



# MONASH University

**Effect of Film Formers and Drying Methodology on**

**Liquid Marble Shape, Structure and Stability**

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*BPharmSci, BEng (Hons)*

A thesis submitted for the degree of Master of Engineering Science (Research) at

Monash University in 2015

Department of Chemical Engineering



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## **Abstract**

This thesis presents a study of liquid marbles and an overview of their applications. It covers the fundamental properties of liquid marbles in cosmetic and hair styling products; the effect of film former on the longevity and drying structure of liquid marbles; and investigates how different drying methodologies influence marble shape, structure and overall stability.

Liquid marbles are made from droplets of fluid coated by a hydrophobic powder. Their distinctive properties such as low friction rolling, gas permeability, isolation from external environment, and the potential to contain up to 98% by weight liquid have made them of interest to researchers. Commercially, cosmetic companies have also found use for these remarkable particles in foundation and hair care products.

Despite the many potential applications, our understanding of liquid marbles is limited. To date the longevity and shelf life of commercial products containing liquid marbles cannot be replicated in the laboratory. In conjunction, the lifetime and stability of liquid marble produced in the laboratory vary significantly between research groups even when similar liquid and powder combinations are used. These discrepancies underpin the motivations behind the need to explore the factors which contribute to the long term stability of liquid marbles.

Commercial products containing liquid marbles were analysed for their formulation, particle size, moisture content and general appearance to gain clues into their significantly longer shelf-life. Based on the results reported in Chapter 4, film former (VP/VA copolymer) was added to a basic water and aerosil formulation to identify the effect of film former on liquid marble stability and longevity. The presence of film former significantly increased drying time and an optimal concentration of 2% (w/v) VP/VA copolymer is ideal, after which the drying time becomes independent of film former concentration and in some cases destabilises the liquid marble and decreases drying time. A unique drying pattern where a ‘rebound’ phenomenon was identified and a potential drying hypothesis is established in Chapter 5.

The effect of other drying methodologies on liquid marble longevity, shape and structure were investigated in Chapter 6. Variations of temperature on the morphology of drying liquid marble were investigated for oven drying. Single droplet drying and freeze drying of liquid marbles and the resultant dried marbles were also investigated to further understand how different drying methods impact the shape and structure of liquid marbles. The ‘rebound’ phenomenon observed in Chapter 5 became less common as temperature increased. Single droplet drying

showed little difference between drying of a pure water droplet and a liquid marble. In Chapter 6, a novel method of freeze drying a liquid marble to produce a resultant spherical structure consisting of a shell and porous center was produced.

The results of this research will enhance the understanding of some of the fundamental aspects of liquid marbles and the factors which contribute to their stability and structure in the long term. In conjunction, it will provide some insight into how different drying methods affect the final size and shape of the final product.

## Declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original paper published in a peer reviewed journal. The core theme of the thesis is the factors contributing to liquid marble shape and stability. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the Department of Chemical Engineering under the supervision of Prof. Karen Hapgood and Prof. Wei Shen.

In the case of the following chapter, my contribution to the work involved the following:

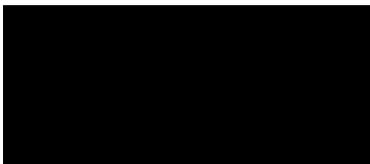
Thesis chapter	Publication title	Publication status*	Nature and extent (%) of students contribution
4	Characterisation of liquid marbles in commercial cosmetic products	Published	100

The above publication has been re-written to comply as a traditional thesis chapter. I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

**Student signature:** 

**Date:** 11/12/2015

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student and co-authors' contributions to this work.

**Main Supervisor signature:** 

**Date:** 14/12/2015



## **Publications during enrolment**

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Yue. S., Shen. W., Hapgood. K.P., “Characterisation of liquid marbles in commercial cosmetic products”. *Advanced Powder Technology*

### **Conference Proceedings**

Yue. S., Shen. W., Hapgood. K.P., (2015) “Effect of film formers on liquid marble stability and drying mechanism”, *Australasian Particle Technology Society 2<sup>nd</sup> Student Conference*, Phillip Island, Australia, 25-27 Sep.

Yue. S., Shen. W., Hapgood. K.P., (2015) “Effect of film formers on liquid marble stability and drying mechanism”, *APCChE 2015*, Melbourne, Australia, 27 Sep – 1 Oct.



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I always knew research was going to be hard, but I never thought it would be this hard. Nor was I truly prepared for all the ups and downs which would follow when I started this journey. While this entire process has been a significant learning curve, it has been an enjoyable one; one which I could only have survived with the help and support of those around me.

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# 1

## Introduction

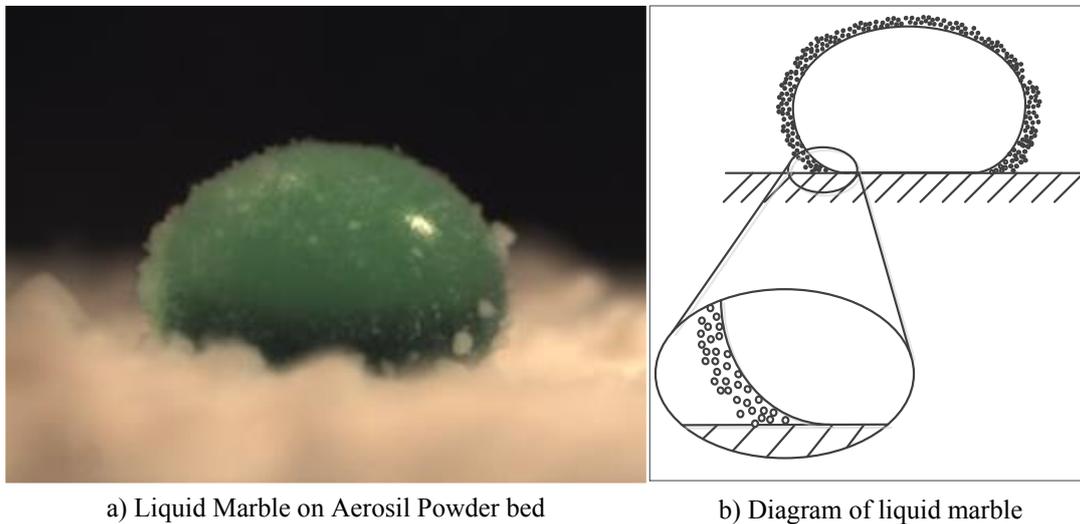
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*“A Journey of a thousand miles must begin with a single step”  
~ Lao Tzu*



## 1 Introduction

Liquid marbles, a term first coined by Quere, Aussillous and Mahadevan in 2001 [1, 2] are droplets of up to 98% fluid coated with a hydrophobic powder [3]. Their unique properties include the ability to roll like a solid but deform like a fluid [1, 4, 5]; gas permeability through a porous shell while maintaining a physical barrier [6, 7]; and a robust encapsulation layer enabling addition and removal of material from inside the marble [8]. In recent times, liquid marbles have found use commercially in cosmetic and hair care products. Despite their commercial use, our knowledge of liquid marbles is still quite limited. Research in liquid marbles only gained popularity in the past decade due to the immense potential of liquid marbles and the vast number of applications which can be achieved by its unique structure.



**Figure 1.1: Example of a) laboratory made liquid marble looks and b) a schematic of liquid marble with multilayer powder shell coating**

Theoretically, any liquid and hydrophobic powder combination can be used to create liquid marbles provided that no drop penetration occurs by the liquid into the powder bed. However, the characteristics of the liquid and hydrophobic powder and their interactions with each other will affect the properties of the resultant liquid marble. To date, many different applications have been discovered, but our ability to commercialise and enable optimisation of systems utilising liquid marble technology is dependent on enhancing our knowledge of these unique particles.

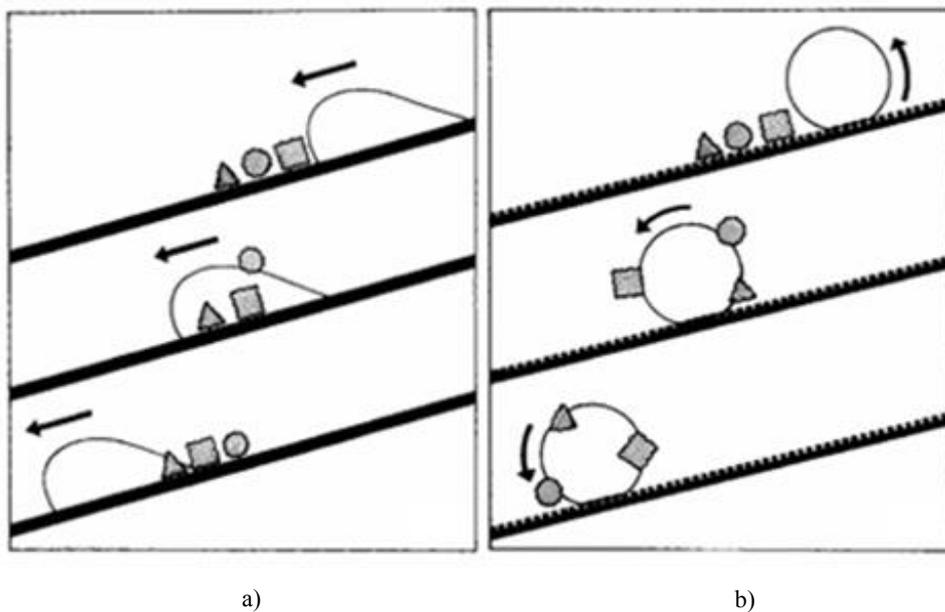
### 1.1 Natural Applications

While the term liquid marbles is relatively new, the phenomenon where solid particles spread around a liquid droplet is common in nature. Surfaces in nature can become contaminated

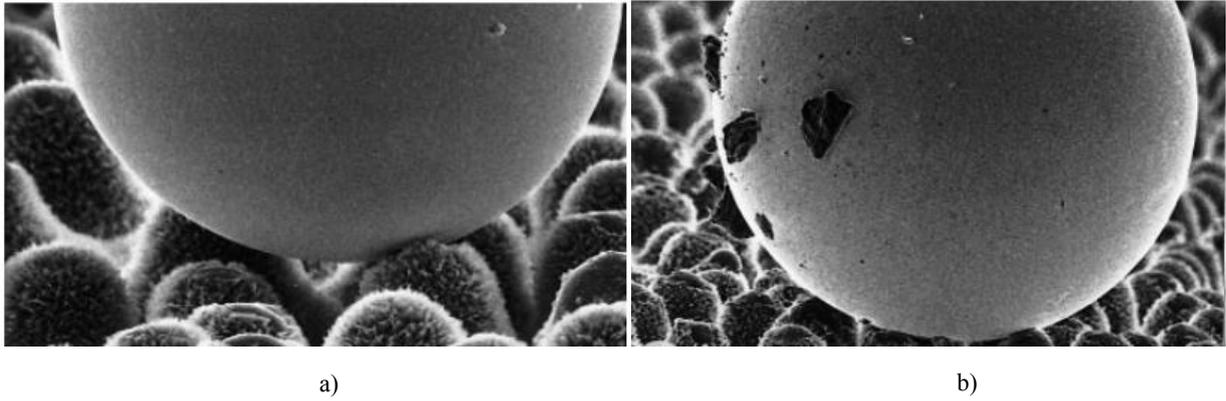
and the ability of biological systems to remove contaminants affects their defence against pathogens and ability to prevent contaminants from entering the system and causing significant damage. Liquid marble formation provides a convenient system to clean surfaces. Two applications utilising liquid marble formation in nature are described below.

