only the vapour diffusion into the surrounding, and therefore it is a basic model describing the droplet evaporation. During the droplet evaporation, the vapour concentration around the surface of the droplet is not homogenous. The vapour concentration at the liquid-vapour interface (c_0) is assumed to equal the saturation concentration (c_s). The vapour concentration decreases away from the droplet interface. The ambient vapour concentration far from the droplet interface (c_∞) is Hc_s . The term H is the gas phase humidity. Thus, the vapour concentration difference in the ambient air $\Delta c = c_s - c_\infty$ is the primary factor

influencing the evaporation. The field of the concentration relies on the mass diffusion balance:

$$\frac{\partial c}{\partial t} = D\Delta c \quad (2.11)$$

where D is the diffusion coefficient of the vapor in the gas phase. Furthermore, the droplet evaporation is a non-saturated process. It is often analysed as a quasi-steady-state process, where the diffusion time of the vapour t_D is lower than the evaporation time t_F :

$$\frac{t_D}{t_F} = \frac{R^2}{Dt_F} \approx \frac{c_s - c_\infty}{\rho_L} \approx \frac{c_s(1-H)}{\rho_L} \ll 1 \quad (2.12)$$

Assuming that the vapour concentration at the drop interface c_0 is much lower than the liquid density ρ_L , this ratio can be simplified as a ratio of densities. The vapor concentration field rapidly regulates before the time to evaporation. For example, the diffusion time for the pure water with the volume of microliter is about 10^{-2} seconds, while its evaporation time is much higher in the order of magnitude of 10^2 seconds.

According to these assumptions, the vapour concentration field can be considered as the solution of the Laplace equation:

$$\Delta c = 0 \quad (2.13)$$

The evaporation mass flux occurring at the interface is determined by the diffusion of molecules at the interface to the surrounding air. Therefore, Fick's law is introduced to explain the outward mass flux called J in any point of the interface:

$$J = -D[\vec{\nabla} \rho]_i \cdot \vec{n} \quad (2.14)$$

where $[\vec{\nabla}\rho]_i$ is the vapor concentration gradient normal to the interface and $\vec{n}$ is the normal vector to the interface. The subscript i shows that the gradient is defined by the interface. Particularly, the evaporation rate $\dot{m}$ is described by the spatial integral of the local mass flux J over the surface ds :

$$\dot{m} = \frac{dm}{dt} = \iint J ds \quad (2.15)$$

As mentioned above, the evaporation is considered as quasi-steady and controlled only by the vapour diffusion. The system is implied as isothermal process. Assuming a spherical droplet of radius R and evaporating into the inert gas surrounding, Maxwell (1877) [115, 116] modelled the evaporation mass as follows:

$$-\frac{dm}{dt} = 4\pi RD(c_s - c_\infty) \quad (2.16)$$

Thus, the local evaporation mass flux is uniform along the interface of the drops. Assuming all the parameters in equation 2.16 are constant, the relation between the droplet radius (or droplet area) and the evaporation time can be deduced that they both have the linear relationship.

Convection of fluids

In fact, the evaporation is also induced by other heat and mass transfer mechanisms such as convection and radiation. In this section, the evaporation is driven by the heat from the substrate. The microgravity setup is used to minimize the effect of gravity. Therefore, additional factors such as the flow of the surrounding gas (Stefan flow) and the flow inside the droplet (Marangoni flow)

are considered. They can produce thermos-gravitational, thermos-capillary, and thermos-solutal convections.

The intermolecular forces attracting the molecules in the liquid phase are typically the van der Waals forces or hydrogen bonds. However, they are applied to the molecules inside the drops rather than the one near the liquid-vapour interface. The concept of the attraction of intermolecular forces is applied to the surface tension. In principle, the surface tension can be described as the force needed to bring a molecule inside the drops of liquid to their interface [117]. It mainly depends on the type of fluid, temperature, and pressure. The surface tension σ is denoted as a function of the temperature T in the pure compound problems as follows:

$$\sigma = \sigma_0 - \varphi(T - T_0) \quad (2.17)$$

$$\varphi = -\frac{\partial \sigma}{\partial T} \quad (2.18)$$

The surface tension relates to Marangoni effect which generally occurs at the interface and induces the flow inside the liquid drops. This effect is well known as the tears along the side of glass wine. The wine which is the combination of water and alcohol rises on the side of the glass by capillary forces and consequently evaporates. During the evaporation, the alcohol which has the lower surface tension evaporates faster and locally increases the surface tension of the wine. As a result, more fluid is drawn to the side of the wine glass, increasing more flow.

As mentioned earlier, flow induced by Marangoni effect is influenced by the concentration and the temperature gradients in the case of droplets. The temperature gradient along the interface produces a tangential stress. Therefore,

the surface tension forces are not in equilibrium and cause the flow from the area which has the lower surface tension (hotter region) to the higher surface tension area (colder region) inside the drops. The flow stops when the equilibrium is reached. If assuming the tangential stress at the liquid-gas interface is zero, the stress can be compensated by the viscous friction in the interface. To conserve the mass flow in the vertical plane, the direction of the speed of the flow in lower layers should be opposed to those in the upper layers near the interface (Figure 2.10b). Furthermore, additional flows due to the buoyancy forces and evaporation-induced outward flow also influence the thermo-gravitational, as shown in Figure 2.10a. The whole phenomena make the complex flow in the evaporating problems.

The thermos-gravitational flow likely pushes the fluid in the cold area by its capillary forces. This flow is predominant when the droplet size is twice the size of the capillary length L_C which is described as follows:

$$L_C = \sqrt{\frac{\sigma_{LV}}{g(\rho_L - \rho_V)}} \quad (2.19)$$

where σ_{LV} is the surface tension at the liquid-vapor interface, g is the gravitation, ρ_L and ρ_V are the liquid and gas density, respectively. The thermos-capillary flow tends to occur when the length reaches the low values, and it shows quantitatively the type of instability that likely to happen. Moreover, the dynamic Bond number (Bd) represents the ratio of the Marangoni number (Ma), describing the Marangoni effect, over the Rayleigh number (Ra) in natural convection:

$$Ra = \frac{\beta g \Delta T L^3}{\nu \alpha} \quad (2.20)$$

$$\text{Ma} = \frac{-\frac{d\sigma}{dT} \Delta T L}{\mu \alpha} \quad (2.21)$$

$$\text{Bd} = \frac{\text{Ra}}{\text{Ma}} = \frac{\beta g \rho}{-\frac{d\sigma}{dT}} \quad (2.22)$$

where β is the thermal expansion coefficient, L is the characteristics length, ν is the kinematic viscosity, α is the thermal diffusivity, and μ is the dynamic viscosity.

Figure 2.10. Two types of flows induced by the temperature gradient: (a) gravitational flow due to density variation and (b) capillary flow due to surface tension variation [117].

2.6.3 The dynamic of the contact line during the evaporation

Considering a pure liquid drop on an ideal solid substrate (smooth and homogenous), the three different phases- that are surface tensions of solid-liquid (σ_{SL}), liquid-vapor (σ_{LV}), and solid-vapor (σ_{SV}) is shown in Figure 2.11. The relation between the three-phase contact lines (TCLs), and the contact angle θ , is explained by Young's equation (1805) [118] as in equation 2.9. As a result of the surface tension from Young's equation, they suggest that only one contact angle is presented at the equilibrium. However, a small range of contact angles can be

found at the equilibrium instead of the certain contact angle. This range is known as hysteresis of the contact angle.

Therefore, these values are always between the upper- and lower-limited contact angles so-called an advancing contact angle θ_a and a receding contact angle θ_r , respectively. The contact angle hysteresis can be derived as the difference between the two angles [119].

$$\Delta\theta = \theta_a - \theta_r \quad (2.23)$$

Both have different effects on the wetting conditions; The advancing contact angle is denoted as an increase in contact area between the liquid and the solid, representing the wetting dynamic on a completely dry substrate. On the other hand, the receding contact angle relates to a decreasing contact angle, which is the results from a retraction on a wet substrate. The value of the hysteresis was typically as large as 50 degrees [120], and often bigger than the measurement error.

Figure 2.11. The schematic of the liquid drops on the solid substrate showing the quantities in Young's equation.

Many studies on the sessile droplet evaporation on hydrophilic [4, 5, 121, 122], hydrophobic [123-125], and even super-hydrophobic [126-128] showed the different modes of evaporation, which depends tremendously on the TCL

dynamics [121, 129-131] and the contact line hysteresis [127]. After the TCL is pinned and then evaporated, a drop that its contact angle decreases over time, but not its radius, is considered to evaporate at a constant contact radius (CCR) mode. While a drop evaporation corresponds to a recession of only the TCL, it refers to the evaporation in a constant contact angle (CCA) mode (Figure 2.12) [121]. In general, drop starts evaporating in the CCR mode and then convert to the CCA mode when the receding contact angle θ_r is achieved. The radius is becoming smaller, and the TCL move toward the centre of the drop. Furthermore, the more complex evaporation mode exists when these two modes, i.e., CCR and CCA modes, are in cooperate, especially at the end of the evaporation process where the switching of these two modes is often found [132].

There is a small region close to the TCL, which is called micro-region [133]. The curvature of the liquid-air interface in this region is influenced by the strength of the solid-liquid interactions. This region is often applied in modelling of drop evaporation when surface temperature is larger than liquid's boiling point [134].

Figure 2.12. The sketch representing (a) the constant contact angle (CCA) mode, and (b) the constant contact radius (CCR) [135].

In fact, the drop evaporation with the pinned TCL is resulting in a global evaporation rate proportional to the wetting radius [4, 136, 137]. The contact angle also changes relative to the evaporation rate [5, 128, 129]. Furthermore, the length of the TCL largely affects the evaporation rate. We can see that the droplet evaporation is related to the TCL dynamic. The TCL dynamic determines the evaporation process (i.e., CCA or CCR mode). Moreover, the TCL dynamic is influenced mainly by two variables: the substrate material properties (surface roughness) and physio-chemical properties (surface energy) [138-141].

The studies of the physiochemical properties of the evaporation process and its mechanism are lesser in terms of number as compared to that of the substrate's roughness. A few works studied the evaporation of the water droplet on the different surfaces such as hydrophobic aluminum [137], hydrophilic glass,

and super-hydrophobic alkylketene dimer (AKD) [142]. They found that the TCL dynamic and the evaporation time changed according to the type of substrate. However, other parameters apart from the surface energy, such as diffusion and surface roughness were not controlled. That means the results of the evaporation in their experiment are not only dependent on the surface energy.

The good example of the study on the effect of the substrate surface properties on the droplet evaporation in the configuration of the pinned TCL is from Sobac and Brutin (2011) [143]. They performed the test by modifying the surface (surface roughness and surface energy) through the micro-coating of the different materials, allowing the identical thermal properties across the surface. Various types of fluid droplets are used under the same atmospheric conditions. Thus, the broad range of properties can be explored, including the dynamic of the TCL and a range of wettability as well as how these parameters influence the dynamics of the evaporation process. They found that the influence of the contact angle is negligible compared with the TCL dynamics when the angle is less than 40° . The evolution of the evaporative power that is the rate of heat absorbed by the droplet from the substrate consequently follows the evolution of the wetting radius, regardless of the behaviour of the TCL. All the experimental data of the effect of surface properties in sessile droplet evaporation are in good agreement with other similar works [5, 111], presenting the evaporation process as the quasi-steady and driven dominantly by the diffusion. The evolution of the drop mass is independent from the drop size and the initial contact angle [128].

Shanahan and Sefiane (2009) [135] provided the preliminary mathematical explanation of this phenomenon. Assuming that a drop with spherical cap geometry possesses the contact angle θ and contact radius R . In this

case, there is no effect of the gravitational flattening. The drop volume (V) and liquid-vapor surface area (A) are given by

$$V = \frac{\pi R^3}{3} \frac{(1 - \cos \theta)^2 (2 + \cos \theta)}{\sin^3 \theta} \quad (2.24)$$

$$A = \frac{2\pi R^2}{(1 + \cos \theta)} \quad (2.25)$$

2.6.4 Fluid flow in evaporating droplets

The macroscopic evaporation of the sessile droplet was mentioned in the previous section. The evaporation mode and time determine the evaporation characteristics of the droplet. The gap from the evaporation of dispersed droplets to the formation of the deposition patterns is still missing. In this section, the fluid flow in the drying droplet will be discussed.

The particle is being deposited when the droplet is pinned. During pinning, the evaporative flux from the droplet surface drives the radial outward flow, which carries the particle to the contact line. The liquid that evaporates at the contact line needs to be replenished by liquid from the interior of the droplet in order to maintain the pinning. Therefore, a compensating flow convoy the liquid from the interior of the droplet to the contact line region [3, 4]. The flow is influenced by the capillary effect. The capillary effect is applied for the droplet with a free surface and settled on the solid substrate. The liquid-vapour interfacial tension across the droplet surface is not uniform, which induces the capillary flows from the droplet surface to the contact line. This capillary flow is a radial outward flow [144]. In addition to the compensating flow, the suspended particles arrive at the microregion, forming a ring-like pattern. The accumulation

of the particles later reinforces the pinning, and hence generate a self-pinning mechanism [7].

Theoretically, the amount of radial flows can be calculated by mass conservation with a known evaporative flux J . For a spherical droplet, it can be considered as an axisymmetric droplet in a cylindrical coordinate system (r, z) . Assuming a small control volume of width dr , located at distance r from the droplet center. Therefore, to satisfy mass conservation, the rate of change of the amount of fluid within the control volume must equal to the inflow of liquid into the control volume minus the amount of liquid that evaporates from the drop surface, as shown in equation 2.26 [4].

$$\frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} Q - \frac{1}{\rho_L} J, \quad (2.26)$$

where $h(r, t)$ is a local drop height, t refers to time, Q is volume flow, and ρ_L represents liquid density. Moreover, $\partial h / \partial t$ can be computed by combining the total rate of volume change with an assumption that the droplet maintains its spherical shape throughout the evaporation. The evaporation flux can be found from a vapor concentration field. Therefore, once those parameters are known, we can obtain the liquid flow Q inside the droplet [145].