### The lotus effect:

The lotus effect describes the process where pollutants on leaves are removed via the formation of a liquid marble as a water droplet rolls over a hydrophobic surface. This effect is seen in plant systems with leaves that are rough and have low wettability [9]. As the water droplets roll over the surface, contaminating particles such as dust, bacteria and fungal spores are picked up as the droplet roll off the leaf surface. A key parameter required for this self-cleaning mechanism to occur is the presence of a low wettability surface, regardless of whether it is plant or animal origin. It was found that plant leaves that had a rough microstructured surface were comparatively more difficult to wet than leaves that had a smooth surface [9, 10] (Figure 1.2). This is due to the high roughness surface decreasing the contact area between liquid and the surface. Air becomes trapped between the droplet and the microstructures on the surface [9], resulting in a strongly hydrophobic structure (Figure 1.3a).



**Figure 1.2: Diagram showing the connection between roughness of surface and self-cleaning. a) On a smooth surface, the contaminants are redistributed by water b) the contaminants adhere to the water droplet and are removed when the droplets roll off [9]**

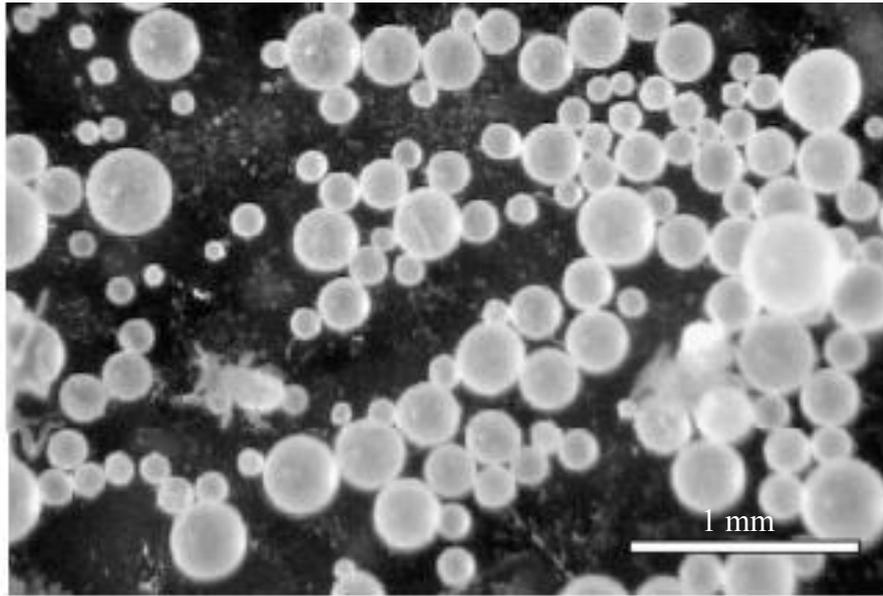


**Figure 1.3: Images showing a) the effect of roughness on wettability b) contaminate particles adhering to droplet surface, which are removed when the droplet rolls off surface [9]**

Wagner et al., extended on the work on low wettability leaves to look at the influence of microstructures on the wettability and contamination of insect wings [10]. Depending on the type of insect, their wing surface will vary in texture, and hence, wettability. It was observed by Wagner et al. that insects with large wings tended to have rougher and more hydrophobic wing surfaces which aided in the removal of contaminants via the lotus effect [10]. The ability to self-clean their wings through the formation of liquid marbles for insects with large wings which cannot be cleaned by their extremities is significant for their survival. Contaminants increase the weight and affect their flight capabilities. Extended flight time is usually crucial to the survival of these insects.

#### **Removal of excrement by aphids:**

Another common use of liquid marbles in nature is removal of excrement by aphids [11]. Gall aphids excrete honeydew which poses two major threats if not removed: entrapment and eventual drowning once the liquid surrounds the insect and surface forces dominate [12]; and pathogen growth [13]. As such, gall aphids use specialised secreted wax to parcel the liquid which is then further coated by a fine wax powder to remain spheroidal and non-wetting [14, 15]. These liquid marbles are then easily transported from the plant gall.



**Figure 1.4: The typical appearance and size range of wax-coated liquid marbles produced by aphids [11]**

## **1.2 Commercial Applications**

Research in the use of liquid marbles have been undertaken in the last decade and to date, while many applications are being studied, commercial use of liquid marbles in pharmaceuticals, cosmetics and food is very limited. Traditionally, encapsulation methods in both cosmetics and pharmaceuticals have used polymer/gel systems [16]. However, the expensive nature of some actives used in anti-inflammatory, dandruff prevention and wrinkle reduction formulations and the resultant degradation after formulation have increased interest in novel delivery systems. It has been suggested that liquid marble technology can be used for active delivery in products such as sunscreens and creams [16].

Despite the general interest in liquid marbles for encapsulation, the cosmetics industry currently seems to have the most products which utilise liquid marble technology. There are two main categories of cosmetics products which utilises liquid marble technology: foundation products and hair styling products. See Figure 1.5 for some example products.



**Figure 1.5: Images of a) examples of some foundation products currently on the market b) examples of some hair styling products currently on the market**

### 1.3 Research Aims

Given the many potential applications of liquid marbles and hollow granules, this thesis aims to increase our understanding of these remarkable particles and the factors which contribute to their long term stability.

Specifically, this research hopes to contribute to our understanding of the following three things:

1. To determine why commercial products containing liquid marble technology are able to have a shelf life of over 2 years compared to laboratory made liquid marbles which have a significantly shorter survival time.
2. To investigate the effect of film former on liquid marble stability in terms of shape integrity and longevity compared to basic water and Aerosil liquid marbles.
3. To investigate the effect of different drying methods on liquid marble stability in terms of shape integrity, size and resultant structure.

### 1.4 Thesis Outline

The following chapters will explore the use of liquid marbles in commercial products, the factors which influence their stability and how different drying processes influence the final structure of the dried liquid marble. An outline of the thesis is shown on the following pages.

***Chapter 2: Literature review***

Previous research conducted on the formation of liquid marbles and subsequently formed hollow granules is summarised in this section. In conjunction, the properties and characteristics of what makes liquid marbles unique is also presented.

***Chapter 3: Material and methodology***

The characteristics of the VP/VA copolymer (Kollidon<sup>®</sup> VA64) solution and Aerosil powder used to create liquid marbles is given in the following chapter. Experimental procedure for determining the liquid properties are also explained here.

***Chapter 4: Characterisation of commercial samples***

Twelve store-bought commercial samples were investigated in terms of their formulation, moisture content, particle size and appearance. A comparison of these parameters allowed for the construction of a basic formulation, which is believed to contribute to the extended longevity of commercial products using liquid marble technology.

***Chapter 5: Impact of film former addition on stability***

Extending on the basic formulation constructed, VP/VA copolymer (Kollidon<sup>®</sup> VA64) solutions of different concentrations was used to produce liquid marbles. Their collapse over time was observed using an optical microscope and compared with plain liquid marbles to observe changes in method of collapse and survival time. In conjunction, a basic drying mechanism is proposed in this section.

***Chapter 6: Drying of liquid marbles***

Air (oven) drying, single droplet drying and freeze drying of liquid marbles was investigated in this section. There is a distinct lack of understanding in how drying affects liquid marbles, and this chapter looks into the effect of these three commonly used commercial drying methods on the final shape and structure of the dried marble.

***Chapter 7: Conclusions and recommendations***

The key findings from commercial sample analysis, addition of film former and investigation into different drying mechanisms and processes are summarised in this section. In addition, suggestions for potential future work are given to enhance current findings and further understanding on liquid marbles and how to increase their stability.

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# 2

## Literature Review

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This Chapter explores previous research conducted and summaries the knowledge on liquid marbles to date.



## 2 Energetics of Liquid Marble Formation

Liquid marbles are structures formed when a droplet of fluid is coated by a hydrophobic powder coating. The final state of powder produced from the combination of liquid and hydrophobic powder is due in part to the energetic aspects of two processes:

1. Wetting and immersion of particles
2. Energetics of the mixing process

Each of these processes will be discussed in turn below.

### 2.0.1 Wetting and Immersion of Particles

There are two possible scenarios when a liquid droplet contacts a solid surface [1]:

1. Complete wetting: The liquid forms a thick layer between the solid and vapour phase. In such a case, the surface tensions are related through Antonow's rule which is expressed as [2]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \quad (eq\ 2.1)$$

Where  $\gamma_{sv}$  = surface tension between the solid and vapour phase

$\gamma_{sl}$  = surface tension between the solid and liquid phase

$\gamma_{lv}$  = surface tension between the liquid and vapour phase

2. Partial wetting: the three phases meet at a common line of contact and is characterized by the existence of a contact angle. The three surface tensions obey Young's law [2]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad (eq\ 2.2)$$

Where  $\gamma_{sv}$  = surface tension between the solid and vapour phase

$\gamma_{sl}$  = surface tension between the solid and liquid phase

$\gamma_{lv}$  = surface tension between the liquid and vapour phase

$\theta$  = contact angle at which the liquid-vapour surface meets the solid substrate.

A wetting transition occurs when a partial wetting system changes to a complete wetting system. On approach to the wetting transition point, the contact angle will slowly decrease until it is zero [2]. However, for liquid marbles, the contact angle between the marble surface and the solid support surface is generally greater than 90° and partial wetting applies.

## 2.0.2 Energetics of the Mixing Process

The energetics of mixing of a solid powder with a liquid can be described by the energy of adhesion which is the difference in energy between the initial two phase states and the final wetted state. Consider Figure 2.1, where the spherical droplet adheres to the liquid surface.

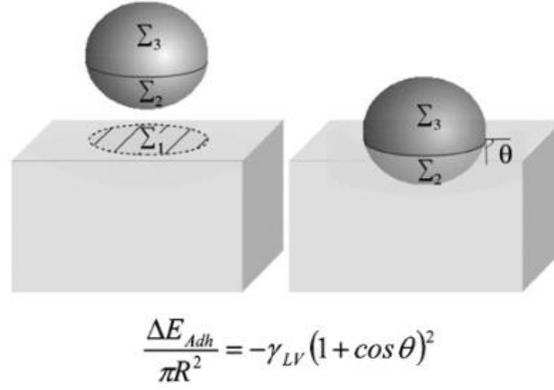


Figure 2.1: Diagram showing energy of adhesion derivation [3]

Assume a gas/liquid interface with known interfacial tension ( $\gamma_{lv}$ ) and a spherical particle with radius  $R$ , the total surface area can be described by the Equation 2.3.

$$\Sigma_0 = \Sigma_2 + \Sigma_3 \quad (eq\ 2.3)$$

Where  $\Sigma_2$  = the proportion of particle in contact with the liquid phase

$\Sigma_3$  = the proportion of particle no in contact with the liquid phase

If the particle is small, gravity can be ignored compared with the interfacial forces. When the particle is brought into contact with the liquid, the particle will adhere to the liquid and partly penetrate until the equilibrium contact angle is reached. This is the process of wetting as described above. From this we can derive the energy of adhesion from an energy balance on the system [3]:

$$\Delta E_{Adh} = \gamma_{sl} \cdot \Sigma_2 - (\gamma_{lv} \cdot \Sigma_1 + \gamma_{sv} \cdot \Sigma_2) = -\gamma_{lv} \cdot \pi R^2 (\cos \theta + 1)^2 \quad (eq\ 2.4)$$

Where  $\Delta E_{Adh}$  = energy of adhesion

$\gamma_{sv}$  = surface tension between the solid and vapour phase

$\gamma_{sl}$  = surface tension between the solid and liquid phase

$\gamma_{lv}$  = surface tension between the liquid and vapour phase

$\Sigma_1$  = liquid surface area to be displaced by particle

$\Sigma_2$  = the proportion of particle in contact with the liquid phase

$\Sigma_3$  = the proportion of particle no in contact with the liquid phase

R = particle radius

$\theta$  = contact angle between particle and liquid

The energy of adhesion is always negative, hence this process is a spontaneous phenomenon which is observed when liquid droplets are rolled across a powder bed resulting in the formation of liquid marbles [4, 5].

The energy of immersion corresponds to the energy required for the particle to move from the air into the liquid to achieve complete wetting and is expressed by the following equation [3]:

$$\Delta E_{Imm} = \gamma_{sl} \cdot (\Sigma_2 + \Sigma_3) - \gamma_{sv} \cdot (\Sigma_2 + \Sigma_3) = -\gamma_{lv} \cdot 4\pi R^2 \cdot \cos\theta \quad (eq 2.5)$$

Where  $\Delta E_{Imm}$  = energy of immersion

$\gamma_{sv}$  = surface tension between the solid and vapour phase

$\gamma_{sl}$  = surface tension between the solid and liquid phase

$\gamma_{lv}$  = surface tension between the liquid and vapour phase

$\Sigma_2$  = the proportion of particle in contact with the liquid phase

$\Sigma_3$  = the proportion of particle no in contact with the liquid phase

R = particle radius

$\theta$  = contact angle between particle and liquid

For hydrophobic particles, the energy of immersion is positive, which means that the particles will try to stay at the gas/liquid interface [3]. However, if more energy is added than their energy of immersion, particles will still exhibit complete wetting and form a foam or suspension depending on the solid-liquid interaction. As such for liquid marbles to be formed, energy less than the energy of immersion must be supplied to prevent the shell from being wetted and collapsing.

## 2.1 Properties of Liquid Marbles

The materials and dynamics governing liquid marble formation have a direct impact on the properties of the resultant liquid marble. However, regardless of its formation, there are a few common properties which are described in the following section.

- I. Low friction rolling – The hydrophobic outer shell prevents the liquid centre from wetting a surface. With the diminished liquid-solid contact area, the marble is able to

be moved with very little force. This allows easy transport of a liquid on a solid surface [5-7]

- II. Robust encapsulation layer – The individual powder particles are a dynamic system on the liquid droplet and can move around to accommodate disturbances at the surface[8, 9]. However, the shell layer must be sufficiently dense to completely encapsulate the liquid centre and have enough powder to self-assemble.
- III. The presence of the hydrophobic powder layer also creates a physical barrier which isolates the inner fluid of the liquid marble from the external environment. This provides many commercial advantages, especially in formulations which contain sensitive ingredients. The barrier prevent degradation caused by contact or exposure to external liquid and light and decrease the rate of volatile material loss [10].
- IV. The hydrophobic powder creates a porous shell around the liquid droplet allowing air and other gases to move freely into the marble while maintaining a physical barrier [8, 9, 11]. Smaller particles tend to collect in the shell layer closer to the liquid core, while larger particles tend to make up the outer shell layer giving a more porous and rough texture [12].
- V. The flexible shell allows material to be extracted out of and introduced into the marble [8, 11]. The number of times a particle can be divided however, it dependent on whether enough powder is present on the surface to rearrange and coat the smaller droplets.
- VI. Liquid marbles have the potential to contain high fluid content, with previous research reporting up to 98% by weight moisture content [10].

## **2.2 Liquid Marble Formation**

Industrially, two methods are used for large scale manufacture of liquid marbles. The first method is via rapid and vigorous agitation of liquid and hydrophobic powder mixture [13, 14]. The second involves atomization of the liquid before being combined with the hydrophobic powder [13].

Commonly, mixers are used for production on a commercial scale. In addition to having a suitable hydrophobic powder, successful liquid marble formation also requires turbulent flow conditions allowing for good stirring properties [3]. It has been found that a combination of both convective axial mixing and shearing action is required to produce liquid marbles [3]. Whether rapid and vigorous agitation of liquid and hydrophobic powder or the atomization

method is used depends on the type of mixers used and the shearing strength of the mixing process.

Large high shear stirring vessels resulting in rapid and vigorous agitation forms liquid marbles progressively as large liquid marbles are reduced in size from macroscopic to microscopic in the high shear process [13]. Saleh et al., further extended on the work conducted by Forny et al., and proposed the following mechanism which is summarised in Figure 2.2 [3]. The liquid is first split into large drops, which requires the presence of air and fumed silica around the impeller creating a convective axial flow. Once these droplets are formed, further mixing leads to more uniform and finer droplets [3]. Depending on the degree of hydrophobicity of the powder and the energy input; a mousse, a suspension or liquid marbles may be formed [3, 15]. Saleh et al. showed that under high shear mixing conditions, only highly hydrophobic particles (with a contact angle higher than approximately  $110^\circ$ ) can produce liquid marbles, while decreasing hydrophobicity of powder coating particles promoted the formation of a mousse [3]. They attributed these differences to the different balance of energetics contributing to the overall mixing process, which was mentioned in Section 2.0.2. A di-phasic mixture is produced when the shear force supplied is not enough to break down the water phase into smaller droplets and provide energy for immersion of the powder into the liquid [3]. Highly hydrophobic powders resist wetting, making the energy of immersion threshold very high, thereby promoting the presence of two separate liquid and solid phases. Liquid marbles are formed when the shear energy given to the system is able to split the bulk liquid into smaller liquid droplets and the excess energy transmitted to the particles from the mixer is lower than the energy of immersion. This forces the water and silica to remain separate phases but allow the solid particles to adhere to the surface of the liquid droplet [3]. Lastly, a mousse will be formed if the mixer imparts enough energy to both break the liquid into droplets and also immerse the particles in the liquid phase [3].

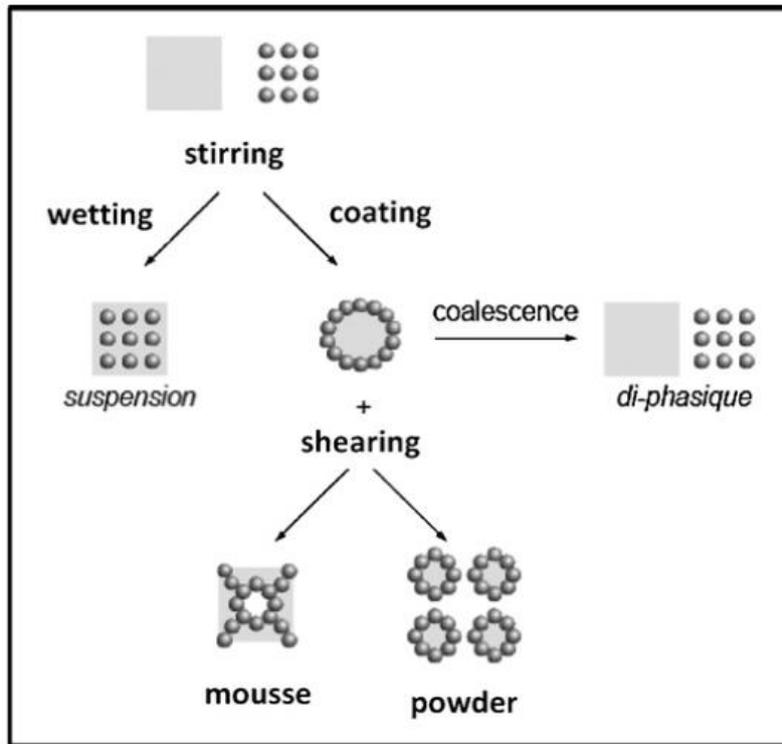


Figure 2.2: Mechanisms of liquid marble formation in stirred vessels [3]

Eshtiaghi et al. [16] later proposed a similar mechanical dispersion regime which is analogous to this process described by Saleh et al. and Forny et al. [3, 17]. Eshtiaghi et al., provided more comprehensive criteria for formation of liquid marbles and will be described later in the chapter.

The second industrial method of liquid marble production is via atomization of liquid before being combined with the hydrophobic powder phase. This is required for low shear mixing processes [13]. In these processes, the water droplets are pre-formed by the atomization system and is coated by free silica particles as the droplets hit the powder bed [13]. Forny et al. noted that formation of liquid marbles through the atomization process is more sensitive to operation conditions compared to the high shear mixing production process. Atomization pressure, stirring conditions and distance between spray nozzle and material had to be precisely controlled to prevent formation of either a mousse or separated powder-liquid mixture [18].

Eshtiaghi et al. later created a more complete systematic criterion for the formation of a liquid marble produced by an atomized spray onto a bed of powder [16], which is described by Figure 2.3.

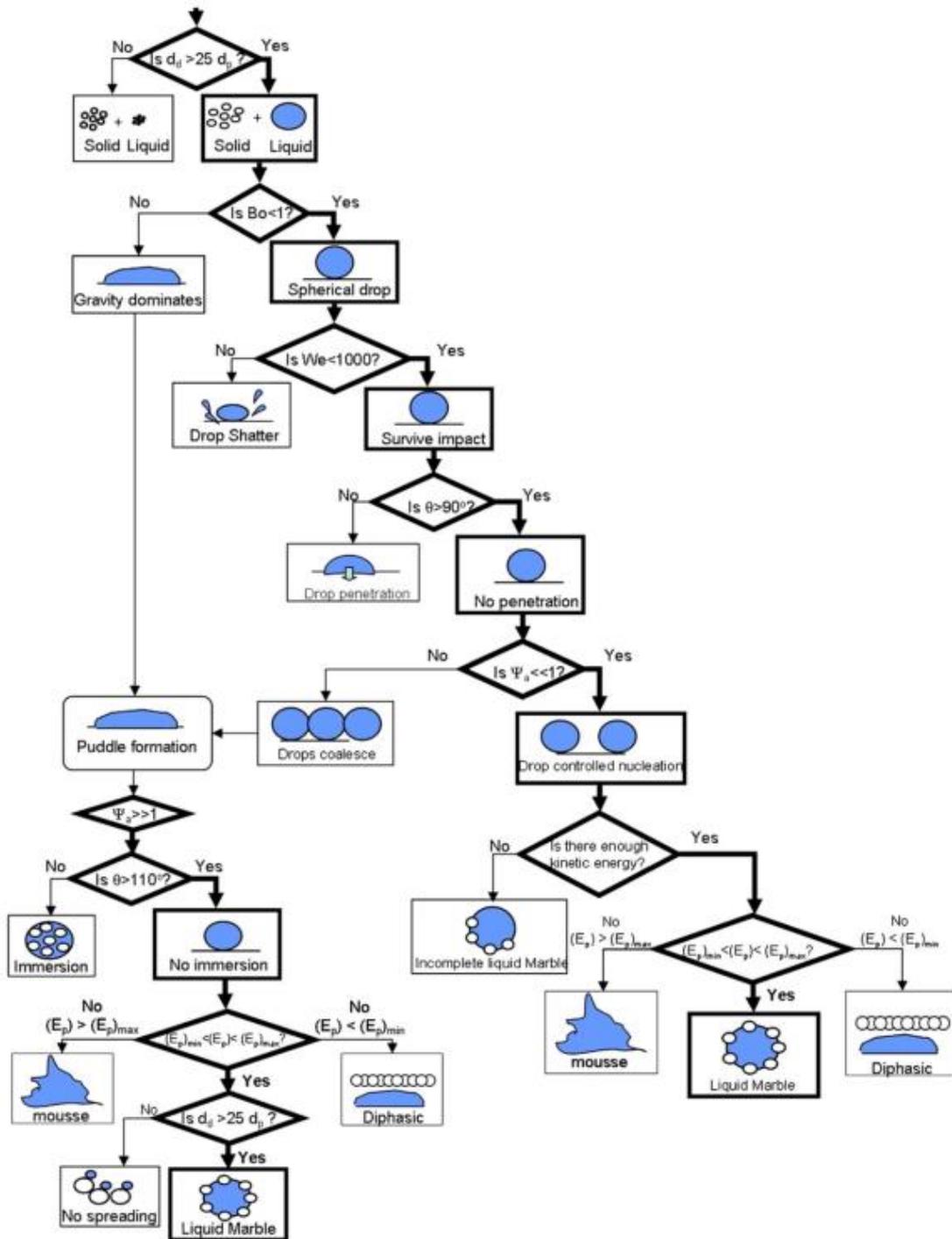


Figure 2.3: Systematic criteria for formation of stable liquid marbles [16, 19]

From Figure 2.3, it can be seen that the formation of a stable liquid marble consists of a few main stages:

- I. The solid particles must be significantly smaller than the droplet diameter ( $d_d \gg d_p$ ) [20-22]. However, the liquid droplet must be small enough for a spherical drop to form, which is influence by the Bond number [8].