Although the volume flow can be found by the mass conservation, the velocity of an actual flow inside an evaporating droplet remains unknown. The lubrication approximation is often used to describe the velocity field inside the droplet with low contact angle [144, 146, 147]. Furthermore, Marangoni stress could influence an additional recirculation near the contact line [6, 148, 149], which has not been addressed in the mass conservation equation. On top of that, if the contact line is not pinned, the moving contact line can contribute to an

addition flow [146, 147]. Therefore, the actual flow field inside the droplet remains unknown and needs accurate experimental investigations to confirm with the theories or simulations.

Figure 2.13. Schematic illustration of an axisymmetric droplet that is evaporating in a cylindrical coordinate system [145].

2.6.5 Sedimentation

Sedimentation is a characteristic behaviour of particles in the suspension to sink to the bottom of the container. It occurs when the density of the dispersed particles is greater than that of the liquid medium. The particles sink to a container bottom as a result of external forces, which can be gravitational force, centrifugal force, and electromagnetic force (depending on magnet position). The larger particle consequently sinks faster. In some cases, a dense packing caused by particle accumulation can be observed [102].

In stokes flow at zero Reynolds number (Re), a spherical particle falls steadily with a terminal velocity u_s . The velocity can be found by balancing the weight of the particle and the drag force acting on it [150]. The weight is caused by the gravitational force f_g as seen in equation 2.27.

$$f_g = \left(\frac{4\pi a^3}{3} \right) \Delta\rho g \quad (2.27)$$

The drag force is influenced by the viscous force,

$$f_d = -6\pi\mu a u_s, \quad (2.28)$$

where a is a radius of the particle, g is gravity, $\Delta\rho = \rho_s - \rho_L$ where ρ_s is the density of the solid particle, ρ_L is the liquid density, and μ is the liquid viscosity. Therefore, the settling velocity of the particle can be described by equation 2.29 [151].

$$u_s = \frac{2\Delta\rho g a^2}{9\mu} \quad (2.29)$$

This Stokes settling velocity is valid in a viscous regime where the viscous force is dominating and $Re \ll 1$. The Reynolds number is dimensionless number describing a ratio of the inertial force to viscous force, as shown in equation 2.30. It firstly introduced by Osborne Reynolds to characterize the transition between laminar flow and turbulent flow.

$$Re = \frac{\rho u a}{\mu} \quad (2.30)$$

Sedimentation can be divided into two systems dependent on the dominant force, either Brownian motion or gravity. The Peclet number (Pe) helps to quantify the dominant driven force. The Pe is a ratio of time for the particle to diffuse its own radius (t_B) to the time the particle takes to fall its own radius (t_u). Thus, the Pe can be seen as in equation 2.31.

$$Pe = \frac{t_B}{t_u} = \frac{u_s a}{D} = \frac{\Delta\rho g a^4}{k_B T}, \quad (2.31)$$

where D is a diffusion coefficient, k_B is Boltzmann's constant, and T is temperature.

A sedimentation system that $Pe \ll 1$ is called Brownian sedimentation in which the particles settle randomly by Brownian motion. Conversely, a system with $Pe \gg 1$ is considered non-Brownian sedimentation. Particle configurations are complex and cannot be predicted during particle settling [152].

After the droplet fully evaporates, the leftover pattern appears on the substrate. The deposition patterns are influenced by many factors. Therefore, the next section will be discussing the involved mechanism of pattern formation.

2.6.6 Formation of deposition patterns

In this section, the typical shapes of the deposition patterns will be discussed as resulted from the internal flows. Three different deposition patterns are shown in Figure 12.4.

The ring-like deposition pattern is formed due to the radial outward flow during the pinning of the contact line. During the pinning, the droplet is assumed to have a no-slip boundary along with the solid-liquid interface and the free surface at liquid-vapour interface with the curvature of spherical shape [144]. The radial flow is caused by the non-uniform evaporation flux at the liquid-vapour interface as the evaporation flux at the TCL is being the highest. At the TCL, the liquid evaporates faster than the droplet's apex. The liquid at the apex must flow to the TCL to maintain the droplet pinning. Therefore, the radial outward flow that is induced by the capillary forces is produced to compensate the loss of liquid at the TCL. The radial flow also carries the particle to be deposited at the contact line [153, 154], forming the ring-like pattern, as shown in Figure 2.14a.

The uniform layer, as shown in Figure 2.14b, has a diameter equal to the initial contact diameter of the droplet. The uniform deposition pattern is formed due to the attractive forces between the particles and the substrate. The attractive forces are electrostatic and van der Waals forces, which can be controlled by the pH level of the suspension or additional surfactants [155].

The temperature gradient along the liquid-vapour interface or non-uniform surface tension caused by a surfactant concentration gradient [156] (or both) can induce the Marangoni flow. The flow recirculates the liquid from the contact line back to the apex [6, 157]. Therefore, the presence of the central bump deposition pattern is shown (Figure 2.14c).

The three different flows can occur concurrently within an evaporating droplet. However, the final deposition pattern is resulted from the combination of these flows, while its morphology follows the most vigorous flow.

Figure 2.14. Three different deposition patterns caused by different internal flows: (a) a coffee-ring pattern, (b) a uniform deposition pattern, and (c) a central bump pattern [155].

2.7 Viscoelastic behaviour of soft substrates

Viscoelastic behaviour combines unique properties of both the elastic and viscous properties. In this section, the viscoelastic property of soft substrates will be discussed. However, the relevant elastic and viscous properties of the soft substrates will also be reviewed.

2.7.1 Elasticity

The elasticity of materials refers to the ability to return to its original shape after deformation. The body deforms under the loading, and it can revert to the original shape after the load was removed. The good example is rubber. It exhibits elastic deformation much more than other kinds of materials. Some of them have the elastic strain up to 1000%, while the crystalline materials only possess that of less than 0.5% [158].

In case of isotropic materials – which have the same properties in all direction – they present the isotropic elasticity. When the uniaxial tension is applied in x-axis, the tensile strain is $\epsilon_x = s_x/E$, where E is Young's modulus, sometimes known as modulus of elasticity, and s_x is the stress in x-axis. Uniaxial tension also causes the lateral strains $\epsilon_y = \epsilon_z = -\nu\epsilon_x$, where ν is the Poisson's ratio. In fact, the stress s_x causes a contribution $\epsilon_x = s_x/E$, and the stress s_y and s_z lead to Poisson contraction $\epsilon_x = -\nu s_y/E$ and $\epsilon_x = -\nu s_z/E$, respectively. Considering these Poisson's contraction, the strain contribution from Hooke's law [159] is given by:

$$\epsilon_x = \left(\frac{1}{E}\right)[s_x - \nu(s_y + s_z)] \quad (2.32)$$

Then, a shear strain which is affected only by the shear stress can be described as:

$$\gamma_{yz} = \frac{\tau_{yz}}{G} = 2\epsilon_{yz} \quad (2.33)$$

where G is the shear modulus. For isotropic elasticity, the similar formula apply to all directions:

$$\epsilon_x = \left(\frac{1}{E}\right) [s_x - \nu(s_y + s_z)] \quad (2.34)$$

$$\gamma_{yz} = \frac{\tau_{yz}}{G} \quad (2.35)$$

$$\epsilon_y = \left(\frac{1}{E}\right) [s_y - \nu(s_z + s_x)] \quad (2.36)$$

$$\gamma_{zx} = \frac{\tau_{zx}}{G} \quad (2.37)$$

$$\epsilon_z = \left(\frac{1}{E}\right) [s_z - \nu(s_x + s_y)] \quad (2.38)$$

$$\gamma_{xy} = \frac{\tau_{xy}}{G} \quad (2.39)$$

In addition, the shear modulus depends on E and ν for the isotropic materials. Their relation is expressed by considering the Hooke's law with the Mohr's strain circle diagram [160, 161]. The shear modulus G is denoted as:

$$G = \frac{E}{2(1 + \nu)} \quad (2.40)$$

Another type of elastic modulus is the bulk modulus B , which is the relation between the volume strain V and the mean stress:

$$\frac{\Delta V}{V} = \left(\frac{1}{B}\right) s_m \quad (2.41)$$

where the mean stress $s_m = (s_x + s_y + s_z)/3$. The bulk modulus is also a function of E and ν . Considering the volume strain produced by a state of hydrostatic stress, $s_m = s_x = s_y = s_z$, the bulk modulus is expressed by:

$$B = \frac{E}{3(1 - 2\nu)} \quad (2.42)$$

The Poisson's ratio ν typically is 0.2-0.4. For the isotropic materials, the ν cannot exceed 0.5, if it does, the bulk modulus would be negative, implying that the increase in pressure causes the rise in volume [158]. As mentioned

earlier, any four elastic constants (E , ν , G , and B) can be rewritten in terms of two others.

The elastic moduli also depend on pressure, temperature, and strain rate. The pressure is a component to determine the tensile stress and Young's modulus. The tensile yield stress and Young's modulus increase with increasing hydrostatic pressure. Moreover, the pressure dependence of the elastic modulus is typically greater for polymers compared to polycrystalline metals. The polymers have high yield stress in relation to their modulus. The ratio of yield stress to bulk modulus of crystalline metals is typically 0.001-0.01, while that of polymers is around 0.02 or higher [162, 163].

The elastic moduli of the polymers are more temperature-sensitive than those of the metals. The temperature dependence of the polymers is related to only thermoplastic polymers, which has significant effect near the glass-transition temperature and the melting point. It is due to the chemical bonding of the polymer molecules. The covalent bonds in the crosslinks break and thus the crosslinked polymers melt. The stiffness of polymers at the ambient temperature depends mainly on glass-transition temperature, geometry, and crystallinity of the polymers [158, 164].

2.7.2 Viscous behaviour

The deformation with viscous behaviour is irreversible. The strain remains after the stress is removed from the fluids. Ideal viscous behaviour is called Newtonian behaviour. It occurs when the relationship between the stress and strain rate is linear. The viscosity of liquids has been mentioned earlier. In

this section, we introduce a dimensionless number to determine the behaviour of the soft substrates, whether elastic, viscous, or viscoelastic responses.

Deborah number (De) is a dimensionless number which is used to characterize the fluidity of the material. In general, the De is a ratio of a material relaxation time λ to the studied time scale t_f of the flow of that material. The relaxation time is computed from a time-dependence flow, whereas the flow time equals to D/V , where D is a characteristic length scale and V is a characteristic velocity of the flow [165]. For dispersions, the De is a ratio of a stress relaxation time λ of the dispersion to an experimental time t_f . Therefore, it acts as a characteristic time for rheological response of the materials to happen. Theoretically, the viscous flow refers to a decay of elastically stored energy in materials. The particles in dispersed systems commonly diffuse from a high-energy state to a lower-energy state. If the system is deformed, its structure will be disturbed which leads the particles into a higher energy state. The system therefore remains a new structure until the particles diffuse to the original low-energy state. The De is given by:

$$De = \frac{\lambda}{t_f} \quad (2.43)$$

If $De \gg 1$, the systems present an elastic response. In contrast, if $De \ll 1$, the systems show a viscous response. When $De \sim 1$, a viscoelastic response is considered [102, 165].

2.7.3 Viscoelasticity

Some of the rubbers exhibit the viscoelastic properties- that is the additional time-dependent deformation. Under the applied loading, there is the elastic response, yet there is the deformation which increases with time. The viscoelasticity is sometimes confused with creep, which is denoted as the time-dependent plastic deformation [166]. Viscoelastic strain in metals and ceramics is usually tiny, so it is always negligible. However, it significantly presents in many polymers, particularly in the rubbers.

Viscoelasticity is in analogy with the damping of the vibration. The viscoelastic strains are often undesirable. It causes interference with the precise measuring system. Also, the damping energy can be released as a heat loss, which typically produces the unwanted temperature rise. Viscoelastic behaviour can be modelled mathematically with the ideal spring and dashpot to represent the elastic and viscous behaviour so-called rheological models [158]. There are several models to describe the viscoelasticity of the materials: Maxwell model [167], Voight model [168], Voight-Maxwell model [169], and Non-linear model [170].

Leaching of an uncured polymer

A widely used substrate that possesses viscoelastic property is PDMS. It has been used in many works because of its unique properties, especially the superior elasticity. PDMS is a crosslinked polymer of a based oligomer and a cross-linking agent. Therefore, it is possible that the residual un-crosslinked oligomer may leach from the bulk polymer due to curing conditions [171]. PDMS

curing depends on time and temperature. It will not reach 100% crosslinking, even after extensive curing. The residual oligomer is left uncrosslinked and can be extracted by organic solvents [172]. The residual oligomer is sometimes called low molecular weight (LMW) species [173-175]. The LMWs can freely diffuse from the bulk polymer to the surface. Therefore, the undesired LMWs can alter the PDMS surface properties. Several studies showed that the LMWs promoted the substrate hydrophobicity, even after the surface treatment by a plasma. To prevent the LMW issues, the uncured oligomer can be eliminated by serial extraction with different organic solvent [172], extended curing time to increase the crosslinking [174], or removal by Soxhlet extraction [173].

2.8 Influence of soft substrates on the droplet evaporation

2.8.1 Influence of soft substrates on the pure water droplet evaporation

Several works demonstrate that the soft substrate has the direct impact on the TCLs of the sessile drop causing by the interfacial forces [19, 20]. It is possible to control the evaporation mode and time by tuning Young's modulus of viscoelastic substrates. In the case of the sessile drop evaporation on a non-heated substrate, the solid-liquid interface has a crucial role due to its influence on the contact line dynamic and hence the evaporation rate.

When the sessile drop is sitting on an ideal substrate at equilibrium, the interfacial forces between three phases are balanced, and tension is consumed on the substrate. The horizontal tensions typically are balanced by the surface energies of the liquid-solid and the solid-gas interfaces. The vertical tension is also counted into the system, in particular for the soft substrates, because its force

deforms the substrate beneath the drop [24]. However, the deformation of the substrate can occur in the case of a thin substrate with the materials that have Young's modulus higher than ~ 100 MPa. The deformation caused by the liquid drop can be determined by the cantilevers sensors [176].