The Bond number describes the ratio of gravity compared to surface tension forces acting on a droplet. Gravity forces the center of mass to drop which promotes the formation of a puddle, while surface tension opposes this action. The Bond number can therefore be expressed as the following:

$$B_o = \frac{\rho g R_0^2}{\gamma} = \frac{\text{gravity}}{\text{surface tension}} \quad (\text{eq 2.6})$$

where  $B_o$  = Bond number

$\rho$  = density of liquid

$g$  = gravity

$R_0$  corresponds to  $\kappa^{-1} = \sqrt{\gamma/\rho g}$  which is the so-called capillary length [8]

Further explanation of the Bond number is given later in Section 2.3.2.

- II. The droplet must be able to withstand the impact force created when the droplet hits the powder surface. If the impact force is greater than the resistance of the drop, the droplet will shatter and break into smaller droplets. This balance of forces can be represented by the Weber number [23] and Ohnesorge number [24].

The Weber number is describes the ratio between the inertial and surface tension force at an interface.

$$We = \frac{\rho d v^2}{\gamma_{LV}} \quad (\text{eq 2.7})$$

Where  $\rho$  = density of fluid

$d$  = diameter of liquid droplet or characteristic length

$v$  = velocity of fluid

$\gamma_{LV}$  = surface tension at liquid- vapour interface

The Ohnesorge number is used to describe the shape and rebound phenomenon of a drop impact on solid surface [24-26]. It relates the viscous forces to the inertial and surface tension forces of the droplet and is described by the following equation:

$$Oh = \frac{\mu}{(\rho \gamma_{LV} R)^{0.5}} \quad (\text{eq 2.8})$$

Where  $\rho$  = density of liquid  
 $\gamma_{LV}$  = surface tension at liquid vapour interface  
 $R$  = drop radius  
 $\mu$  = viscosity

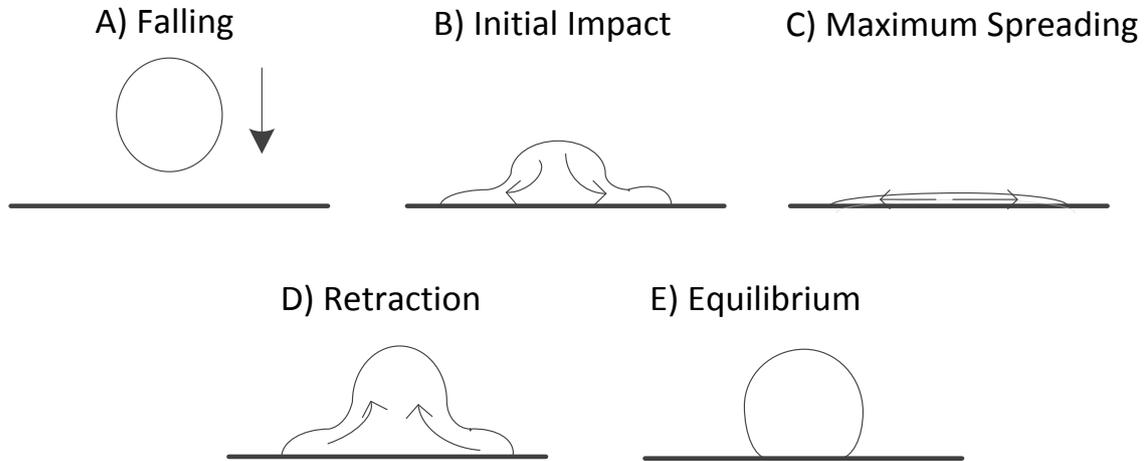
It has been found that a liquid marble tends to be formed when the Weber number is less than 1000 and the Ohnesorge number is greater than 0.05 [19]. Later research conducted by Eshtiaghi and Hapgood showed that to prevent droplet shattering, the criteria where Weber number has to be less than 1000 is crucial, while the requirement of Ohnesorge number greater than 0.05 is not always consistent with experimental data [16]. This may be due to the Weber number accounting for the velocity of the fluid during a drop while the Ohnesorge number does not as the retraction rate of a droplet is independent of impact speed [24]. The critical Ohnesorge number of 0.05 instead represents the crossover between two different retraction mechanisms [24]. Further explanation on the Ohnesorge number will be given in Section 2.3.2.

- III. The liquid droplet must have a contact angle greater than  $90^\circ$  with the powder bed to prevent penetration into the powder bed. The powder particles must then spread around the droplet at the air-liquid interface to form an external shell. The extent of droplet coverage is dependent on a combination of parameters including the energy input when the droplet contacts the powder bed and the powder particle size and density [13, 19, 27, 28].

One of the major mechanisms by which the powder spreads over the liquid droplet is the bulk flow mechanism where the initial spreading of particles on the liquid surface is driven by the internal flow of the bulk liquid which traps the solid particles and drags them over the surface as the droplet reforms [28].

Figure 2.4 shows that the droplet on impact spreads radially with the rate of spreading driven by inertia and opposed by viscous effects and deforms into a thin disk (Figure 2.4A - C). As the inertia energy dissipates, maximum spreading is reached and flow circulation begins in the middle of the disk caused by compressed air between liquid and solid [29]. A retraction action then occurs as the liquid flows from the edge to the

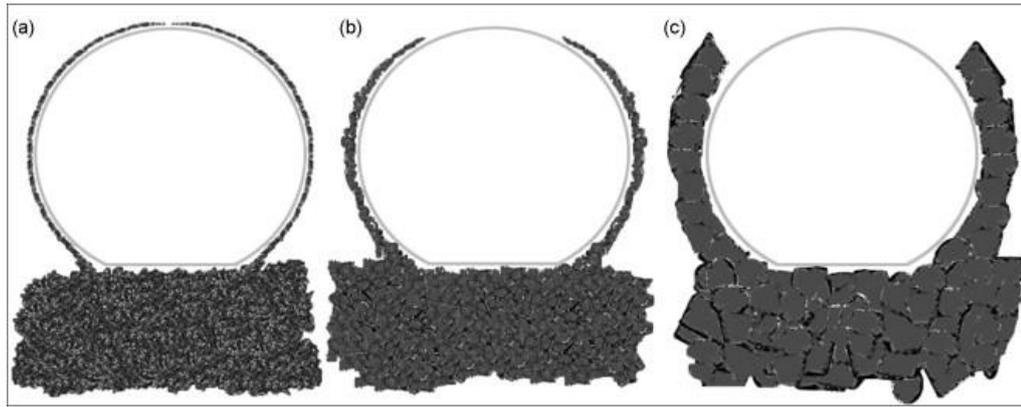
centre [18, 30]. For the case where there is powder on the solid surface, this fluid motion corresponds to a surface flow which will draw the powder over the liquid droplet.



**Figure 2.4: Sketch of droplet impact on solid surface. A) As droplet is falling B) On initial impact C) maximum spreading D) retraction and E) Equilibrium (Adapted from [18, 29, 30])**

In this mechanism, increasing the kinetic energy of the marbles via agitation increases the coverage of solid particles over the liquid droplet [13, 19, 27]. However, droplet viscosity will resist the rebound motion of the droplet and when the kinetic energy is too high, some of the energy is dissipated by the deformation of the droplet. Therefore, a balance of kinetic energy is required to ensure the reformation of the liquid marble droplet [13].

In conjunction to the energy input, the particle size and density of the hydrophobic powder has been found to affect the ability of the powder mass to encapsulate the liquid droplet. Larger particle sizes will result in lower coverage of the liquid droplet resulting in a higher powder mass to droplet surface area ratio. Conversely, smaller particles will result in higher obtainable droplet surface coverage, leading to a lower powder mass to droplet surface area ratio. Figure 2.5 illustrates how the obtainable surface coverage decreases with increasing hydrophobic powder mass [28].



**Figure 2.5: schematic diagram of typical attainable powder-water surface coverage for increasing particle size [28]**

- IV. The spray flux ( $\psi_a$ ) must be low to maintain individual droplets without significant overlap and therefore prevent coalesce [16, 17]. If the spray flux is less than 0.1, most drops will land individually on the powder without significant overlap and liquid marbles may be formed from each drop [16]. If the spray flux is larger than 1, liquid marble formation is still possible, however, it will occur via a mechanical dispersion process [16]. The mechanical dispersion framework is shown in the bottom left of Figure 2.3. While both low and high spray flux may result in liquid marble formation, it has been observed that resultant hollow granules produced at high spray flux contain multiple cavities compared to single cavity granules observed when low spray flux conditions are used [16, 31].
- V. The energy applied per unit mass of powder ( $E_p$ ) is a crucial parameter for liquid marble formation [3]. For liquid marble to form, the energy input must be between an  $(E_p)_{\min}$  and  $(E_p)_{\max}$ . Below  $(E_p)_{\min}$  the powders will remain as two separate phases but above the  $(E_p)_{\max}$ , the mixture will become a mousse [16].
- VI. The powder shell must be able to form a sufficiently dense layer to completely encapsulate the liquid center and form an effective barrier. If the shell is not uniform or it is too thin, the powder may not be able to efficiently self-assemble causing weak areas where the liquid may leak and hence cause the marble to rupture on the supporting surface [10].

## 2.3 Size and Shape of Liquid Marbles

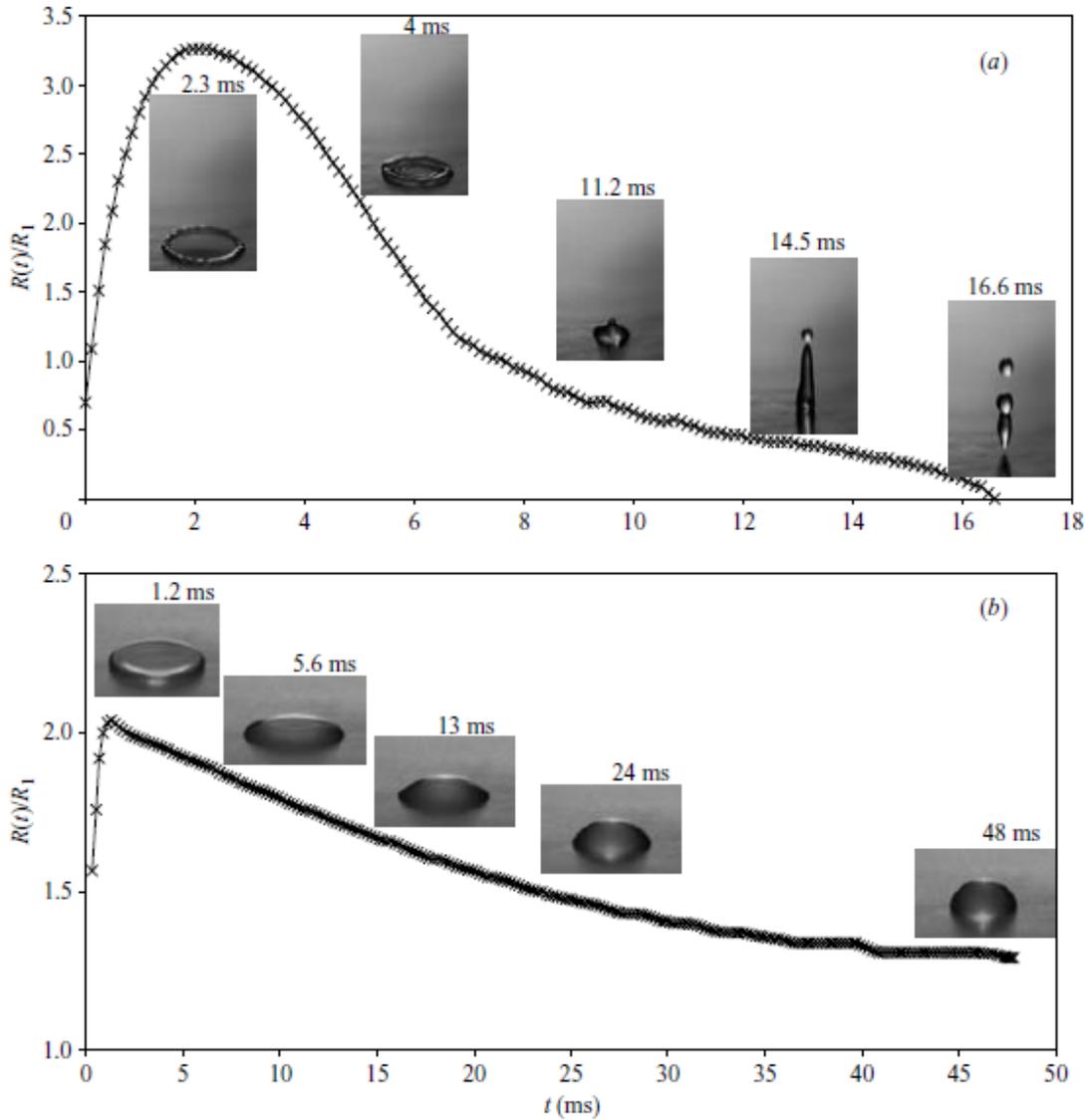
### 2.3.1 Size of Liquid Marbles

Liquid marbles generally range in size between 20-400  $\mu\text{m}$  in diameter [10]. However, marble size is highly dependent on the drop size of the liquid during manufacturing [14]. Measuring the size of liquid marbles is difficult due to their delicate nature and sensitivity of liquid marbles to shear. To overcome this, Forny et al. used laser diffraction to measure the diameter of liquid marbles [10]. While this method is gentle on the marble, its accuracy is dependent on the marbles having a spherical shape. While theoretically laboratory made marbles are usually spherical, commercially made marbles are usually a lot more diverse in their size and shape.

### 2.3.2 Shape of Liquid Marbles

The shape of a liquid marble may change throughout its lifetime. During impact with the powder bed, the shape of a liquid marble is affected by the impact speed and the rebound process [32]. Throughout this process, there are usually three forces which need to be balanced; the capillary, viscous and the inertia forces of the droplet. The Ohnesorge number is used to relate the viscous forces to the inertial and surface tension forces (Eq 2.8) [24]. It has been found that the maximum drop recoil is greater on hydrophobic substrates compared to hydrophilic surfaces [33], and the rebounding of a droplet on impact with a solid surface depends on impact velocity [34, 35]. However, the drop retraction rate does not depend on impact velocity if the velocity is high [24].

Figure 2.6 shows the two different drop retraction regimes have been proposed. A capillary-inertial regime is defined when  $Oh < 0.05$  (Figure 2.6a) and a capillary- viscous regime is present when  $Oh > 0.05$  (Figure 2.6b). In both cases, capillary force drives the retraction and opposed by either the inertial force in capillary-inertial regime or the viscous force in the capillary-viscous regime.



**Figure 2.6: Shape of droplets at different stages of retraction. Droplet radius of 1 mm with impact speed of  $2 \text{ ms}^{-1}$  for: (a) Pure water, (b) viscous water-glycerol mixture with viscosity of  $50 \text{ mPa s}$  [24]**

This phenomenon is consistent whether a droplet impacts on a solid or powder surface [23]. In both cases a critical Weber number of 1000 is used to determine whether a droplet will break on impact or not. If the Weber number is  $< 1000$ , the droplet will stay intact [23].

The final shape of a liquid drop after hitting a surface can be expressed by the Bond number (Eq. 2.6) which describes the ratio of gravity compared to surface tension forces acting on a droplet. Gravity forces the center of mass to drop which promotes the formation of a puddle, while surface tension opposes this action.

From the Bond number, the contact zone length may be calculated. When gravity is negligible and ( $R_0 \ll \kappa^{-1}$ ), a spherical droplet results and the contact zone length is equal to:

$$l = \sqrt{\left(\frac{2}{3}\right)R\kappa} \quad (\text{eq 2.9})$$

When gravity dominates and ( $R_0 \gg \kappa^{-1}$ ), a puddle like structure will result and the contact zone length is equal to:

$$l = \sqrt{\left(\frac{2}{3}\right)R^{(3/2)}\kappa^{(1/2)}} \quad (\text{eq 2.10})$$

where thickness of the puddle  $h = 2\kappa^{-1}$ .

Doganci et al, suggested that the overall shape of the resultant droplet can usually be defined using the following four parameters: drop height, liquid-solid contact length, contact angle and radius of spherical drop, where the drop height is not always equal to the radius as in some cases, the resultant droplet does not maintain a spherical shape through drying. [36].

## 2.4 Stability of Liquid Marbles

The stability of a liquid marble is defined in this thesis as the combination of longevity of a liquid marble and the ability to maintain its spherical shape. The stability of liquid marbles or dry water is dependent on a combination of factors including the type of hydrophobic powder used, presence of excipients, the production process, the chemical nature and the liquid used to form the marble [36, 37]. Previously, it has been shown experimentally that the stability of a liquid marble infused with inert graphite particles is double that of a pure water droplet of the same size [38]. Ionic liquid marbles using fluoride containing polymers in the powder shell were able to float on water for a week, compared to hydrophobised silica liquid marbles which only lasted a minute before coalescing [39]. pH responsive marbles have been made using poly(2-vinylpyridine) particles stabilised with hydrophobic polydimethylsiloxane macromonomer, which is highly stable at pH greater than 4.9 [40]. This can be explained by the weakly basic nature of poly(2-vinylpyridine) which becomes protonated in acidic conditions. The protonation of the poly(2-vinylpyridine) leads to the shell of the marble to become hydrophilic and hydrogen bond with surrounding liquids, leading to the rupture of the marble.

The liquid evaporation rate from the liquid marble also has a significant effect on the gradual deformation and eventual collapse of a liquid marble. The deformation and collapse of the liquid marble can be characterised in general by the following stages [36]:

1. Marble starts to shrink as liquid evaporates
2. Powder on marble surface becomes more dense on the liquid surface due to decreasing surface area
3. Marble buckles as the powder reaches maximum packing density [38]

The time it takes for different marbles to progress through each of these three stages varies significantly depending on the marble itself and also external conditions which affect the evaporation of the liquid from the marble. The exact effect of the powder encapsulation layer on the drying kinetics has not been studied. Previous research has shown that the lifetime of the marble is dependent on the humidity which is known to affect water evaporation rate. Lower ambient humidity results in a faster water evaporation rate which has been shown to reduce marble lifetime[41]. The stability of the marble can be increased by up to four hours just by increasing humidity from 5% to 86% [41].

The hydrophobicity of the powder also influences the stability of liquid marbles during formation. More hydrophobic powders, which will have larger contact angle will promote the formation of liquid marbles. As powders become more hydrophilic, foams tend to be formed instead [15, 42] as seen in Figure 2.7.

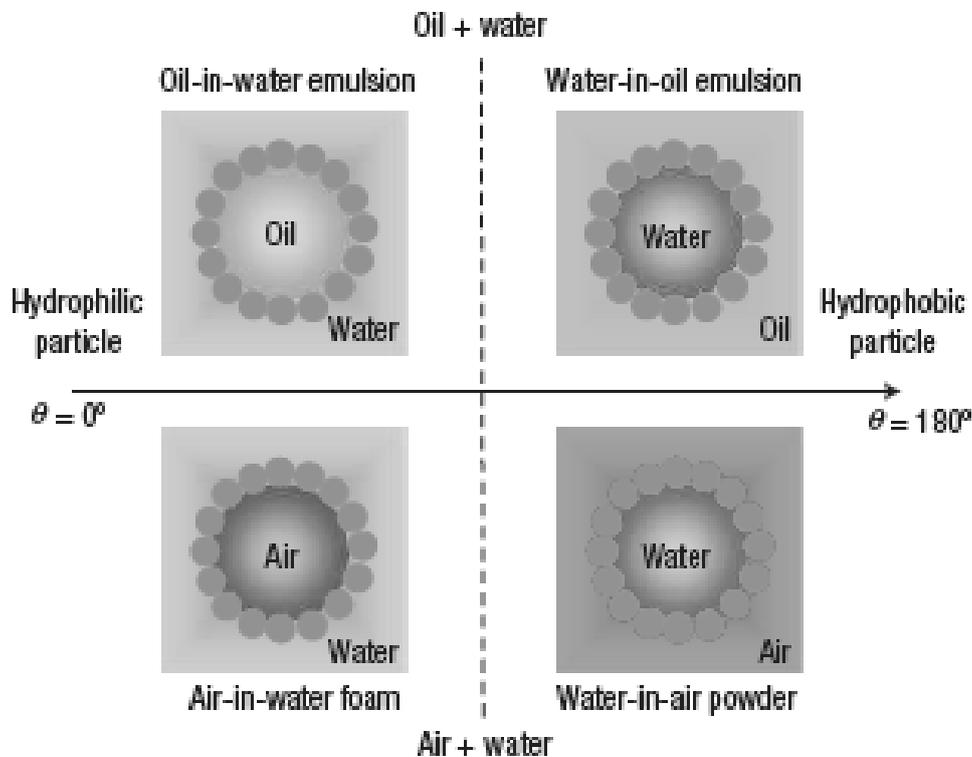


Figure 2.7: Dispersed systems prepared from fluid mixtures and colloidal particles [15]

The size of the particles in the powder layer is also a contributing factor to the mechanical robustness and evaporation rate of liquid from the liquid marble. Most studies to date use microparticulate materials as the encapsulation powder [8, 39, 43]. Nano particles have shown to create a more uniform coverage compared to microparticles which results in lower evaporation rate [44]. This is believed to be due to increased particle-particle interaction which results in the formation of an elastic membrane which protects the marble from evaporation and also increases the mechanical robustness of the marble [10, 44]

In conjunction to the size of the particles in the powder layer, the thickness of the powder shell will also affect liquid marble integrity [12]. The resistance of liquid marbles to mechanical deformation decreases as the powder wall thickness decreases or when the particles become less hydrophobic. This is attributed to the dependence of liquid marble stability on the hydrophobic interactions which exist between the powder particles [12]. The highly hydrophobic powder layer interacts within the powder shell layer through short range Van der Waal forces. The greater the contact area between particles, which is more likely in multi-layer powder shell cases; the greater the van der Waals forces, which helps the liquid marble to withstand external compression forces exerted on the liquid marble due to a stronger shell [12]. In addition, there is a lack of hydrogen bonding between the liquid center and the hydrophobic powder particles at the solid - liquid interface. This lack of bonding between the powder shell and the liquid center and the strong hydrogen bonding between the bulk water molecules encourages the water to stay within the center of the liquid marble [12]. These two factors together promote structural integrity and stability of liquid marbles.