Lopes and Bonaccorso [19] performed the test showing that deformation of the viscoelastic substrate caused by the interfacial and capillary forces affects the evaporation of sessile drops of pure water (18.2 M Ω cm ultra-pure water). The result showed that the deformation could control the evaporation. Therefore, they came up with the relation between the evaporation mode and the substrate stiffness. To investigate this relationship, the substrates are cast via a spin-coating process by varying the mixing ratio of the oligomer (base) and the cross-linker (curing agent) of the PDMS. The substrates with a range of elasticity are made (Young's modulus ranging from 0.02 to 1.5 MPa, and a thickness of 60 μ m). The drop evaporation is recorded by the top and side view using two Charge-coupled device (CCD) cameras, which were placed orthogonal to each other. Thus, the initial contact angle and the initial contact radius are measured, independent of the substrate.

All drops initially have similar contact radii. In the initial phase of evaporation, their evaporation rates when drops are evaporated in CCR mode exhibit the same trends, assuming that the evaporation rate is proportional to the contact radius of the drop [177-179]. As the evaporation continues, the influences of the substrate start to affect the evaporation rate, which increases the difference between the drop volume on different substrates. They found that the drops on less stiff substrates (lower Young's modulus) evaporate faster than on the stiffer substrates (higher Young's modulus). In addition, the thicker PDMS substrates

reduce the contact angle of the drops, which therefore produces slightly shorter evaporation time.

The mechanism behind the effect of the stiffness on the evaporation time of identical drops is described as follows: The normalized contact radii to the initial contact radii are plotted as a function of the evaporation time. The drops on the less stiff substrates tend to have a longer evaporation time in the CCR mode. When the normalized contact radii are plotted as a function of the contact angles, they found that the drops evaporate in the CCR mode and consequently switched to the CCA mode when the contact angle θ reach the receding contact angle θ_r . Then, the contact radius of the drops decreased rapidly, which leads to the changes of the drop geometry due to the high evaporation rate.

To sum up, the elasticity of the substrate affects the drop evaporation on the substrate. During the evaporation, the receding contact angle determines the transition time from CCR to CCA mode. The less stiff substrates tend to have the smaller receding contact angle, which lengthen the duration of the CCR mode and hence shorten the total evaporation time. Therefore, by tuning the substrate elasticity, it was possible to control the dynamic of the TCL and to predict the total evaporation time of the drops.

2.8.2 Influence of soft substrates on the suspension droplet evaporation

Previously, we have discussed the drop evaporation of the pure liquid which left no strain on the substrate after the evaporation. In this topic, a particle deposition from the evaporation of a suspension droplet is presented. The evaporation of nanoparticle suspension droplets on the surface can create many

types of the deposit patterns, including a single ring (so-called coffee ring) [180-182], multiple rings [183, 184], central bump [182], and uniformly distributed pattern [13]. These deposits are usually the results from the interplay of the process associated with the evaporation of the water/ solvent [180] such as the pinning and receding of the TCLs [106, 180, 185], the evaporative cooling, and the convective flow inside the drop due to Marangoni effects [144, 147, 186]. However, there are many more factors results in a wide range of pinned and receding TCLs such as advancing and initial contact angles; solute and particles concentration and compositions; surface roughness of the substrate; and the surrounding conditions (mainly the temperature and the humidity).

As mentioned in the previous section, the evaporation mode and time are possible to control by tuning the elasticity of the substrates. Instead of the pure liquid, the water-silica suspensions are then used to investigate the influence of substrate elasticity on particle deposition patterns. The diameter of the silica particle is $2.01 \pm 0.22 \mu\text{m}$. The PDMS with different mixing ratio is used, giving a range of the elasticity with a thickness of 3 mm. The suspensions are prepared by the diluting a silica suspension in ultra-pure water with different loading content. All experiments are done in the controlled environment (controlled temperature and humidity). The setup is similar to that of the drops evaporation of the pure water, except the inverse microscope to observe the contact line of the drop from the bottom view.

As shown in Figure 2.15, the movement of the TCLs can be described by balancing the main forces acting on them. Lopes and Bonaccorso [20] found that the receding velocity of the TCL during the evaporation of pure liquids acting on

them is derived by the balancing of the driving and resisting contributions as follows;

$$\sum \dot{W} = 0 \rightarrow \dot{W}_{cap} + \dot{W}_{def} + \dot{W}_{CL} = 0 \quad (2.44)$$

where $\dot{W}_{cap}$ is the work rate done by the capillary force to move the contact line and can be expressed by

$$\dot{W}_{cap} = 2\pi R U_r \sigma_{LV} (\cos \theta_r - \cos \theta_0) \quad (2.45)$$

The receding speed of the contact line $U_r = -dR/dt$, σ_{LV} is the surface tension of the liquid, R is the drop's contact radius, θ_r and θ_0 are the receding and equilibrium contact angle, respectively. While the rate of change of work related to the deformation $\dot{W}_{def}$ is derived by the deformation energy as

$$\dot{W}_{def} = 2\pi U_r h_{rim} \sigma_{LV} (1 - \Delta) \quad (2.46)$$

where h_{rim} is relatively proportional to $\sigma_{LV} \sin \theta / E$ [178, 187], E is the Young's modulus of the substrate. The constant Δ represents the dissipation part [188]. The third term is the rate of change of work occurred when the contact line resists the movement, also known as contact line friction dissipation. Thus,

$$\dot{W}_{CL} = -2\pi R \mu_f U^2 \quad (2.47)$$

where μ_f is a friction parameter and U is the spreading speed. The receding velocity of the contact line is the result after derived the above equation;

$$U_r = \frac{\sigma_{LV}}{\mu_f} \left(\cos \theta_r - \cos \theta_0 + \frac{C \sigma_{LV} \sin \theta_r}{RE} (1 - \Delta) \right) \quad (2.48)$$

The term C is the proportionality constant. This equation is well suited theoretically, and experimentally the contact line velocities of evaporating water drops during the movement of the contact line on the CCA evaporation mode on

deformable substrates. However, it only exists if the contact radius R is much larger than the distant ξ .

Figure 2.15. The schematic drawing of the sessile drop of pure water sitting on a deformable substrate. The deformation of the substrate is not to scale [20].

The evaporation of the water-silica droplet is similar to the evaporation of the water drops on the deformable substrate and can be controlled by the substrate's elastic modulus. The main difference is that there are three stages, instead of two stages in the water drop evaporation, during the water-silica drop evaporation as presented in Figure 2.16. The third stage, which is the final stage of evaporation, appears in the suspension evaporation because of a renewed pinning of the contact line. This second pinning, known as self-pinning [189, 190], results in a thin film of silica particles after the drying of the water.

Figure 2.16. The plot between the normalized contact radius and the contact angle of an evaporating droplet of the water-silica suspensions [20].

In this case, the receding contact angle of the suspension was found to be smaller than that of the pure water, indicating an extra force applied on the contact line due to the accumulation of the particles in the region near the contact line [180, 189, 190]. Thus, the longer pinning time and flow toward the inside of the drop result in the accumulation of the particles at this region.

The deposition patterns and profiles are shown in Figure 2.17. The deposits are rarely found in the outer region on the stiffer substrates, and the particles deposition mostly occurred during the self-pinning period [191], which leads to more particles deposited at the rim of the inner region than the centre of the ring. The second pinning of the drops leaves the deposited particles in the inner region. On the other hand, the outer region represents the area between the initial contact area and the inner region. Also, the maximum height of the deposit is relatively proportional to Young's modulus of the substrates. The deposition in this inner region occurred at the last moment ($t < 2s$), leading to the

readjustment of particle confinement inside the drop. Therefore, the deposited patterns largely depend on the particles distribution inside the drops in the final stage of evaporation. In this work, the particles accumulate at the contact line during the CCA mode, receding of the contact line. However, other works found that the large mobility of the particles occurs when the CCR evaporating mode is dominant [4, 192], increasing the flow toward the contact line.

As mentioned earlier, the softness of the substrate affects the deposited patterns. On stiffer substrates (Young's modulus $E = 1.5$ MPa and 0.22 MPa), there are no deposits in the outer region during the passing of the contact line. While, there is particles agglomeration during the contact line contraction on the less stiff substrate (Young's modulus $E = 0.8$ MPa and 0.02 MPa), leaving the deposited pattern in the outer region.

Figure 2.17. (a) The stains left after evaporation of the water-silica drop on substrates with different Young modulus. (b) the average height profiles of the silica deposits on different substrates [20].

Chapter 3: Thermographic investigation of an evaporation dynamics of a suspension sessile droplet on soft solid substrates

3.1 Introduction

Drying of a droplet on solid surfaces is a complex phenomenon involving many physical branches such as mass and heat transfer, fluid flow, phase transition, and sedimentation of particles. The physical mechanism of droplet evaporation provides fundamental understanding to many research and industrial applications such as inkjet printing [47, 60], thin-film fabrication [193], surface coating [194], and biosensors [195]. Theoretically, the evaporation of a suspension droplet containing dispersed particles can be described as follows: The evaporation begins when the vapor concentration at the liquid-vapor interface is greater than that of the ambient. In particular, the evaporative flux is higher at the contact line. It generates a gradient of evaporative flux across the liquid-vapor interface, which later induces an outward radial flow. The dispersed particles subsequently are deposited upon the completion of the evaporation, forming a ring-like pattern. The formation of the deposition patterns, also known as the coffee-ring effect, has been the subject of intense research efforts in the past two decades [3]. The coffee ring formation is found to dominantly induced by pinning of the contact line [3-5] and suppression of Marangoni flows inside the droplet [6]. Moreover, the coffee-ring formation can be found in most of evaporating systems dispersed with large undissolved colloids [7, 196], nanoparticles [197, 198], and even individual molecules [199]. It is useful in some applications such as self-assembly of particles into dense and ordered

structures [191, 200]. Nonetheless, in applications such as printing [75, 201] and coating [202, 203], the coffee-ring stain may be problematic and need to be suppressed, e.g., by using non-spherical particles [204] or using the additional effect from electrowetting [205].

Among numerous factors affecting the evaporation process, it was found that evaporation mode and time depend most significantly on the liquids and surface properties, as well as the ambient conditions. For instance, liquid density, thermal conductivity, and volatility control the evaporation process and subsequently the deposition patterns [109, 206]. A liquid drop containing higher particle concentration promotes longer pinning time [16, 17]. Surface temperature and wettability also affect the mode of evaporation [207]. Moreover, a heated substrate promotes the evaporation of a sessile droplet to be only in constant contact radius (CCR) mode [17]. It was shown that the constant contact angle (CCA) mode is more profound for evaporating droplets on hydrophobic substrates, whereas the CCR mode is typically prevalent for droplets on hydrophilic substrates [16, 18]. Eventually, higher humidity of the surrounding can prolong the evaporation process [208].

Despite the mentioned factors affecting the evaporation of a sessile droplet and the resulting deposition patterns, the effect of elastic modulus of the surface remains largely unexplored [19, 20]. Theoretically, the liquid-vapor interfacial tension can deform the area vertically at a three-phase contact line (TCL) of the soft surfaces [178]. The elevated height depends on the surface elastic modulus. From the literature, it was demonstrated that a water drop remains pinned for a longer period on a substrate with lower elastic modulus. In particular, the evaporation rate of a sessile droplet depends on droplet geometry,

so surface elastic modulus is bound to affect the evaporation process. Typically, a liquid droplet evaporating in CCA mode requires a longer time to dry than a drop with identically initial contact radius, contact angle, and height, and volume, evaporating in CCR mode [209]. Due to enhanced contact line pinning, a liquid drop evaporating on a soft surface experiences a longer CCR mode of evaporation. This leads to shorter overall evaporation time on soft surfaces. All these factors make use of soft surfaces ideal for optimizing drop evaporation.

3.2 Thermographic measurement of a sessile droplet

Thermography is a non-contact, non-invasive, and non-destructive measuring technique. It is captured using an infra-red (IR) camera, which can detect radiant heat emitted from an object. Theoretically, the object that has its temperature above an absolute zero releases the infrared heat. The amount of heat directly associates with the temperature of the object [210].

The thermographic observation of a sessile droplet evaporating on solid surfaces has been previously conducted [17, 211-213]. From the literature, the IR camera is often placed from the top of evaporating droplets, displaying the temperature distribution across the liquid-vapor interface. However, the sessile droplet typically has a shape of spherical cap or semi-circle, which is not homogenous in shape. Therefore, the thermographic quantities associated with the droplet height must be carefully used.

The works associated with IR investigation of evaporating droplets are presented: Fabien *et. al.* [212] have experimentally investigated, for the first time, the evolution of interfacial temperature across the liquid-vapor interface of the

droplet using the infrared thermography. A sessile water drop is placed on a heated substrate. The interfacial temperature is measured as a function of substrates temperatures. Non-uniform temperature distribution across the droplet interface was observed. The measurement demonstrates a linear increasing trend in the interfacial surface temperature with time. Therefore, a local temperature at the contact line and its dynamics can be found due to these quantitative results. In addition, a local mass flux can be calculated from the measured temperature gradient. Moreover, Patil *et. al.* [17] report the effect of substrate temperature coupled with particle concentration on the deposition patterns. They formulated a regime map for predicting the variation of deposition patterns under the influence of the substrate temperature, particle concentration, and substrate wettability. In their work, the IR camera is used to measure the temperature at the liquid-vapour interface. The temperature data is later used to verify a theoretical model, describing the droplet evaporation.

Theoretically, the kinematics of the drop evaporation is a complex problem because various phenomena are strongly coupled. For instance, several factors have involved in this phenomenon: conduction/ convection inside the liquid droplet, convection/ diffusion in the gas phase, droplet shape correlation with interaction at the liquid-substrate interface, and the conduction induced by the heated substrates [211]. Therefore, there were no direct solutions to solve heat transfer problems at the contact line. Many works have been conducted using several approaches: experimental investigations using visible cameras [214, 215], numerical simulations [5, 129, 216], and theoretical approaches [217-219]. However, the infrared thermography is yet to examine the droplet evaporation on a non-heated and soft substrate. The IR measurement on the non-heated substrate

is more challenging because the droplet has a lower temperature gradient without the heating.

Despite several advantages of the thermography, a dominant uncertainty of the measurement is an IR emissivity (ε) of an investigated object. The value of the ε is often unknown and sometimes is dependent on the viewing angle of the IR camera. Therefore, a correction of emissivity is needed. The selected range of the emissivity must be applied to the object's surface in order to obtain a correct temperature [220]. In principle, the emissivity is a dimensionless number, that is a ratio of radiant energy of the object over that of an ideal black body. A black body is an ideal system that emits the greatest amount of energy at a given temperature. The emissivity is ranging from zero to one as the zero is an absolute reflector, while the black body has the emissivity of one. The emissivity mainly depends on the material and nature of the surface. For instance, an identical material with rough surface exhibits higher emissivity than a smooth-shiny surface under the same observation conditions [221]. Therefore, the correct value of emissivity must be carefully calibrated.

This chapter aims to experimentally investigate the dependence of the surface's elastic modulus on the profile evolution of sessile droplets containing microparticles. From the literature, an evaporative mass rate is indirectly found by the reduction of droplet volume. The contact angle and contact radius are often used to calculate the reduction rate. In this chapter, we focus on the profile temperature of the liquid-vapor interface, together with the profile evolution data, which can be used to compute a local evaporative mass flux [222]. Besides, the experimental results can be useful for validating theoretical predictions and modelling of droplet evaporation [223].

3.3 Experimental methods

3.3.1 Preparation of microparticle suspension

The suspension was prepared by dispersing dry powder of polymer microspheres (FMO-1.3, Cospheric) into pure ethanol (99.9%, Sigma-Aldrich). The microspheres have a diameter of 1-5 μm . The suspension has a concentration of 0.01 wt%, and its density is 790 kgm^{-3} . Prior to the experiment, the suspension was sonicated in an ultrasonic bath (ALD-40100-28H, Alstron) for 30 minutes to ensure the homogenous dispersion of the particles.

3.3.2 Fabrication of elastic substrates

The elastic substrates are made of PDMS (Slygard®184, Dow Corning). The PDMS is well known for high stretchability. The elastic modulus of the PDMS substrates was controlled by varying the mixing ratio between a base monomer and a crosslinking agent: higher the mixing ratio results in substrates with the lower elastic modulus (lesser stiff substrates). The monomer and crosslinking agent were mixed using a magnetic stirrer (MR Hei-Standard, Heidolph) with the spinning speed of 100 rpm for 10 minutes, to ensure a homogenous distribution of the crosslinking agent. The PDMS mixture was subsequently degassed by a vacuum desiccator (F42025-0000, Bel-Art Products). The glass slide (Deckglaser) of dimension $22 \times 22 \text{ mm}^2$ was used as a solid support. The glass slide was cleaned by sonicating in ethanol, deionized water, and dried by an air blow gun to remove contaminations. A spin coater (Spin150i, Spincoating) was used to spin-coated the PDMS mixture on the glass surface with a spinning speed of 4000 rpm for 120 seconds. Consequently, the coated

PDMS samples were cured using an oven set at 80 °C for 48 hours. In this chapter, four sets of substrates were selected by the mixing ratio of 10:1, 20:1, 40:1, and 50:1. The resulting elastic moduli or Young moduli (E) of the substrates were 1.5MPa, 0.7MPa, 0.35MPa, and 0.02MPa, respectively. The Young moduli were measured using a tensile testing machine (Instron 5569, Instron). The thickness of the coated PDMS layer was measured by a laser scanning confocal microscope (VK-X200, Keyence). The measured thickness was $61.14 \pm 3.87 \mu\text{m}$.

3.3.3 Tensile testing

The samples for tensile testing are prepared using ASTM D412 standard with the modification of a one-fourth standard size of the dumbbell-shaped test specimens [100]. The ASTM D412 is commonly used for measuring the tensile properties of thermosetting rubbers and thermoplastic elastomers. The specimens are dumbbell or dogbone shape. The dimensions of the specimens are shown in Figure 3.1. The thickness is 0.2 mm. The specimens were cast in a custom-made silicone mould.

Figure 3.1. Schematic illustration of a dumbbell specimen used for tensile testing. The dimensions are in millimetre and are one-fourth the size of the ASTM D412 standard.

The tensile testing of the PDMS specimens was investigated by an Instron 5569 materials testing system. All specimens were clamped tightly in manual testing grips and were placed parallel to the extension direction. The testing grips were attached to a 10-Newton load cell. The maximum load that can be applied to the specimens is 10 N. The dimensions (i.e., length, width, thickness) of the specimens were measured manually. The specimen's dimensions are pre-determined to the machine. The machine can record the extension through the distance of a moving stage. The rate of grip separation was 1 mm/s. Three replicated specimens for each mixing ratio were used. The tensile testing was performed at room temperature ($\sim 25\text{ }^{\circ}\text{C}$).

Young modulus is used to define the elastic behaviour of materials. It is the ratio of stress over strain within the elastic regime. In fact, Young modulus is an intrinsic property of materials. In this measurement, the machine automatically defines Young modulus within the elastic regime. The average Young modulus is shown in Table 3.1.

Table 3.1 The measured tensile properties of the PDMS.

PDMS mixing ratios	Tensile stress (MPa)	Maximum tensile strain (%)	Young modulus E (MPa)
10:1	4.87 ± 0.67	108 ± 5	1.5 ± 0.20
20:1	3.54 ± 0.86	127 ± 8	0.7 ± 0.14
40:1	1.53 ± 0.59	151 ± 18	0.35 ± 0.03
50:1	0.29 ± 0.13	198 ± 27	0.02 ± 0.007

The elastomers can exhibit elastic behaviour up to very high strain levels. However, the linear elastic behaviour can be calculated via Hooke's law at a

strain level below 40% [224]. Moreover, the measured Young modulus is comparable to other reports [19, 20, 100, 225, 226].

3.3.4 Experimental procedure

Prior to the experiment, the suspension was stored in a water bath (Ultrasonic cleaner, Alstron) set at room temperature (25 °C) for at least 60 minutes. It was mixed thoroughly via the ultrasonic bath before depositing on the surface. A 0.5 mL droplet was generated using a pipette. The droplet was placed onto the PDMS substrates, which is fixed in the custom-made setup (Figure 3.2). A high-speed camera (SA5, Photron) was used to record the droplet geometry from side view, while an infrared (IR) camera (ImageIR® 8300, Infratec) displays the temperature distribution across the liquid-vapor interface of the evaporating droplet (see Figure 3.3). The ambient conditions were monitored throughout the entire experiment to ensure consistent environment conditions. The measured room temperature (T_{room}) was 24.7 ± 0.3 °C, and relative humidity (RH) was $59.1 \pm 1.3\%$. At least five replicated samples were used to ensure consistent results.

Figure 3.2. Schematic drawing of the experimental setup. The mixing ratios (i.e., 50:1, 40:1, 30:1, 20:1, and 10:1) of the PDMS relate to the elasticity and the elevated height.

3.3.5 Visualization of the droplet

The side-view observation is captured by the high-speed camera equipped with 5x zoom lens (MP-E65mm, Canon). The camera provides the images with a pixel size of $4\ \mu\text{m}$ and the acquisition rate of 1 Hz. The side-view images of the droplets are used to measure the contact radius r , contact angle θ , droplet height h . The droplet volume (v) is consequently calculated using a formula as following [227]:

$$v = \frac{\pi r^3 (2 - 3 \cos \theta + \cos^3 \theta)}{3 \sin^3 \theta} \quad (3.1)$$

The measurement is carried using an image analysis software (ImageJ, plugin DropSnake) [228, 229]. The software uses B-spline fitting to extract the contact

radius and contact angle of the droplets. The height was measured from the droplet's base to the apex.

3.3.6 Thermographic measurements

The IR camera equipped with a 3x zoom lens (Infratec) provides the temperature profile with a resolution of 5 μm / pixel. The camera has a thermal resolution of 20 mK and its spectral range of 2.0-5.7 μm . It should be noted that the emissivity of the working suspension and the PDMS surface are different; therefore, the emissivity should be carefully used within a particular area. We used the emissivity of the ethanol, $\varepsilon_e = 0.86$ [211], to observe the temperature distribution across the liquid surface. The emissivity of the PDMS substrates was adjusted by matching the reference temperature measured by the thermocouple attached to the surface of the PDMS substrates with the measured temperature from the IR camera. The temperature accuracy of the camera is ± 1 $^{\circ}\text{C}$. As ambient light may contribute to the experimental uncertainty, we performed all experiments in a dark environment

3.4 Results and discussions

In Figure 3.3, series of snapshots of an evaporating droplet is presented. The droplet is sitting on a stiffer substrate ($E=1.5$ MPa) with an initial radius (r_0) of 0.88 mm. The snapshots were recorded from the side and the temperature profile from the top surface. From the side-view images, it is observed that the droplet maintains its spherical cap shape throughout the evaporation. The droplet

initially evaporated in the CCA mode. The contact line was first pinned after 90 seconds and subsequently the evaporation process changes to the CCR mode. At time $t = 130$ s, the depinning occurred, but the droplet quickly repined to the substrate at $t = 140$ s. This second pinning results from particles accumulation at the contact line known as self-pinning [189, 190]. This mode is characterized by stick-slip motion, which lasts until the end of evaporation. Toward the end of evaporation ($t = 210$ s), the droplet is like a thin film instead of a spherical cap shape. Therefore, the contact angle becomes so small that the measurement is not feasible. The droplet lasts for around 250 seconds.

Figure 3.3. Series of snapshots represent the evaporation of a droplet on non-heated PDMS substrate: Visualization from the side-view regards the geometry evolution as shown in the pictures on the left. The IR images taken from the top surface are shown on the right.

The IR images display the temperature profile measured across the liquid-vapor interface, and on the bare PDMS substrate. It was observed that the temperature at the contact line was larger than that at the droplet's apex. However, the temperature difference becomes smaller as the drop evaporates due to heat transfer mechanism. The heat dissipates from the contact line to a region at the apex. The larger amount of heat is moving towards the apex where the temperature is lower. Subsequently, a stain of microparticles appears on the surface after the liquid fully evaporates. The temperature was slightly different between the stain ($\epsilon \approx 0.78$) and the bare PDMS substrate ($\epsilon \approx 0.80$) due to a difference in emissivity value of the materials.

3.4.1 The evolution of droplet geometry during the evaporation

In this chapter, the substrate Young modulus E is varied from 0.02 MPa to 1.5 MPa. The variation in droplet geometrical characteristics is observed as the droplet evaporates. The initial droplet dimensions of all samples are similar. The initial contact radius (r_0) is 0.88 ± 0.03 mm. The initial contact angle (θ_0) is 39.16 ± 3.28 degrees. The initial droplet height (h_0) is 0.31 ± 0.02 mm. The dependence of the evolution of the normalized contact radius r/r_0 on E is presented in Figure 3.4a. It was demonstrated that the droplets evaporating on the substrate with lower E (0.7 MPa, 0.35 MPa, and 0.02 MPa) immediately dried in the CCR mode. The droplet subsequently converted to the CCA mode. On the other hand, the evaporation behaviour on the substrate with the highest value of E ($E=1.5$ MPa), is remarkably different. The droplet initially evaporated in the CCA mode before transitioning to the CCR mode. The delayed CCA mode for

surfaces of lower E suggests that pinning of the contact line is more dominant on less stiff surfaces.

The evaporation behaviour for the surface with $E=1.5$ MPa is reminiscent of the behaviour observed for the droplet evaporation on rigid hydrophobic surfaces. The receding contact line follows the stick-slip motion. The sticking of the droplet to the substrate is due to saturation of dynamic contact angle to its receding value. The liquid at the contact line depletes towards the evaporation. Therefore, the contact line recedes when the liquid depletion is sufficient, yet the particles are left behind at a particular position. On the other hand, the slipping continues until the sufficient number of particles accumulate at the contact line; therefore, the droplet subsequently sticks.

Figure 3.4. Evaporation dynamics of a $0.5 \mu\text{L}$ suspension droplet on the non-heated PDMS substrates with varying Young moduli. (a) Evolution of normalized contact radius r/r_0 . (b) Evolution of normalized contact angle θ/θ_0 . (c) Evolution of normalized droplet height h/h_0 . (d) Evolution of normalized droplet volume v/v_0 .

In Figure 3.4b-d, the effects of substrate Young modulus on the evolution of the normalized contact angle θ/θ_0 , droplet height h/h_0 , and droplet volume v/v_0 are demonstrated, respectively. It was observed that less stiff the surface (lower E), lower is the receding contact angle value. This is a natural consequence of increased surface deformation at the contact line. The surface deformation promotes the pinning of the contact line and longer duration of the

CCR mode. Except for the substrate with $E=1.5$ MPa, the droplets remain in the CCA mode for $t \leq 40$ s, and hence the θ/θ_0 , h/h_0 , and v/v_0 decrease with a higher rate at the beginning. For the evaporation on the substrate with $E=0.7$ MPa, droplets depinned at $t \approx 100$ s. Such depinning is presented with an abrupt jump in the contact angle (see Figure 3.4b). Consequently, the second pinning happens at $t \approx 110$ s. The depinning of the droplet on the substrate with $E=0.35$ MPa can still be observed momentarily from the recording even though it is not obviously seen in the plot of r/r_0 against t . The depinning is followed by subsequent pinning, which occurs at $t \approx 100$ s. On the softest substrate ($E=0.02$ MPa), it appeared that the pinning occurred when the droplet contact radius is relatively large, i.e., $r/r_0=0.74$. It can be implied that the substrate deformation is sufficiently large so that it resists the contact line tension and enhances the pinning of the contact line.

The total evaporation time is also influenced by the substrate elastic modulus, which is in a good agreement with previous reports [19, 20]. Notably, the substrate with higher E can increase the total evaporation time because the liquid's surface tension is not sufficient to deform the substrate. Hence, the receding contact line spends more time to surf the surface, resulting in a longer total evaporation time. In that event, the total evaporation time is shorter for the droplet on the substrate with $E=0.02$ MPa as compared with those substrates with higher E . Furthermore, the droplet remained as a thin film for 50 s before it was completely dried.