It has also been suggested that stable liquid marbles requires a combination of low-surface energy particles and high-surface-energy liquids [5, 8, 9, 39, 40, 45]. Until recently, the majority of liquid marbles had been made from water or glycerol as the liquid phase and hydrophobized lycopodium, reactive polymer or silica as the hydrophobic phase for that reason [42]. However, both the liquid and hydrophobic phase are potentially reactive and are hence restricting in their use in chemical applications [39]. Ionic liquid marbles have since been created by Gao and McCarthy using chemically inert fluoropolymer particles (OTFE) as the stabilising powder. These marbles have shown higher stability, existing for weeks floating on water [39] compared to marbles made from hydrophobized silica which may float for around one minute before coalescing [8]. This may be due to the OTFE powder coating which contains a liquid component [46] and will stabilise the powder coating with an extra

adhesive interaction compared to pure hydrophobic interaction in water and hydrophobized silica marbles [39].

## 2.5 Drying of Liquid Marbles

The drying of liquid marbles is crucial as it usually sets the foundation of liquid marble stability. For a plain water droplet, the smaller the droplet, the shorter the time required for drying. This is expected as the drying rate is controlled by vapour diffusion in air and the changing surface area which is dependent on the wetting properties [47]. Research by Hu and Larson showed that droplets with a low initial contact angle of less than  $40^\circ$  have a constant overall evaporation rate. [48]. Previous researchers [36, 38] estimated evaporation rate of liquid marbles by assuming their shape to be a spherical cap drop shape. This shape is taken when the liquid drop is sufficiently small and surface tension dominates over gravity [49]. For the spherical cap drop shape, there are four main parameters (Figure 2.8): height of the drop ( $h$ ); liquid-solid contact radius ( $r_b$ ); equilibrium contact angle ( $\theta$ ); and the radius of the spherical drop ( $R$ ) [36, 50-52].

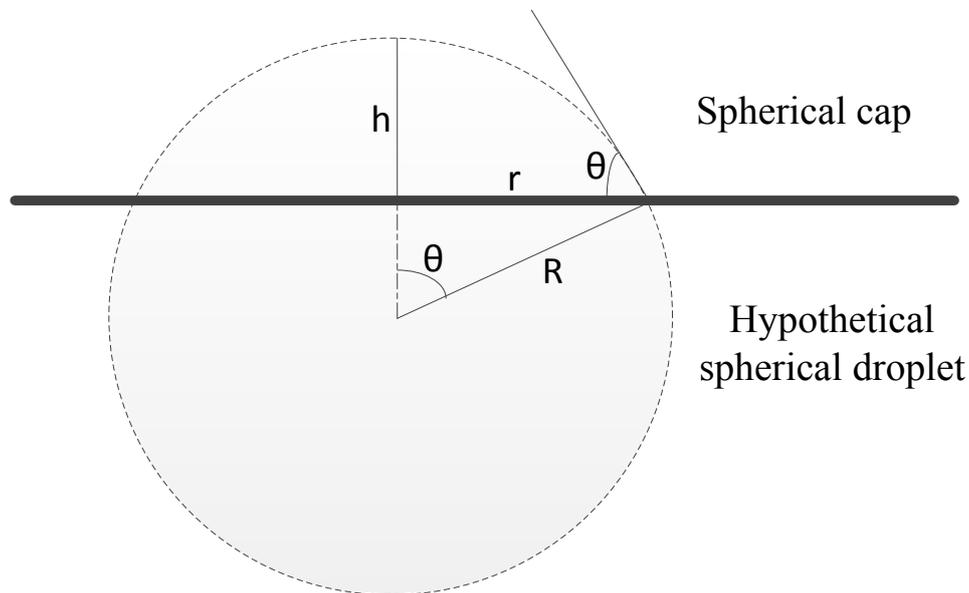


Figure 2.8: Diagram of the spherical cap drop shape and the contributing parameters. Adapted from [36]

The two radii and the contact angle can be calculated based on the spherical geometry [36, 50-52]:

$$r_b = R \sin\theta \quad (\text{eq 2.11})$$

and

$$R = \left[ \frac{3V}{\pi(2 - 3\cos\theta + \cos^3\theta)} \right]^{\frac{1}{3}} \quad (\text{eq 2.12})$$

Where  $V$  = volume of the drop. The volume has to be calculated from  $h$  and  $r_b$ , which can be measured from the drop profiles during droplet evaporation using Equation 2.13 below [52]:

$$V = \frac{\pi h}{6} (3r_b^2 + h^2) \quad (\text{eq 2.13})$$

For a liquid drop having a spherical cap shape, the rate of volume decrease with time where evaporation is diffusion controlled is given in equation 2.14 [53, 54]:

$$-\left(\frac{\delta V}{\delta t}\right) = \frac{4\pi D}{\rho_L} R(C_o - C_\infty)f(\theta) = Kf(\theta)V^{\frac{1}{3}} \quad (\text{eq 2.14})$$

Where  $t$  = time

$D$  = diffusion coefficient of the vapour

$\rho_L$  = density of the liquid

$C_o$  = vapour concentration at the surface

$C_\infty$  = vapour concentration at infinite distance from the surface

$\theta$  = equilibrium contact angle which is constant during this process

The  $f(\theta)$  term represents the retardation of evaporation due to the presence of the solid surface [36, 53, 54]:

$$f(\theta) = 4.4785 * 10^{-5} + 0.31665\theta + 5.8 * 10^{-2}\theta^2 \\ -4.439 * 10^{-2}\theta^3 + 5.165 * 10^{-3}\theta^4 \quad (\text{eq 2.15})$$

Where  $\theta$  = equilibrium contact angle (radians)

In equation 2.14, the  $K$  represents a constant which is independent of the drop volume and has to be calculated using the following volume correlation which is derived from anti-

differentiation of equation 2.14. This correlation has been reported to correlate well with experimental results in other diffusion controlled evaporation publications [36, 38, 49, 55, 56].

$$V^{\frac{2}{3}} = V_i^{\frac{2}{3}} - \left(\frac{2}{3}\right) Kf(\theta)t \quad (\text{eq 2.16})$$

The vapour concentration difference values in equation 2.14 can be calculated from equation 2.17 [36, 53, 54] :

$$(C_o - C_{\infty}) = \left(\frac{M_w P_{vs}}{RT}\right) (1 - RH) \quad (\text{eq 2.17})$$

Where RH = relative humidity of water vapour in the closed chamber

$M_w$  = molecular weight of water

$P_{vs}$  = saturation water vapor pressure at the given temperature

R = gas constant

T = Temperature

However, it is also possible to experimentally determine the vapor concentrations.

La Mer et al. later derived a specific evaporation resistance parameter,  $\phi$  to investigate the rate of evaporation when the surface of a liquid is covered with a monolayer of powder [57, 58].

$$\phi = A(C_o - C_{\infty}) \left( \frac{dt}{dm_M} - \frac{dt}{dm_L} \right) \quad (\text{eq 2.18})$$

Where A = the initial surface area of the evaporating medium

$m_M$  = mass of the coated droplet (liquid marble)

$m_L$  = mass of the pure uncoated liquid droplet

The La Mer equation provides a means to compare the drop evaporation resistance of both pure and liquid marbles where a powder surface coating is present.

Despite, the relative consensus in theoretical drop evaporation modelling using the spherical cap droplet method above, there is a lack of consensus from experimental results in literature on drying of liquid marbles and the effect of the powder coating. In many instances, the time needed to dry the liquid marbles seem to vary based on experimental set-up, size and nature

of the marble and independent of the type of powder shell present. Aberle et al, reported that liquid marbles formed with graphite shell had similar drying times to that of bare water droplets at temperature above the Leidenfrost temperature [59], while Dandan and Erbil reported almost doubling of drying time due to graphite shell [38]. Likewise, Tosun and Erbil reported longer survival time for liquid marbles coated with microsized polytetrafluoroethylene particles (PTFE) compared to bare water droplets [60] while Bhosale et al., found reported a shorter drying time compared to bare water droplets despite using similar microsized PTFE [44]. A study by Laborie et al., showed that droplets coated with a monolayer of hydrophobic particles dry faster than normal sessile water droplet, while a liquid marble covered with multilayer of particles tend to dry slower compared to a normal pure liquid droplet, with the drying rate dependent on shell coating thickness relative to the droplet size [47]. The faster drying of droplets with monolayer coating can be attributed two things:

1. Diffusion flux does not change with addition of a monolayer of particles compared to a bare droplet [47] and the evaporation rate due to a monolayer is constant regardless of pore size [61].
2. The surface area remains relatively constant over the drying time due to the incompressibility of the shell compared to the normal diminishing surface area of a bare droplet [47].

For multilayer droplets, the presence of a porous layer due to aggregation of the particles around the interface is believed to slow down drying as vapour diffusion from the center is retarded [47].

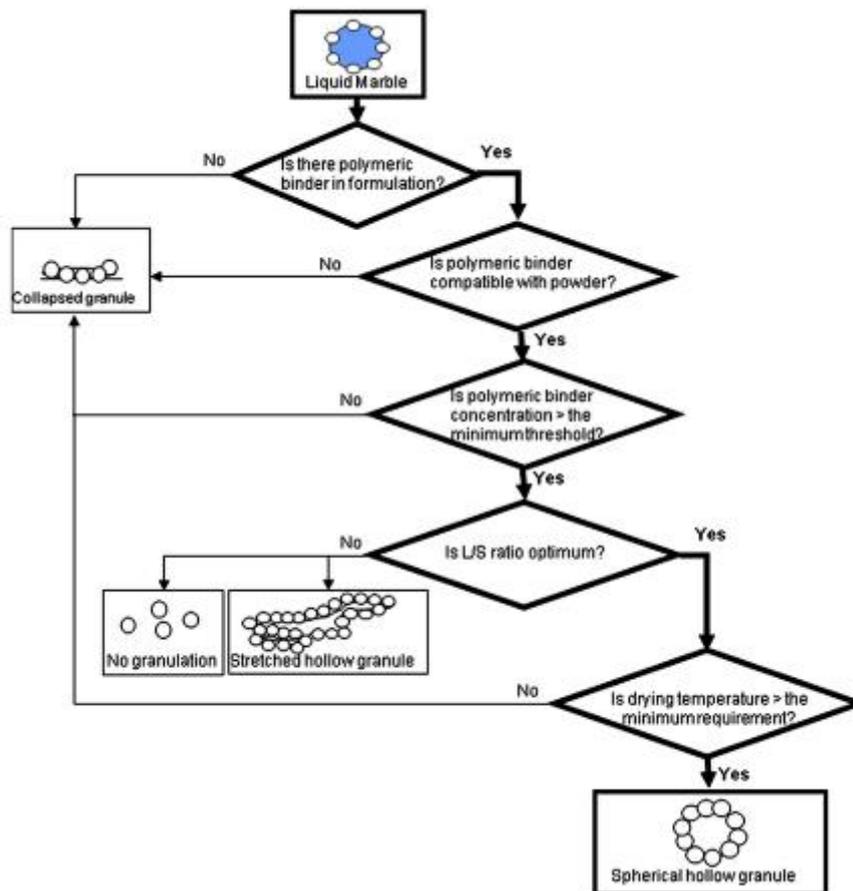
## **2.6 Hollow Granules**

An extension of liquid marbles is hollow granules. Hollow granules are the structures formed when the liquid inside the liquid marbles is dried leaving just the external hydrophobic shell. It has been observed that hollow granules between 100 and 300  $\mu\text{m}$  in diameter are spherical or slightly elliptical [62]. The existence of hollow granules is useful in the pharmaceutical industry as they allow for more controlled granule size, have good flow and compression properties and can contain a high hydrophobic drug content [62].