3.4.2 The evolution of temperature profile during the evaporation

The temperature profile evolution of evaporating droplets on substrates with varying Young modulus is presented in Figure 3.5. We measured the spatial temperature distribution across the liquid-vapor interface of the droplet, which covers from the droplet's apex to the area near the three-phase contact line (TCL). Prior to the droplet deposition, we displayed the temperature distribution of the PDMS substrate (square markers), and also after the droplet fully evaporates (star markers). There was a slight shift in temperature due to the emissivity difference by the left-over stain. From the recording thermography, it was demonstrated that the temperature at the contact line (T_{CL}) is always larger than that at the droplet's apex (T_A). The temperature difference is due to the delayed heat transfer from the contact line towards the apex. The droplet height is smaller at the contact line, so the heat dissipation actively happens in this area. The general behaviour obtained from the results is a monotonically declining temperature from the contact line to the apex.

Figure 3.5. The graphs represent an evolution of temperature profile of the droplet on the substrates with varying Young modulus: (a) $E = 1.5$ MPa, (b) $E = 0.7$ MPa, (c) $E = 0.35$ MPa, and (d) $E = 0.02$ MPa. The spatial resolution is 0.10 mm. A dot-line displays droplet symmetry where the radius $r = 0$ mm.

In figure 3.6, the plot of the substrate elastic modulus against the evolution of droplet temperature profile is shown. The profile temperature is compared with the normalized contact radius r/r_0 at particular timing ($t = 0$ s, 30 s, 60 s, and 90 s). The measurement of the evaporating sessile drop was done when the contact line remains pinned, excluding the measurement of asymmetry of the droplet. On the substrate with the highest value of elastic modulus ($E = 1.5$ MPa), the droplet started to recede at an earlier stage ($t \approx 10$ s), therefore, it has

the shortest time spent in the CCR mode. From the IR images, it is found that the temperature difference between the contact line and the apex is larger than the droplets evaporating on other substrates. The temperature difference is influenced by a larger thickness of the droplet, which induces higher thermal resistance. Subsequently, the slower heat transfer event from the contact line to the apex occurs. On the substrate with $E=0.02$ MPa, the presence of the contact line pinning throughout the evaporation process is observed. During the pinning, the radial flow replenishes the area near TCL, causing a reduction of the droplet height. As a result, the temperature difference becomes smaller as the droplet evaporates. In addition, the temperature distribution is almost equivalent at $t=90$ s. A lower thermal resistance of the thinner droplet induces the heat to dissipate faster from the contact line to the droplet apex.

Figure 3.6. The graphs show the dependence of the droplet with normalized contact radius r/r_0 on the interfacial temperature at the liquid-vapor interface T_{LV} against the different substrate Young moduli at a particular time: (a) $t = 0$ s, (b) $t = 30$ s, (c) $t = 60$ s, and (d) $t = 90$ s.

3.4.3 The evolution of the interfacial temperature at the apex and contact line of the droplet

The evolution of temperature at the droplet apex T_A is shown in Figure 3.7a. If one compares the T_A of the evaporating droplets that are initially pinned to the substrate (excluding the substrate with $E=1.5$ MPa), it is found that the T_A of drops evaporating on the substrate with $E=0.02$ MPa has the lower value. This is due to larger drop thickness induced slower the temperature dissipation to the apex. Nonetheless, the rates of change of the T_A were similar in all cases. Figure 3.7b presents the evolution of the temperature at the contact line T_{CL} . No significant differences in the evolution of the T_{CL} was observed. In fact, the rates of change of the T_{CL} for all substrates with varying Young modulus were comparable. Moreover, the shorter total evaporation time of the droplet evaporating on the substrates with $E=0.7$ MPa and $E=0.35$ MPa is because we did not measure the temperature profile when the droplets evaporate with an asymmetrical shape. In this case, it was observed that the droplets did not prolong their symmetry after depinning. Meanwhile, the droplets evaporating on the substrates with $E=1.5$ MPa and $E=0.02$ MPa maintain their symmetry until the droplet fully dries.

Figure 3.7. (a) The evolution of the droplet temperature at the droplet's apex (T_A). (b) The evolution of the droplet temperature at the contact line (T_{CL}).

3.4.4 The deposition patterns

In Figure 3.8, microscopic images of the deposition patterns that were left after the droplet fully evaporated on the substrate with varying Young modulus. The deposition patterns with a radius of $569.30 \pm 9.78 \mu\text{m}$, $884.64 \pm 39.69 \mu\text{m}$, $873.42 \pm 58.86 \mu\text{m}$, and $821.31 \pm 45.41 \mu\text{m}$, are revealed on the substrate with Young modulus $E=1.5$ MPa, $E=0.7$ MPa, $E=0.35$ MPa, and $E=0.02$ MPa, respectively. As a result, the substrate Young modulus can be one of the factors

that contributes to the deposition patterns. The substrate Young modulus can cause the different evaporation mode and variation of evaporation time, which consequently result in a variety of deposition patterns. However, other factors also contribute to the deposition patterns, such as liquid's thermal properties, substrate thermal conductivity, roughness, and environmental variables.

The radius of deposition pattern on the substrate with $E=1.5$ MPa is the smallest, whereas the other deposition patterns shared similar size. The deposition pattern should be formed during the event of second pinning. We found that the droplet's contact radius at the second pinning was approximately $570\text{ }\mu\text{m}$, which is similar in length with the radius of the deposition patterns. According to the deposition radius, it is implied that a strong radial flow which occurs at the second pinning conveys the particles to the contact line, forming a ring-like pattern. Moreover, we observed deposition patterns with a two-ring deposit: an outer ring is likely thinner in terms of a deposited radius than the inner ring. The patterns were found after the droplets fully evaporated on the substrates with $E=0.7$ MPa, $E=0.35$ MPa, and $E=0.02$ MPa. For the deposition patterns on the substrate with $E=0.7$ MPa and $E=0.35$ MPa, the outer rings were produced during the first pinning at $t \approx 70$ s and $t \approx 80$ s, respectively. It is confirmed by the contact radii of the droplet during the pinning. The inner rings were formed due to the radial flow during the subsequent pinning at $t \approx 110$ s and $t \approx 100$ s, respectively. The contact radii of the droplets, which were $760\text{ }\mu\text{m}$ and $740\text{ }\mu\text{m}$, are also similar to the radii of the inner rings. On the least stiff substrate ($E=0.02$ MPa), The droplet evaporated in two modes: the droplet initially pinned until $t \approx 80$ s and converted to dry in CCA mode until the end of evaporation. Although the droplet is pinned at the beginning, the deposition patterns appeared that they

were not placed at the earlier stage, indicating the radial flow was not sufficient to settle the particles. Hence, the particles were placed as the contact line was receding. Moreover, the inner deposited ring was produced at almost the end of evaporation ($t \approx 120$ s).

Figure 3.8. Microscopic images of the deposition patterns on the substrate with Young modulus of (a) $E=1.5$ MPa, (b) $E=0.7$ MPa, (c) $E=0.35$ MPa, and (d) $E=0.02$ MPa. The second column shows the higher magnification images at the edge of the deposition patterns, while the third column displays the photos of the central region.

3.5 Conclusions

This chapter presented an experimental investigation of suspension-laden sessile droplet evaporating on soft PDMS substrate with a variation of elastic moduli using thermographic approach. The dependence of surface Young modulus on the evaporation process was also reported. As a result, the droplets have a shorter evaporation time on the least stiff substrate ($E=0.02$ MPa) as compared with the evaporation on the substrates with higher Young modulus. In this experiment, we can categorize the evaporation process into two types: the droplets initially in the CCR mode (pinning) before transitioning to the CCA mode. The delayed in the CCA mode suggests that pinning is more dominant on the substrates with lower E , i.e., $E=0.7$ MPa, $E=0.35$ MPa, and $E=0.02$ MPa. The longer pinning time is indirectly associated with the substrate deformation. Moreover, the second pinning was found only for the evaporation on the substrates with $E=0.7$ MPa and $E=0.35$ MPa. Concurrently, the monotonically decreasing temperature from the contact line to the apex of the droplet is observed. The temperature distribution across the interface becomes smaller as the droplet evaporates due to the reduction of droplet thickness or droplet height. Consequently, the heat dissipates faster from the contact line to the apex of the droplet. Afterward, the deposition pattern is formed upon completion of the evaporation process. The left-over stain appeared to have a two-ring pattern. The outer ring is likely caused by the first pinning, whereas the second pinning caused the formation of the inner ring. Furthermore, the deposition radius on these substrates is relatively larger than the substrate with $E=1.5$ MPa.

Another type of evaporation process occurs when the droplet is evaporating on the stiffer substrate ($E=1.5$ MPa). The droplet is immediately

gone into the CCA mode before transitioning to the CCR mode. An abrupt jump of the normalized contact radius was found, determining the presence of the depinning. The second pinning occurs after the depinning. Moreover, the radius of the deposition pattern is the smallest as particles accumulated mainly at the circumference of the ring. The deposition pattern was formed during the second pinning when strong radial flows brought the particles towards the contact line. From the thermography, the larger difference in temperature was observed. It could be because of the bigger droplet thickness which influenced a higher thermal resistance. As a result, the temperature gradually increases towards the apex.

In conclusion, qualitative and quantitative results of the droplet evaporation on soft substrates are presented using the proposed thermographic approach. The evolution of droplet geometry is determined, together with the temperature distribution.

Chapter 4: Evaporation dynamics of a sessile droplet containing non-spherical nanoparticles

4.1 Introduction

Additive manufacturing (AM) or 3D printing of electronic components has been intensively studied [47, 230-232]. Droplet-based printing techniques such as inkjet printing and aerosol jet printing are often used. They involve deposition of functional inks onto a substrate and formation of deposition patterns. The inks are usually suspensions and nanofluids such as metallic nanofluids [233, 234], graphene pellets [235], carbon nanotubes (CNTs) [236], and polymer-based suspensions [237, 238]. These functional inks have been demonstrated in various applications, such as sensors and actuators [239, 240], light-emitting diodes (LEDs) [241], and energy storages [242].

A fundamental study of the evaporation of sessile droplet is commonly conducted to model the droplet-based printing techniques. It has demonstrated that the evaporation could be influenced by several factors: surface roughness [243], hydrophobicity [244], substrate temperature [17], liquid's properties [109, 206], and ambient conditions [245]. However, those studies were conducted using suspensions of microparticles; limited studies are conducted for nanofluids [246-250].

The evaporation dynamics of a sessile droplet are categorized into two modes: constant contact radius (CCR) mode and constant contact angle (CCA) mode. The CCR mode (pinning) occurs when the contact radius remains constant while the contact angle decreases. In contrast, the droplet evaporation that

correlates with the recession of the contact line is referred to the evaporation in CCA mode [121, 135].

Another important aspect for printed electronics is an arrangement of particles. A homogenous deposition is preferable because it promotes a better electrical conductivity [251]. However, several studies [204, 252] suggested that coffee ring effect is often found after the liquid fully evaporates. The coffee ring effect is controlled by several factors: hydrodynamic flows inside the droplet, contact line dynamics, particle concentration, particle geometry, substrate temperature, particle-substrate interaction, and external forces [253, 254].

The particles arrangement on solid surfaces has been well studied [191, 252]. The particles deposition occurs at the micro-region at the three-phase contact line (TCL). The TCL relates to the balance of surface tensions, which is described by the well-known Young's equation [117]. The particle arrangements at the contact line strongly depend on the shape of particles. It was discovered that the spherical particles organized in a sequential square or hexagonal assembly near the contact line, while a disorder organization was found away from the contact line [191]. Similarly, the elongated nanotubes tended to align parallelly along the contact line, while nanotubes that were away from the contact line were placed perpendicular to the contact line [255]. Furthermore, the degree of alignment of the nanotubes is also dependent on some variables, such as substrate temperature, nanotube length, surface charges of the nanotubes, ionic strength of the solvent, and pH of the solvent [256].

CNTs are 1-dimensional materials that possess good electrical conductivity and mechanical properties. CNTs are flexible and have a high aspect

ratio (~100). They have various forms dependent on diameters, lengths, chirality, and chemical functionalization [257, 258]. CNTs have garnered much interest in the area of flexible printed electronics [259, 260] due to their superior properties. In addition, aligned CNT's with desired orientation can improve mechanical properties, electrical and thermal conductivities of the printed thin-films [193].

Many investigations of the evaporation of dispersed droplets have been conducted to study the dependence of evaporation dynamics on the arrangement of deposition patterns. However, the dispersed materials mainly are spherical particles [261], micro-sized elongated beads [262], and rigid nanotubes [256]. There were limited studies on the evaporation dynamics of droplets containing elongated particles, such as nanorods and CNTs [255, 263, 264]. Moreover, restricted studies did not show a dependence of a polymer substrate, which is often used for printed flexible electronics, on the evaporation dynamics of droplets. In fact, the effect of an interplay between the substrate temperature and CNT concentration on the evaporation dynamics of droplets and the arrangement of CNTs is missing.

Therefore, this study aims to experimentally investigate the dependence of substrate temperature and CNT concentration on evaporation dynamics of a droplet and the alignment of the CNTs.

4.2 Experimental methods

4.2.1 Preparation of CNT dispersion ink

The CNT ink is a single-walled CNT suspension in water with a concentration (φ) of 0.2 wt% (NINK 1100) and was purchased from Nanolab[®]. The ink contains a non-ionic surfactant (<1 wt%). The CNTs are also functionalized with carboxyl groups. The carboxyl group has negative surface charges, which keeps the CNTs isolated and free from agglomeration. Moreover, the suspensions were prepared by using the sonication method to ensure the uniformity of the dispersion [265]. It was observed that there was no CNT sediment settled at the bottom, and the CNTs did not form aggregates after 15 minutes of sonication. The CNTs have an average length of 1300 μm with a standard deviation of 615 μm . Their average diameter is 1.5 nm according to the datasheet from the supplier. The ink was diluted with deionized water to prepare three other nanofluids with different concentrations (0.07 wt%, 0.02 wt%, and 0.007 wt%).