Hollow granule shells can be formed after drying poly-methylmethacrylate (PMMA), PTFE and two types of treated fumed silica powder encapsulated liquid marbles [28, 44]. The high

surface area of nanoparticle materials creates a more uniform powder shell and also forms a more elastic layer which results in the ability to withstand higher compressive forces during drying. This increases the likelihood of hollow granules formation.

A quantitative framework for the formation of hollow granules was proposed by Eshtiaghi and Hapgood [16]. For hollow granules to be formed, the powder shell must be sufficiently self-supporting to avoid collapse during the drying process of liquid marbles [19]. The formation of stable hollow granule from a liquid marble precursor is outlined in Figure 2.9 below [16], concentrating on the use of a polymeric binder to strengthen the powder shell by forming inter-particle bridges. While direct polymerisation of the shell is possible [28], use of polymeric binders promote the formation of a porous crust which prevents rupture or deflation during drying [63].



**Figure 2.9: Framework for formation of hollow granules from liquid marble precursor [16]**

Polymeric binder behaviour is dependent on their physical and chemical properties and hence, they must be compatible with the properties of the powder to exhibit desired response. A minimum binder concentration is required to provide sufficient strength to the crust as the

liquid marble dries [64]. It has been show that increasing the binder concentration reduces particle distortion and surface rupture [63].

An optimal liquid to solid ratio needs to be determined during formation of liquid marbles to maximise the number of spherical, single cavity granules and minimise foaming [15, 31]. To date, optimal liquid to solid ratio is determined using trial and error for different powder and liquid combinations.

The drying temperature is the last parameter which is believed to contribute significantly to the formation of stable hollow granules. Each powder/binder combination requires a different minimum temperature. Generally, increased temperature increases the survivability and quality of hollow granules produced, although not all binders follow this trend [16].

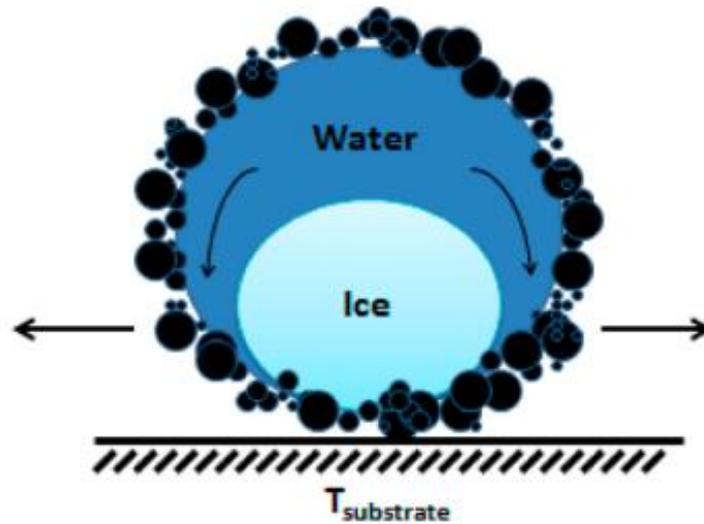
The resultant shell of the hollow granules can be categories into three crust types [64, 65]:

1. Crust is rigid and porous: the surface appearance of the marble does not change during drying.
2. Crust is rigid and non porous: a fracture phenomenon occurs on the air-liquid surface to allow air into the particle. The fracture may remain open resulting in solidification at the particle surface or in the crust structure. Otherwise, the fracture may close and crystals will form at the surface.
3. Crust is pliable and non porous. Rupture of marble and buckling will eventually occur as the crust thickens and stiffens.

## **2.7 Freezing of Liquid Marbles**

The effect of freezing liquid marbles has not been studied in much detail to date, with only two major papers published by Hashmi et al. [66] and Zang et al. [67]. Hashmi et al. made liquid marbles from de-ionised water and lycopodium particles which were cooled on a thermo-electric cooler. Compared to a water droplet freezing on a superhydrophobic surface; liquid marbles undergo a gradual deformation and a ‘flying saucer-shaped’ ice marble results [66]. The observations were attributed to the Marangoni convection and preferred nucleation principles, where it was proposed that the particles coating the liquid marble acts as an icing inhibitor, resulting in liquid flow of the water around the ice core as the marble freezes [66].

Figure 2.10 shows the cross sectional sketch of a liquid marble with the arrows indicating the flow of water due to the Marangoni effects.



**Figure 2.10: Cross-section sketch of a liquid marble with a proposed gap between the freezing front and the powder coating due to preferential nucleation. The arrows indicate the flow of water to the gap due to Marangoni effects. Replicated from [66].**

Zang et al. further extended on this work by looking at the effect of the coating powder hydrophobicity on the final shape of the liquid marble on freezing. It was observed that marbles with coating of powders which were more hydrophobic resulted in a frozen marble with a pointed protrusion on top; while marbles created with a lesser hydrophobic powder coating adopted a flying saucer shape similar to that observed by Hashmi et al. [66, 67]. Zang et al. attributed this difference to the different nucleation site present depending on where the particles sit at the air-liquid interface. For very hydrophobic particle coatings, ice crystals grows on the convex surface of the particles, while for less hydrophobic particle coatings, the ice nucleation site is in the concave cavities between particles. The growth of ice crystals between the particle cavities then extends into the liquid droplet; causing lateral stretching of the surface shell network, resulting in a flying saucer shaped frozen marble.

## 2.8 Novel Applications

The unique properties of liquid marbles and the simple concept behind their formation have resulted in numerous novel application trials in fields such as biology, electronics and reaction engineering. While many are still in the conceptual and lab-scale stage, the diversity of the applications is astounding, with many researchers exploiting the seemingly infinite

combinations of liquid and hydrophobic powder available. A few of the major applications have been described below.

On the biological front, liquid marbles for the cultivation of microorganisms have been created. Liquid marbles are ideal for growing micro-organisms due to their robustness and gas permeability of the shell which allows the free transport of oxygen and carbon dioxide across the marble shell [11]. A combination of the above characteristics means respirable bioreactors such as those created using liquid marbles provide a suitable environment for the growth of aerobic micro-organisms and it was determined that cell concentration increased more rapidly in liquid marbles compared to conventional incubation methods [11]. Hep G2 (hepatocellular carcinoma cells) have also been grown in the liquid core of a liquid marble. The constrained internal structure of liquid marbles allows the 3D growth of cancer cells compared to conventional 2D plate grown cells. The resulting cells therefore better reflect *in vivo* physiology of tumours [68].

Liquid marbles as micro-bioreactors for use as diagnostic assays for blood typing have also been studied [69]. Compared to conventional blood typing methods, liquid marble bioreactors have the added advantages of requiring smaller amounts of samples and reagents, reduced biohazards through isolation of sample and are cheap and relatively easy to control [69]. The authors used blood as the liquid phase and either precipitated calcium carbonate (PCC) treated with stearic acid or polytetrafluoroethylene (PTFE) as the hydrophobic powder phase to make these blood liquid marbles [69]. These marbles changed colour when an antigen was added resulting in an effective method for blood typing.

The use of liquid marbles as micro-reactors is not restricted to the biological field. Xue et al. created magnetic liquid marbles to mimic miniature reactors using organic solvents as the liquid phase [70]. Organic solvents tend to have low surface tension, which is generally unfavourable for the creation of liquid marbles. However, this was overcome by Xue et al. through use of a fluorinated decyl polyhedral oligomeric silsesquioxane (FD-POSS). FD-POSS showed strongly repellent behaviour to the organic liquids tested such as dimethyl sulfoxide (DMSO), toluene, hexadecane and ethanol, enabling the formation of liquid marbles [70]. Xue et al. further modified the FD-POSS powder to include  $\text{Fe}_3\text{O}_4$  nano particles to render the powder shell with magnetic properties for better control of the liquid marbles as small reactors [70]. Other groups have since also studied the characteristics of magnetic liquid marbles including their robustness; ability to open and close the powder shell

on demand to either add or remove liquid reagents; and ability to have more controlled movement of the resultant liquid marble in the presence of a magnet [70-72]. Iron oxides in the  $\text{Fe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  form are commonly added to the hydrophobic powder to render the powder shell of the liquid marble magnetic. However, Zhao et al., observed the detachment of iron particles over time which resulted in decreasing magnetic responsiveness and also deformation of the marble [71]. This problem was later avoided when the hydrophobic powder used itself contains magnetic properties. Ionic liquid marbles which uses chemically inert fluoropolymer particles as stabilizing agent has also been investigated as ionic liquids are non-volatile and can be used as solvents for chemical reactions [39]. Gao and McCarthy used oligomeric tetrafluoroethylene (OTFE) as the hydrophobic powder phase which can be used to a range of aqueous liquids including hexadecane, aqueous sulphuric acid and aqueous sodium hydroxide [39].

Remotely controllable liquid marbles have also been studied for the possibility of delivery of water-soluble reagents to trigger chemical reactions [73]. In order to achieve this, a specially designed shell made of a silica-coated magnetite core and a mesoporous silica shell grafted with poly (2-vinylpyridine-b-dimethylsiloxane) was created and used. The shell is loaded with photoacid generator (PAG), which generates  $\text{H}^+$  ions locally when illuminated with UV light. This causes a hydrophilic transition of the outer shell which causes the rupture of the marbles [73]. The stability of these marbles also varied significantly depending on the pH of their environment. The marbles ruptured in less than 10 seconds at pH less than 2 and as pH increased their survival time also increased to more than 12 hours at pH around 8 [73]. This is similar to other pH-responsive liquid marbles created with shells made from stabilized latex particles, chemically grafted PDEA chains and PDMS-P2VP latex [74, 75]. The addition of UV responsiveness in the marbles created by Zhang et al. provides the additional advantage that such marbles can be controlled without the need to change pH of the bulk liquid [73].

The concept of using nanomaterial coated liquid marbles to act as heavy metal ion sensors have also been tried. This holds implications in the field of soft electronics. Liquid metal marbles which have been encapsulated by semi-conducting and insulating micro - particles and nano - particles have been made to achieve this [7]. Such marbles have been shown to have enhanced heavy metal ion sensing sensitivity. Compared to the conventional water based marbles, metal marbles have higher surface tension and are able to withstand heavier load as a result [7]. They are also able to be used at higher temperatures as well as in a vacuum.