4.2.2 Experimental procedures for droplet evaporation

Prior to the experiment, the ink was kept at room temperature. A substrate is a polyimide (PI) sheet with a thickness of 50 μm (Kapton[®] B, Dupont). Its modulus is 3.0 GPa [266]. It was prepared by cleaning with soap water and sonicating with ethanol to remove any contaminations on its surfaces. The PI sheet was attached to a glass slide to ensure that it was flat. The surface roughness was measured using a confocal microscope (VK-X1000, Keyence). The average surface roughness (R_a) of the substrate was found to be 0.60 μm . A heater with

a control feedback loop was used to adjust the substrate temperature (T_s) to be 30 °C, 50 °C, 70 °C, and 100 °C. A droplet with an expected volume of 0.5 μL was placed onto the substrate by a micro-pipette. The side-view images of the droplet were recorded by a high-speed camera (SA5, Photon Inc.) equipped with a 5x zoom lens (MP-E 65mm, Canon). Captured rate was set at 1 Hz. From the recorded side-view images, the contact angle (θ), contact radius (r), and volume (v) of the sessile droplet were measured using an image analysis software (ImageJ plugin DropSnake) [267]. The reproducibility of the result was verified by repeating each condition at least six times.

4.2.3 Characterization of CNT deposition

After the droplet is fully dried, deposition patterns appear on the PI surface. The deposition patterns were characterized by optical microscope (CKX41, Olympus) to obtain their optical images; by field emission scanning electron microscopy (FESEM) to obtain CNT arrangement and orientation.

4.3 Results and discussions

The evaporation dynamics of the CNT droplet is presented in Figure 4.1. The evolution of the normalized contact radius (r/r_0) and contact angle of the CNT droplet with different concentration are plotted against the substrate temperature. The substrate temperature could control the evaporation mode and time. The evaporation time of a droplet at substrate temperatures of 30 °C, 50 °C, 70 °C, and 110 °C was recorded to be approximately 230 s, 55 s, 25 s, and 9 s,

respectively. The droplet receives a more substantial amount of heat from the increasing substrate temperature. Therefore, it evaporates faster on the substrate at higher temperatures. At higher substrate temperature, the droplets that had lower CNT concentration evaporated in CCA mode before they converted to dry in CCR mode. The switch between the CCA and CCR mode is called stick-slip motion [268]. The higher droplet temperature can reduce the liquid surface tension, which causes the unbalanced Young's force at the TCL. The droplets consequently repined at lower contact angle where Young's equilibrium has reached again.

The dependence of CNT concentration on the contact line dynamics and resulting deposition patterns is shown in Figure 4.2. The droplets with different CNT concentration were dried on the substrate at 30 °C. It appeared that the droplets with lower concentration such as 0.007 wt% and 0.02 wt% initially evaporated in CCR mode; however, when the contact angle reached its critical angle, the droplets converted to dry in CCA mode. The droplets depinned, and the contact radius receded. On the other hand, the droplets with higher CNT concentration such as 0.07 wt% and 0.2 wt% evaporated in CCR throughout the evaporation. The droplets are pinned while their contact angles are decreasing.

Figure 4.1 Graphs present the evolution of the normalized contact radius (r/r_0) and contact angle (θ) of the CNT droplets evaporating at the substrate temperature of (a) 30°C , (b) 50°C , (c) 70°C , and (d) 110°C [269].

The pinning and depinning phenomena are explained by aggregated-induced pinning [270]. The CNT aggregation at the contact line halts the moving of the contact line. It was observed that the coffee ring effect appeared in all

samples. The coffee ring is formed during the pinning of the contact line. The evaporation induces the radial capillary flow inside the droplet to move toward the contact line. The CNT were moved along with the flow and aggregated at the contact line, forming the coffee ring effect. There were no residual CNTs within the ring of a droplet with lower concentrations, that are 0.007 wt% and 0.02 wt%. Therefore, the results suggest that the insufficiency of aggregate-induced pinning influences the depinning of the droplet with lower CNT concentrations. On the other hand, the residual CNTs were found in the deposition patterns of the higher concentration droplet. A sufficient amount of CNTs leads to aggregate-induced pinning. This result agreed with several studies where enough particles can induce pinning and resulting coffee ring effect [3, 4, 7, 204].

The coffee ring effect is not only induced by the radial flow but also affected by the recirculation flow due to the temperature-induced Marangoni stress [6]. The recirculation flow is stronger at the higher substrate temperature. The flow can bring the particles at the contact line to the middle of the droplet; therefore, the coffee ring effect can be hindered. The depinning of the contact line was observed for droplets with a lower CNT concentration, whereas the pinned contact line was presented throughout the evaporation of CNT droplet with a higher concentration.

The SEM images (Figure 4.3) present that the deposition patterns of CNTs can be categorized into three regions based on the arrangement: an aligned region, a transition region, and a randomly oriented region. The CNTs were aligned parallel to the contact line in the aligned region. The arrangement near the contact line is due to the radial flow and surface tension at the TCL. In the transition region, the arrangement was observed in the direction both parallel and

perpendicular to the contact line. This region is where the radially aligned CNTs meet a group of nematic CNTs. The CNT dispersion can exhibit nematic liquid crystal behaviour because of its rod-like shape. The CNTs were self-aggregated to have long-range directional order parallelly to their long axes. In the third region, The CNTs were randomly oriented and located further away from the contact line due to the formation of the nematic phase CNTs and lower CNT concentration. These regions of deposition were found in all samples regardless of CNT concentration and substrate temperature.

Figure 4.2 Images of the evaporation dynamics of CNT sessile droplets with different concentration: (from left to right) $\phi = 0.007$ wt%, $\phi = 0.02$ wt%, $\phi = 0.07$ wt%, and $\phi = 0.2$ wt% at the substrate temperature of 30 °C. The deposition patterns are shown as the bottom images of each concentration [269].

The effect of substrate temperature and CNT concentration on the arrangement of the CNTs near the contact line is shown in Figure 4.4. For $T_s = 30\text{ }^{\circ}\text{C}$, the CNTs are aligned parallel to the contact line regardless of all CNT concentrations. Most CNTs are aligned to the contact line at $T_s = 70\text{ }^{\circ}\text{C}$. However, there were some regions where noticeable misalignment of the CNTs can be observed. The random alignment of the CNTs can be found when $T_s = 110\text{ }^{\circ}\text{C}$. Moreover, there were no significant differences among all CNT concentrations that dried at the same substrate temperature. In summary, the CNTs were becoming more misaligned with an increase in substrate temperature. However, the effect of CNT concentration alone showed no difference to the CNT arrangement. The misalignment of the CNTs at the higher temperature is due to shorter evaporation time and an increase in motion of the CNT particles. The total evaporation time decreases from 230 s to 9 s when the substrate temperature is heated up from $30\text{ }^{\circ}\text{C}$ to $110\text{ }^{\circ}\text{C}$. The given time is not enough for the particles to adjust themselves via inter-particle forces. Another factor is the increase in Brownian motion of the CNT particles due to the decrease in fluid viscosity [271, 272]. The combined effect can prevent the well-aligned network of the CNTs. Therefore, the randomly oriented CNT network is found at the higher substrate temperature.

In this work, the effect of the substrate's modulus might not be significant on the evaporation dynamics and the deposition patterns of the CNTs. Tsai *et al.* [273] reported that Young's modulus (E) of the PI decreased almost linearly with increasing temperature. However, the range of temperature used in the experiment is small ($30\text{--}110\text{ }^{\circ}\text{C}$). The modulus E of the PI sheet is 3.0 GPa at room temperature ($25\text{ }^{\circ}\text{C}$), while that at $110\text{ }^{\circ}\text{C}$ is approximately 2.8 GPa. Hence,

the effect of substrate temperature on the modulus E of the PI sheet might not be significant. Moreover, the PI sheet is very stiff that the surface tension of the nanofluid cannot deform the substrate. Therefore, the PI substrate stiffness dependence on the temperature has no significant effect on the evaporation dynamics of the nanofluid.

The increasing temperature also affects the viscosity of the CNT nanofluid. Some reports [274-276] presented that the viscosity of the CNT nanofluid decreases with increasing temperature. The increase in temperature lower the intermolecular attraction between the liquid molecules, which reduces the fluid's viscosity. The evaporation of the liquid also involves. The lower content of liquid, while the volume of particles remains the same, causes the increase in viscosity of the dispersion as well. Therefore, the substrate temperature affects the fluid's viscosity, which later influences the evaporation dynamics of the droplet (Figure 4.1) and the morphology of the CNT deposition patterns (Figure 4.4).

Figure 4.3 (a) SEM image showing three distinct regions of CNT arrangement: (b) aligned region, (c) transition region, and (d) randomly oriented region. (e) Schematic diagram presents the CNT alignment mechanism during the solvent evaporation [269].

Figure 4.4 SEM images displaying the morphology of the CNT thin film at the contact line for different substrate temperatures and CNT concentrations. The contact line is located horizontally at the top of the images [269].

4.4 Conclusions

In conclusion, the dependence of substrate temperature and suspension concentration on the evaporation dynamics of a sessile droplet containing CNT nanoparticles and CNT deposition patterns was experimentally investigated. It is observed that the droplet evaporated in CCR mode (pinning) throughout the evaporation at higher substrate temperature. The pinning also induces the coffee ring effect via evaporative self-assembly mechanism. It is also found that the droplet with higher concentration evaporated in CCR mode throughout the evaporation, whereas the depinning is observed for the evaporation of the lower concentration droplets. The depinning is attributed to the insufficiency of aggregate-induced pinning. Furthermore, the substrate temperature could control the degree of alignment of the CNT network at the contact line.

Chapter 5: Effects of substrate's elastic modulus on performance characteristics of printed patterns

5.1 Introduction

The soft electronic devices are often made via direct writing techniques due to a wide range of available deposit materials, a capability of printing on non-planar surfaces, and a high resolution with accurate alignment patterns [47, 232]. The droplet-based printing techniques, such as inkjet and aerosol-jet printing, are one of the selected techniques to fabricate the functional electronic devices. The fabrication via droplet-based printing techniques involves direct writing of ink onto a substrate. The ink is placed and subsequently dried, forming a thin film of printed patterns. Therefore, both the substrate and deposit materials play a major role in the properties of the printed patterns.

Several studies focus on the functionality and durability of the printed components on the soft substrates [81, 85, 277]. For example, Valentine *et al.* report a hybrid 3D printing method for fabricating soft electronics that combines direct ink writing with automated pick-and-place of surface mount components. They developed a conductive ink that is highly stretchable. The printed patterns on the soft substrate can be elongated up to 240% strain before losing their conductivity [278]. Moreover, Ramuz *et al.* present an optical pressure sensor that is not only transparent but also highly stretchable with good cycling stability. It can sense a weight as low as ten of milligrams. The sensor shows great potential in the applications of touchscreen-based devices such as smartphone or tablet for human-electronic device interface [279].

Other works investigated factors affecting the performance characteristics of the printed patterns: Park and Moon demonstrate that particle deposit morphologies of the ink-jetted microdroplets depend on particle concentration and solvent composition [251]. The optimum ink concentration produces a homogenous layer. Soltman and Subramanian inkjet-printed features of conductive deposits. They found that the substrate temperature can control the topology of the printed patterns, either reversing or enhancing the coffee ring effect [252]. Perelaer *et al.* presented a single-step process for the fabrication of conductive features on flexible substrates. The higher sintering temperature and longer sintering time lead to lower resistivity value of the printed features [280]. However, the effect of the substrate elastic modulus on the properties of deposition patterns has not entirely investigated.

In this chapter, we experimentally investigated the dependent of the substrate elastic modulus on the performance characteristics of printed patterns. This understanding can lead to the development of soft electronic devices in the near future.

5.2 Experimental methods

5.2.1 Preparation of silver nanoparticle ink

The commercial ink is nanofluid containing spherical silver-nanoparticles with 40% loading (UTDAg40TE, UT Dots Inc.). The particles with an average size of 10 nm are dispersed in organic solvents. The silver nanoparticles ink is often used for printing electronics due to its high conductivity. Moreover, silver nanoparticles are stable in ambient condition due to a small amount of proprietary

additive. The ink's viscosity is approximately 1-10 centipoise (cP), which is printable using the droplet-based printing techniques.

5.2.2 Printing processes

Before printing, A designed pattern is drawn using CAD software. The pattern is a straight line of serpentine patterns with a dimension of $1 \times 10 \text{ mm}^2$. The PDMS substrates with different elastic modulus were prepared, as described in Chapter 3.3 (section 3.3.2 – Fabrication of elastic substrates). They were kept in a dry cabinet to prevent swelling of water molecules from the ambient environment. The ink was loaded into an ultrasonic atomizer unit of Aerosol jet printer (Aerosol jet 5X systems, Optomec Inc.). The printing parameters were fixed to produce consistent thin films among all samples. A sheath gas was kept at 20 SCCM. An ultrasonic atomizing power was fixed at approximately 0.6 Ampere. An atomizing pressure was set at 30 SCCM. A $300 \text{ }\mu\text{m}$ nozzle was used in this study. The printing process is running with a serpentine line. A printing speed of 10 millimetres per second (mm/s) was selected to achieve a line width of approximately $200 \text{ }\mu\text{m}$ on PDMS substrates. During the printing, the platen below the substrates was heated up to $80 \text{ }^\circ\text{C}$. The patterns were printed with three different layers (1, 5, and 10 layers). The ink was placed on the substrate, and the solvent subsequently evaporated. For five and ten printed layers, the consequent layer is printed on top of the previous layer.

5.2.3 Sintering processes

The printed samples were sintered in a convection oven (Venticell, MMM group) with a temperature of 140 °C for 4 hours to ensure that the solvents fully evaporate, and particles properly solidify. Moreover, the PDMS can withstand the temperature of 140 °C. It starts to decompose at the temperature above 200 °C [281, 282]. The samples are kept in the dry box after the sintering.

5.2.4 Characterisation

After the samples are cured, their surface profiles, particle arrangement, and electrical property were measured. The surface profiles of the printed patterns were measured using a 3D laser confocal microscope (VK-X1000, Keyence) with 10x and 20x zoom lens. In particular, a printed morphology is captured, and thickness of printed patterns is measured. The arrangement of silver nanoparticles is observed using a field-emission scanning electron microscope (FESEM, JSM-7600F, JEOL) in the GB-low mode. All samples are first coated with platinum to ensure good electrical conductivity. The SEM images are analysed using commercial software (Mipar image analysis software) to extract the average particle size of the microstructures. At least five images of the same sample are taken from different locations to ensure the reproducibility of the results.

A resistance of the printed thin films was measured using a two-point probe (115 True RMS Digital Multimeters, Fluke corporation). The electrical resistivity (ρ_e) is calculated using a formula as follows:

$$\rho_e = R \frac{A}{L} \quad (5.1)$$

where R is measured resistances of the printed line, A is a cross-sectional area, and L is a length of the printed line. The rectangle area A is therefore calculated from an average of a measured line width multiply with an average of a measured line thickness. The length L of 10 mm was selected. At least three replicated samples are measured for each experimental condition.

5.3 Results and discussions

We varied the substrate Young modulus (E) and printed a single line on the substrate, as shown in Figure 5.1. From the images, the width of the printed line is measured, and its morphology is observed. The images show that the particles mainly accumulate at the centre of the line, while a presence of overspray at the side is also observed (see Figure 5.2). The overspray is determined as a loss of materials because the overspray is a disconnected island of silver particles. Therefore, the line is not conductive. Moreover, the overspray reduces a line spacing, which is crucial in some applications (e.g., electrodes for field-effect transistors (FETs) [80, 283], micro-heaters [284], and radio frequency (RF) components [285]) where a sharp and narrow spacing is required. The overspray is one of the disadvantages of the aerosol jet printing technique [286].

Figure 5.1. Optical images present the printed single line with 1, 5, and 10 layers on the soft substrates with varying Young modulus (E).

Figure 5.2. (a) a printed single line on a substrate. (b) the SEM images show the microscopic of the overspray.

The printed single layer on the substrate with Young modulus $E=1.5$ MPa, shows a line without any cracks. The line on the substrate with $E=0.7$ MPa and 0.35 MPa, has small cracks horizontally to the line. The cracks are formed during the sintering process due to a shrinkage of the printed film and thermal stress. The heat induces a solidification of silver particles, establishing a network of silver particles. However, the PDMS substrate is also heated up, which can affect its Young modulus. Once the heat is being removed, the substrate retracts. In particular, a coefficient of thermal expansion (CTE) for the printed silver film and the underlying PDMS substrate is different. The CTE of the PDMS is found to be ten times larger than that of the silver thin film [287]. The difference in CTE between the printed pattern and the underlying substrate causes thermal stress within the film [288, 289]. Moreover, the printed pattern shrinks with densification and the evaporation of the organic solvent during sintering. Therefore, the thermal stress and the shrinkage of the printed pattern result in the presence of cracks across the printed samples [290]. The horizontal cracks in the

printed single line are due to a drying gradient in a radial direction [291]. In our work, we found that the silver particles accumulate mainly at the centre and decrease toward the lateral sides, as shown in Figure 5.3a. The drying gradient should be in radial direction regarding the amount of deposition material. The drying at lateral sides is faster compared with the central area due to lower thickness. Therefore, the crack formation in the horizontal direction is due to the drying gradient in the radial direction that is resulted from the different amounts of deposited material.

Moreover, the printed line on the least stiff substrate ($E=0.02$ MPa), shows many small cracks randomly across the printed line. It is possible that the printed patterns are contaminated by the PDMS because the jetting stream is strong enough to penetrate the substrate superficially. In addition, a residual uncrosslinked oligomer may leach into the ink during the evaporation of the solvent. The leaching of the residual oligomer is often found on the substrate with a higher mixing ratio (i.e., 40:1, 50:1, and 60:1). During sintering, the solvent is evaporated, but the oligomer remains within the film because its decomposition temperature is above 200 °C. The oligomer might lower the densification of the silver film.

Another major issue of the printing technique is the inconsistent amount of ejected materials. This is due to a clogging of the ink inside the nozzle and the connecting tubes. Once the clogging happens, driven pressure changes as well as the amount of printed material.

Figure 5.3. The surface profile of (a) a ten-layer printed single line on the substrate with $E=1.5$ MPa, and (b) a ten-layer printed pattern on the substrate with $E=1.5$ MPa. The deposited materials mainly accumulate at the centre of the printed line.

The plot between the substrate Young modulus and the width of the printed single line is presented in Figure 5.4. The width of the single-layer and five-layer printed line is comparable, independent of the substrate Young modulus. However, the width was larger on the least stiff substrates ($E=0.02$ MPa) for the ten-layer printed line. The ink spreading on the substrate with lower Young modulus and the overspray might increase the line width. Therefore, the substrate Young modulus did not significantly affect the width of the fully sintered line.

Moreover, the line width increases with the increasing number of the printed layer. This is due to the spreading of ink on the substrate. The more the

printed layers, the larger the amount of the ink wet the substrate, resulting in the larger line width. However, the wetting behaviour of the ink changes. The wetting of the first layer is due to the interface between PDMS and the ink. The wetting of the consequent layer attributes to the properties of the ink's droplet and the wetting thin film. There will be changes in surface roughness and material composition.

Figure 5.4. The graph between the substrate with varying Young modulus (E) and the width of the printed single line (W_L) with varying number of layers.

The printed single line is commonly non-conductive due to a thin layer, and a narrow line making the measurement difficulty. Thus, we printed a thin film with a dimension of $1 \times 10 \text{ mm}^2$ and measured its electrical resistance and surface profile. The images representing the printed patterns with the different number of layers (1, 5, and 10 layers) on the substrate with varying Young modulus, as shown in Figure 5.5. We measured the width and thickness of the

printed patterns. The dependence of substrate Young modulus on the width of the printed patterns is displayed in Figure 5.6.

Figure 5.5. Optical images represent the printed patterns with 1, 5, and 10 layers on the soft substrates with varying Young modulus E .

Figure 5.6. The graph shows the dependence of the substrate Young modulus (E) on the printed line width (W) of 1, 5, and 10 layers, respectively.

The width of the printed patterns increases with increasing numbers of layer. The increased layer indicates more amount of ink on the substrate. The ink can wet a larger area of the substrate, resulting in bigger line width. Moreover, the overspray can be seen in all samples, and it is one of the factors in the variation of the line width. However, the line width is not significantly influenced by the substrate Young modulus, as the width of the printed patterns with the same number of layers is comparable. The substrate's deformation might be insufficient to control the droplet of ink during the deposition and evaporation. In fact, the ink properties, substrate properties, and the printing process are the main parameters affecting the printed line width.

In addition, cracks are found in all samples. Some cracks are horizontal lines or vertical lines to the printed pattern, while others are random crack lines. The printed patterns with five and ten layers on the substrates with $E=1.5$ MPa, 0.7 MPa, and 0.35 MPa, have the cracks horizontally to the line direction, similar to the printed single line. The horizontal cracks relate to the densification of the printed patterns. The printed pattern is produced by overlapping the printed single line. The amount of deposited materials is varied in the radial direction due to the effect of the printing process and the evaporative driven flows. We found that the silver particles accumulate mainly at the centre and decrease toward the lateral sides of each line, as shown in Figure 5.3b. The drying gradient should be in radial direction regarding the amount of deposition material. The drying at lateral sides is faster compared with the central area due to lower thickness. Therefore, the variation of deposited materials leads to the different densification rates at particular locations, which induces the crack formation horizontally.

The cracks are further analysed using Mud-cracking method [292]. Mud cracks or desiccation structures are formed by the evaporation of liquid content from the surface of sediments. The cracks originate as shrinkage cracks due to a reduction in volume from the loss of the liquid. Consequently, tensile stresses are generated in all directions. The stresses are compensated by the formation of polygonal cracks on the mud's surfaces [293]. In this work, all images were processed using ImageJ software. Three images from the same sample were used to investigate the crack profile. Figure 5.7 presents the characterization process of crack patterns via image processing and analysis.

From Figure 5.7, a contrast of a raw image of crack patterns was enhanced to further divide the crack and printed silver film. Then, the raw image was

converted to an 8-bit grayscale image. Consequently, the areas that are not covered by the printed pattern were cropped out. That image was changed to a binary image by auto thresholding. Close and Despeckle operators were used to eliminate small residual defects. Next, the black pixels were measured as a crack area. The image was skeletonized, which was a process to reduce the width of the crack to a single pixel. The total pixels of the crack line were measured and were used to calculate the total crack length.

Figure 5.7. Characterization process of crack patterns using image processing and analysis.

The percentage of total crack areas is represented by Crack Intensity Factor (CIF). In particular, the CIF is defined as a percentage of the total crack area to entire areas of the sample. Figure 5.8a shows the plot of the CIF of all samples on the soft substrate with varying Young modulus. The CIF for the substrates with $E=0.7$ MPa, 0.35 MPa, and 0.02 MPa, is similar. The CIF for ten layers is relatively higher, indicating that the crack area is relatively higher. The CIF for the substrate with $E=1.5$ MPa is lower compared to other cases, especially for the ten-layer printed film, which shows that the presence of cracks is lesser.

The numbers of cracks are counted manually from the unconnected cracking lines regardless of the crack length. The numbers of cracks for all printed samples is displayed in Figure 5.8b. The thinner the printed layer, the higher the numbers of cracks. The higher numbers of cracks on a single printed layer are due to the mismatch between the values of the coefficient of thermal expansion (CTE) of both the PDMS substrate and the printed silver film, and the shrinkage of the printed film during sintering. The numbers of cracks of the printed patterns with five and ten layers are lower, but their average crack widths are higher. We can imply that the presence of cracks is lesser, but the cracks are wider.

(a)

(b)

Figure 5.8. (a) The plots represent the CIF of all printed patterns on soft substrates. (b) The numbers of cracks of the printed patterns dependent on substrate Young modulus.

Moreover, the total crack length is found using the skeletonized images. Figure 5.9a presents the total crack length of all printed samples on different substrates. The average crack width of all samples is plotted in Figure 5.9b. On the least stiff substrate ($E=0.02$ MPa), the total crack length is slightly higher for the thinner film. The average crack width is lower for the thinner film as well, which indicates that the crack is narrower, but the presence of cracks is more compared to that of the printed film with five and ten layers. The numbers of cracks (see Figure 5.8b) also double confirm with this finding.

On the substrate with $E=0.35$ MPa and 0.7 MPa, the results of both the total crack length and the average crack width have the opposite trends. The total crack length is relatively higher for the printed single layer, while its crack's width is relatively smaller – the cracks are narrower, but higher numbers of cracks are found. These are also in good agreement with the numbers of cracks in Figure 5.8b. The total crack length for both five and ten layers is similar, but the average crack width is relatively higher for the printed ten layers due to crack propagation from the film's surface down to underlying layers [294]. In fact, the cracks usually propagate from the film's surface down within the film layers. However, the crack propagation in a thicker film results in a broader crack width.

The total crack length of the five-layer film on the stiffest substrate ($E=1.5$ MPa) is the highest. The total crack length of the five-layer film is higher than that of the single-layer film, while their average crack widths are comparable. Moreover, the total crack length of the ten-layer film is the lowest, but its crack width is the largest compared with other printed layers, indicating that the presence of the cracks is lesser, but the crack is broader. The broader

cracks are also due to crack propagation from the film surface downwards the film thickness.

Figure 5.9. (a) Graphs display the total crack length of all printed patterns on substrates with varying Young modulus. (b) The average cracks width of the printed patterns dependent on the substrate Young modulus.

The effect of substrate Young modulus on the thickness of the printed patterns is presented in Figure 5.10. It is found that the thickness increases with the number of layers. The more the amount of ink deposited on the substrate, the larger the thickness of the printed patterns. Moreover, it shows that the substrate Young modulus has no significant effect on the thickness of the printed patterns, except the printed patterns with five and ten layers on the substrate with $E=1.5$ MPa and $E=0.02$ MPa. The slightly lower thickness might be due to the densification/ shrinkage of the film or the measurement error.

Figure 5.10. The graph presents the dependence of the substrate Young modulus (E) on the thickness (t_p) of the printed patterns with varying number of layers.

We also investigated further into the microstructure of the printed patterns. Figure 5.11 displays the SEM images of the printed patterns with a different number of layers on the substrate with varying Young modulus. The microstructures of the printed patterns on the substrate with $E=1.5$ MPa, 0.7 MPa,

and 0.35 MPa, are a film-like microstructure which includes fully sintered particles and some voids. Moreover, particle boundaries are seen within the microstructure. On the substrates with $E=0.02$ MPa, the particles come into contact but not fully sintered, forming a cluster of particles. There were a lot of voids in the microstructure. We suspected the voids might be filled in with the leaching oligomers from the bulk PDMS. Some particles showed slightly necked particles. In particular, the printed patterns with ten layers on these substrates demonstrated slightly necked particles and some particles with neck growth (see Figure 5.12). The growth of necked particles shows that the particles are partially sintered. Moreover, it was difficult to achieve a clear SEM image, indicating the printed microstructure has low conductivity.

Figure 5.11. The SEM images showing the arrangement of silver nanoparticle of the printed patterns with a different number of layers on the substrate with varying Young modulus.

Figure 5.12. The images represent the necked particles: (a) FESEM image of the printed pattern with ten layers on the substrate $E=0.02$ MPa. (b) The image shows the area of the particles in green. (c) schematic representing the spherical particles with necking.

Comparing with the microstructure of the printed patterns on the rigid substrate such as polyimide (PI) sheet, the patterns that were printed with the same conditions were fully sintered with a particle boundary, as displayed in Figure 5.13. The sintered microstructure has smaller voids or microcracks ($\sim 4.81\%$), that is favourable for printed electronic applications [295]. The results suggest that the void area is lesser on the rigid PI substrate compared with soft substrates. Hence, the density of the printed pattern on PI substrate is higher than that of the soft substrate. The difference in the density could be due to the CTE mismatch between the silver thin film and each substrate as well as other surface properties.

Figure 5.13. The SEM image of the printed pattern on the polyimide sheet after sintering at 120 °C for 4 hours [295]. The measured void area is approximately 4.81%.

Figure 5.14 shows a measured feature of the particle size using the image analysis software. The average particle size (D_p) is represented by the average of the equivalent diameter of the particles, which equals to the diameter of a symmetrically circular area. The plot between the average particle size and the substrate Young modulus is presented in Figure 5.15.

On the substrate with $E=0.02$ MPa, the particle size is relatively smaller compared with that for other substrates. The smaller particle size might due to the leaching of oligomers into the printed thin film. The oligomers might diffuse into the liquid ink before the ink fully evaporates. The oligomers cannot be eliminated because their decomposition temperature is above 200 °C, while the sintering temperature is 140 °C. The remained oligomers in the film likely prevent the densification of the silver film. Therefore, the particle size is smaller. The measured particle size (Figure 5.15), the presence of voids (Figure 5.16), and

the cross-section image (Figure 5.17) are used to support this conclusion. On the substrate with $E=1.5$ MPa, 0.7 MPa, and 0.35 MPa, the particle size is similar. The dependence of substrate Young modulus on the particle size is not significant. It suggests that the particle size mostly depends on the sintering conditions.

The void areas of each printed pattern are shown in Figure 5.16. The void areas are found by the summation of the black pixels in the images. As a result, the void areas of the printed pattern on the least stiff substrate ($E=0.02$ MPa) are relatively higher compared with that of other substrates. The larger percentage of voids is due to lesser densification of the silver film through the contamination of the PDMS. A cross-sectional image of the film on the least stiff substrate (see Figure 5.17b) presents the silver film with some contaminations. Moreover, the presence of the voids is more dominant in the printed patterns with five and ten layers. The larger void areas indicate that the thicker films have lesser densification. Apart from PDMS contamination, the lesser densification might occur due to other impurities, such as gases and moistures from the ambient air. The printing process is a layer-by-layer process, which might entrap the ambient gases (i.e., oxygen and nitrogen) and moistures in between the printed layers.

To conclude, the substrate Young modulus might not have a significant effect on the microstructure of the printed patterns. The average particle size for each number of layers shares a similar value, except for the pattern on the least stiff substrate. We believe that the smaller particle size is due to the leaching of the oligomers into the printed film during sintering, which lower the densification of the sintered film.

Figure 5.14. (a) Measured features of the particles size, and (b) size distributions (Equivalent diameter) of the silver nanoparticles from FESEM images.

Figure 5.15. The plot between the substrate Young modulus (E) with the average particle size (D_p) of the printed microstructure.

Figure 5.16. Graph showing the void area in the microstructure of the printed patterns dependent on substrate Young modulus (E).

Figure 5.17. The SEM images show a cross-section of the printed single-layer pattern on the PDMS substrate with (a) $E = 1.5$ MPa and (b) $E = 0.02$ MPa.

Lastly, the electrical resistivity of the printed patterns (ρ_e) is plotted against the substrate Young modulus, as shown in Figure 5.18. The resistivity of printed patterns on the substrate with $E = 0.02$ MPa cannot be measured. The reason is because of lesser densification of the printed pattern and the presence of cracks, which can be found across the samples. The cracks disconnect the network of silver particles, which prevent electrical conduction. Moreover, the residual oligomers that leach from the substrate might lower the densification process. The smaller particle size (see Figure 5.15) and larger volume of voids (see Figure 5.16) indicate the lesser densification of the silver film.

On the other hand, the printed patterns on the substrates with $E = 1.5$ MPa, 0.7 MPa, and 0.35 MPa, are conductive. The electrical resistivity increases with increasing numbers of printed layers. The thicker layers have the broader line width and the larger thickness, which can cause the increases of the resistance following Equation 5.1. Moreover, the particle size is comparable for different printed layers, while the presence of voids is higher for the thicker film. The higher percentage of void area also results in the larger electrical resistance of the

printed film. Furthermore, the electrical resistance also increases with a reduction of the substrate stiffness. From Figure 5.16, the void area enlarges when the substrate stiffness is lower. The increase of void area might occur due to the shrinkage of the film during sintering and the CTE mismatch between the film and the PDMS substrates. Furthermore, the smaller particle size influences the higher resistivity of the printed patterns [296]. Therefore, the increase of void area and the smaller particle size are lower the electrical resistance.

The electrical resistivity is directly governed by the parameters described in Equation 5.1. However, the electrical resistance is influenced by the physical contact of the sintered particles. The presence of voids resulted in a higher electrical resistance due to the increase of contact resistance between silver particles. In addition, the resistivity also decreases with increasing particle size [296-298]. The presence of defects and impurities within the microstructure can also increase the electrical resistivity [299]. In this work, the electrical resistivity is consistent with the results of the particle size and void area.

Moreover, the resistivity of the printed patterns is compared with that of bulk silver. The electrical resistivity of the bulk silver is $1.59 \times 10^{-8} \Omega\text{m}$ at 20°C [300, 301], which is smaller than that of the printed silver film by two orders of magnitude. The higher value of the electrical resistivity of the printed film can be implied that the particle size and the arrangement of the particle influence the electrical resistivity. The bulk silver has a well-ordered structure of silver atoms, so its electrical resistivity is extremely low. The bulk silver deficiently resists the flow of electrons. Hence, it conducts a very high electron flow. In fact, silver has the highest electrical conductivity among all metals.

Figure 5.18. The plot between the substrate Young modulus (E) with the electrical resistivity (ρ_e) of the printed thin film of varying number of layers.

5.4 Conclusions

The patterns of silver nanoparticles on PDMS substrate with varying Young modulus were printed using the aerosol jet printer. The patterns were printed with varying number of layers (1, 5, and 10 layers). The overspray is found in all samples. It appears that the width of the printed patterns measured after sintering is similar for the samples with equal numbers of layers. The slight variation of the width is due to the overspray. The cracks are more profound in the printed patterns with the thicker layers. The crack formation is caused by the densification/ shrinkage of the printed thin film and the thermal stress during sintering. Moreover, the increasing number of printed layers could result in a larger printed width, but the width is not depended on the substrate Young

modulus. The relationship between the thickness of the printed patterns after sintering and the substrate Young modulus also shows no significant dependence.

The microstructure of the printed patterns is investigated. It reveals that the film-like microstructure consisting of fully sintered particles and some voids is observed. The particle size of the printed patterns on substrates with $E=0.35$ MPa, 0.7 MPa, and 1.5 MPa, shares a similar diameter. The silver nanoparticles are excellent for both thermal and electrical conduction. Hence, the particle size might not depend on the thickness or the increased amount of the particles. On the least stiff substrate ($E=0.02$ MPa), the particle size is relatively smaller due to the reduced densification. The contamination of residual oligomers can be one of the factors in the reduction of densification. Moreover, the electrical resistivity of the printed pattern on the substrate with $E=0.02$ MPa, cannot be measured due to the reduced densification and the presence of cracks/ voids. However, the electrical resistivity of other samples follows the results of particle size and the presence of voids. The smaller particle size and the higher percentage of voids in the microstructure result in the larger electrical resistivity, regardless of the governing parameters in Equation 5.1.

Chapter 6: Conclusions

6.1 Conclusions

In this chapter, we have concluded the key finding of this work and the suggestions to further determine the evaporation dynamic of the sessile droplet on soft substrates as following:

6.1.1 Thermographic investigation of an evaporation dynamics of a suspension sessile droplet on soft solid substrates

This chapter aims to experimentally investigate the dependence of substrate elastic modulus on the evaporation dynamics of suspension-laden sessile droplet using thermographic approach coupled with optical images. We found two main kinds of the evaporation process when the substrates Young modulus (E) is varying from 0.02 MPa to 1.5 MPa.

The first kind of evaporation process is found when the droplet evaporates on the substrate with $E=0.7$ MPa, $E=0.35$ MPa, and $E=0.02$ MPa. The droplets initially evaporate in the CCR mode before transitioning to the CCA mode. The delay in the CCA mode indicates that pinning is more dominant on the substrate with lower Young modulus. Several factors can influence the longer pinning duration, one of which is the substrate deformation at the droplet's contact line. From the thermographic images, the temperature decreases from the contact line toward the droplet apex. The temperature distribution across the liquid-vapor interface decreases as the droplet evaporates. The decrease in temperature is associated with the droplet thickness (height). Consequently, a two-ring deposition pattern is found, which combines a thinner outer-ring and a thicker

inner-ring. The formation of the outer ring occurs during the first pinning, whereas the second pinning generates the inner ring.

Another type of evaporation process happens when the droplet is evaporating on the stiffest substrate ($E=1.5$ MPa). The droplet is quickly dried in the CCA mode before converting to the CCR mode. During the mode transition, an abrupt jump of the normalized contact radius was seen, indicating the droplet depinning to the contact line. Subsequently, the second pinning occurs. The radius of deposition patterns on this substrate was found to be the smallest. The particles accumulated mainly at the circumference of the ring. The deposition patterns were formed during this second pinning due to strong radial flows. The temperature difference is found to be larger due to the bigger droplet thickness induced higher thermal resistance.

To conclude, the proposed thermographic approach provides both qualitative and quantitative results of the evaporating droplet sitting on the surface of soft substrates. The evolution of droplet geometry is determined as well as the temperature distribution across the droplet surface.

6.1.2 Evaporation dynamics of a sessile droplet containing non-spherical nanoparticles

We experimentally investigated the effect of substrate temperature and suspension concentration on the evaporation dynamics of a sessile droplet containing CNT nanoparticles and the resulting deposition patterns. It is demonstrated that the higher substrate temperature influences the droplet to evaporate in the CCR mode (pinning) throughout the evaporation. The pinning

subsequently produces the coffee ring effect via the evaporative self-assembly mechanism. It is found that the temperature could also affect the degree of alignment of the CNT network in the vicinity of the contact line. Moreover, the evaporation in the CCR mode is found with an increased droplet concentration. On the other hand, the depinning is seen for the evaporation of the lower concentration droplets. Such depinning is due to the lack of aggregate-induced pinning from lower concentration suspensions.

6.1.3 Effects of substrate's elasticity on performance characteristics of depositions patterns

The patterns of silver nanoparticles on PDMS substrate with varying Young modulus were printed using the aerosol jet printer. The patterns were printed with varying number of layers (1, 5, and 10 layers). The overspray is found in all samples. It appears that the width of the printed patterns measured after sintering is similar for the samples with equal numbers of layers. The slight variation of the width is due to the overspray. The cracks are more profound in the printed patterns with the thicker layers. The crack formation is caused by the densification/ shrinkage of the printed thin film and the thermal stress during sintering. Moreover, the increasing number of printed layers could result in a larger printed width, but the width is not depended on the substrate Young modulus. The relationship between the thickness of the printed patterns after sintering and the substrate Young modulus also shows no significant dependence.

The microstructure of the printed patterns is investigated. It reveals that the film-like microstructure consisting of fully sintered particles and some voids

is observed. The particle size of the printed patterns on substrates with $E=0.35$ MPa, 0.7 MPa, and 1.5 MPa, shares a similar diameter. The silver nanoparticles are excellent for both thermal and electrical conduction. Hence, the particle size might not depend on the thickness or the increased amount of the particles. On the least stiff substrate ($E=0.02$ MPa), the particle size is relatively smaller due to the reduced densification. The contamination of residual oligomers can be one of the factors in the reduction of densification. Moreover, the electrical resistivity of the printed pattern on the substrate with $E=0.02$ MPa, cannot be measured due to the reduced densification and the presence of cracks/ voids. However, the electrical resistivity of other samples follows the results of particle size and the presence of voids. The smaller particle size and the higher percentage of voids in the microstructure result in the larger electrical resistivity, regardless of the governing parameters in Equation 5.1.

6.2 Recommendations

Despite the proposed experimental investigations, the following works might be helpful to determine further the effect of substrate elastic modulus on the evaporation dynamics of the sessile droplet containing undissolved particles.

6.2.1 Particle image velocimetry (PIV) of dispersed particles

The PIV is used for determining the flow field of the fluids. The flow field at a particular area can be visualized. The PIV uses trace particles to visualize flow velocity and patterns. The tracers move along with the fluid flows. The tracer's density must be comparable to that of the surrounding fluid to eliminate the effect of gravity. The PIV can be used to visualize the particles

deposition within the drop, specifically at the contact line. One of the challenges is the visualization of the flows at the contact line during evaporation. The TCL of the soft substrates behaves differently from that of the solid substrates under the influence of the sessile droplet. Therefore, the dynamics of fluid flow near the contact line will deviate according to the substrates. The results can be used to describe fundamentally the dynamics of moving droplets as well as to validate theoretical and numerical modelling.

6.2.2 Enlarging the studied range of substrate elastic modulus

Although this work has found significant differences in the evaporation dynamics and the resulting deposition patterns as affected by the substrate Young modulus, it could be useful to have a larger range of Young modulus. The effect of those substrates with an extended range of Young modulus on the consequent evaporation dynamics may show new insight into the evaporation mechanism of the sessile drop.

In this work, the substrate Young modulus is controlled by the PDMS mixing ratio. The higher mixing ratios can be theoretically used, e.g., 60:1, 70:1, 80:1, or even higher ratios. However, the mixing process may not homogeneously disperse the curing agent within the monomers. Moreover, intensive curing is unavoidably required. As a result, the leaching of small polymer molecules is often found. They contaminate the liquid drops and alter the substrate Young modulus. To overcome this issue, instead of using PDMS, other elastic materials such as silicones, hydrogels, and oils, should be integrated.

In addition, the elastic substrates should be stable and highly resistant to any chemical solvents.

6.2.3 The mechanical testing of the thin-film deposition pattern

The mechanical testing such as tensile testing could be conducted to measure the mechanical properties of the thin film of deposition patterns. In this work, we focus only on the morphology of the deposition patterns because the deposition is very thin. The study of the mechanical properties of the thin films leads to the reliability of thin films, e.g., the stress level that leads to the film fracture or delamination from the substrate, the elastic response of the film compared with the supporting substrate. Besides, the mechanical testing can be used to double confirm with the structure and chemical composition of the thin film. In addition, the mechanical testing of the thin films investigates the strength and durability of deposition patterns, which is beneficial in many applications, such as sensor, painting, data storage, and MEM device [302-304].

6.3 Publications

- Saengchairat, N., Tran, T., & Chua, C. K. (2017). A review: Additive manufacturing for active electronic components. *Virtual and Physical Prototyping*, 12(1), 31-46.
- Goh, G. L., Saengchairat, N., Agarwala, S., Yeong, W. Y., & Tran, T. (2019). Sessile droplets containing carbon nanotubes: a study of evaporation dynamics and CNT alignment for printed electronics. *Nanoscale*, 11(22), 10603-10614.

- Tan, H. W., Saengchairat, N., Goh, G. L., An, J., Chua, C. K., & Tran, T. (2020). Induction Sintering of Silver Nanoparticle Inks on Polyimide Substrates. *Advanced Materials Technologies*, 5(1), 1900897.

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