The idea of using liquid marbles as micropumps has been explored by Bormashenko et al. [45]. It functions according to the principle that droplets coated with different powders and of different radius have different surface tensions. As a result of the pressure difference formed, a liquid flow will occur between the two connected marbles [45].

Liquid marbles for gas sensing have been created by utilising the property of the hydrophobic shell which isolates the liquid core from the external environment but allows gases to transport through [9, 11]. Tian et al. studied the use of liquid marbles for gas sensing of ammonia and hydrochloric acid gases, using colorimetric and fluorescent indicators respectively [9]. The colour change within the liquid marble not only confirms the fact that the porous shell of the marble allows effective gas transport, but also provides the possibility of providing cheaper and faster acting detection mechanism for gas leaks.

In conjunction to the novel use of liquid marbles found in a laboratory setting, these remarkable particles have also found commercial uses. Currently, liquid marble technology is utilised in foundation and hair styling products in the cosmetic industry. Their ability to store large amount of fluid by weight, dry feel until subjected to shear force whether the inner liquid is then released has given them an almost magical quality which has been marketed with terms such as ‘magic liquid powder’ and ‘aqua powder’. They have also been found to last over two year compared to laboratory made marbles which survive for a fraction of that time. However, due to the secrecy surrounding commercial products, their formulation and exact production methodology, there is little know about liquid marbles found in commercial products.

## **2.9 Literature Summary and Research gap**

Research on liquid marbles has gained a lot of interest in the past decade and the diversity of literature available reflects the potential that these remarkable particles have. Although a basic understanding of how liquid marbles are formed, their unique properties and reactions to various chemical and physical manipulations is available in literature; our understanding of liquid marbles and the effects of formulation and environmental conditions on liquid marble stability is still in its infancy. To date, there has been minimal research conducted on why they are stable, the interactions between the air, solid and liquid interfaces and how the powder shell affects things such as the drying kinetics and drying mechanism of liquid marbles. This thesis focusses on the following three aspects:

1. How can liquid marbles be made to survive longer and what are the conditions which govern their long term survival?
2. How does a film forming additives such as a copolymer affect their shape during drying and their longevity?
3. How does different drying methodologies such as oven drying, single droplet drying and freeze drying affect the shape and structure of a liquid marble and their resultant dried structure?

As commercial products containing liquid marble technology start to enter our community, a better understanding of the above aspects is required to better design and optimise the uses of liquid marbles in the future.

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# 3

## Material Characterisation

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This Chapter describes the properties of materials used and methodology for production and characterization of liquid marbles studied in this thesis.



### 3 Material Characterisation

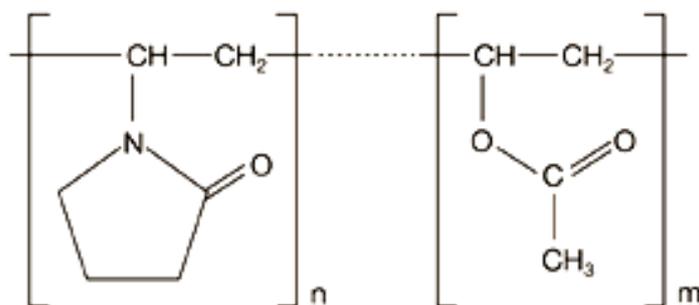
This chapter describes the properties of materials used for the study of liquid marble formation and their stability. The physical and chemical properties of liquid marbles are dependent on the interactions which exist in the powder encapsulation layer, the powder – liquid interface, and the internal fluid interactions. Knowing the properties of the materials used will help provide an insight into the fundamental interactions between the different components of the liquid marble and to better define the parameters which dictate whether stable marbles can be formed.

Given that commercialisation of these remarkable particles are seen mostly in the cosmetics industry to date, it is crucial that the selection of material is reflective of common excipients found in the cosmetics and pharmaceutical industry. This is to ensure this research may be extended into industry and that safety of products will not be compromised by inherent material properties or through interactions between the different types of materials.

#### 3.1 Liquid Characterisation - VP/VA Copolymer Solution

The liquid phase is a key component of liquid marble formation. Distilled water was used as the control and aqueous solutions of 2% and 5% (w/v) VP/VA copolymer (Vinyl-Pyrrolidone/Vinyl- Acetate copolymer) were used. VP/VA copolymer is sold under the name of Kollidon® VA64 by BASF. Kollidon® VA64 was chosen after the analysis of formulations of common commercial products, which had been identified as containing liquid marbles (see Section 4.1). It was found that a film former was included in the formulation of 75% of hair products and 25% of foundation products, however, those which included a film former showed more apparent liquid marbles and the most common film former used was VP/VA copolymer.

Kollidon® VA64 is also known as polyvinylpyrrolidone-vinyl acetate copolymer, VP/VA copolymer and copovidone. Kollidon® VA64 is a copolymer powder consisting of 6 parts N-vinylpyrrolidone and 4 parts vinyl acetate [1]. Figure 3.1 shows the constituent monomers of VP/VA copolymer.



**Figure 3.1: Molecular structure of Kollidon VA 64 copolymer [1]**

Kollidon<sup>®</sup> VA64 is a pharmaceutical grade product and fulfils the requirements of the “copovidone” and “Copoly-vidone” monographs in the European Pharmacopoeia and Japanese pharmaceutical excipients texts [1]. It has an extremely high solubility in hydrophilic liquids as well as in some hydrophobic solvents. However, at high concentrations; the viscosity of the solution can be quite high. In pharmaceuticals, it is used as a binder and granulating aid in tablets; a film former in tablet coatings; and matrix forming agent in sustained-release and fast-release dosage forms [1].

Food dye (Queens Fine Food Ltd.) was added to the liquid solutions to differentiate between the different concentrations of marbles and to aid in visual observations of drying patterns. It is assumed that the addition of the dye does not change the solution properties significantly [2].

### 3.1.1 Liquid Solution Properties Measurement

Surface tension of the VP/VA copolymer solution is measured using the capillary rise method. In a capillary, the Laplace pressure will push a liquid up the capillary. The height which the liquid travels up is dependent on the balance between the Laplace pressure and pressure due to gravity. This can be expressed by the following equation:

$$h = \frac{2\gamma\cos\theta}{\rho gr} \quad (\text{eq 3.1})$$

where  $h$  = height of liquid in capillary

$\gamma$  = surface tension

$\theta$  = contact angle

$\rho$  = density of solution

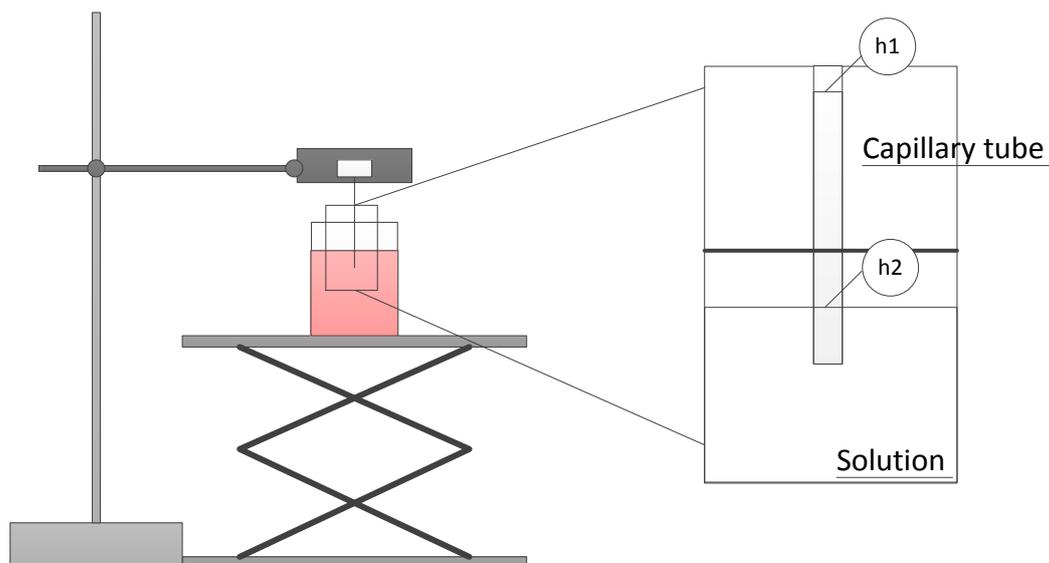
$g$  = gravity

$r$  = capillary radius

Rearrangement of equation 3.1 allows the calculation of surface tension:

$$\gamma = \frac{1}{2\cos\theta} h g \rho r \quad (\text{eq 3.2})$$

In order to determine the height of the capillary rise, the following apparatus was used. The solution was held in a beaker to allow enough depth to raise and lower the liquid in the capillary a few times. This ensures that the receding contact angle is used which is close to zero degree. The height at  $h_1$  and  $h_2$  is measured using a cathetometer. The height used in equation 2 to calculate the surface tension is the difference between  $h_1$  and  $h_2$ .



**Figure 3.2: Systematic diagram of apparatus used to determine capillary rise**

The density of the VP/VA solutions was measured using a Mettler Toledo densito 30PX at approximately 22 °C.

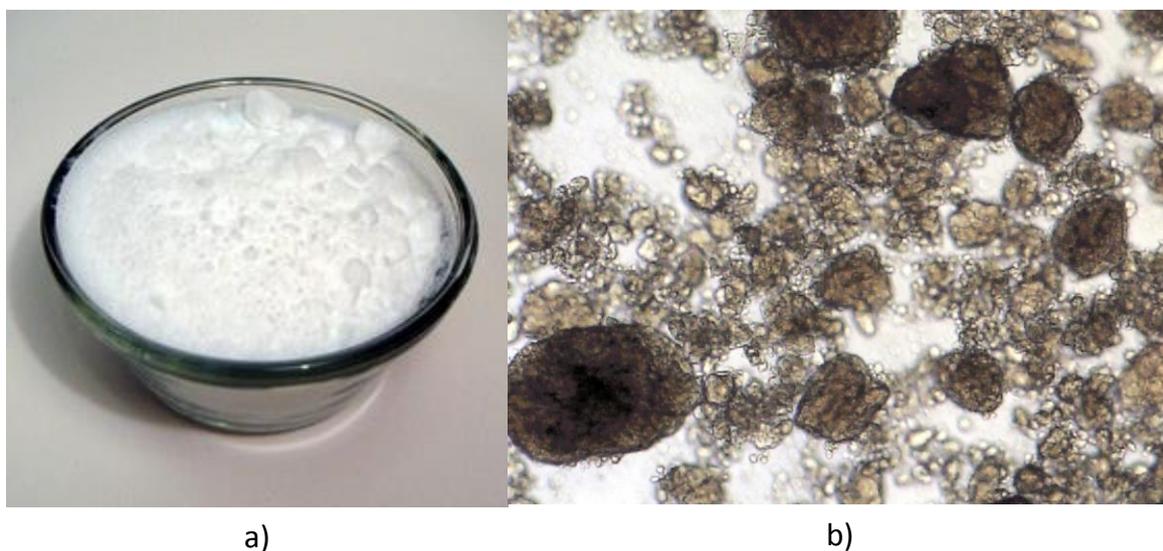
The properties for the liquid solutions used are summarised in Table 3.1.

**Table 3.1: Liquid properties of water and film former solutions**

<b>Liquid Property</b>	<b>De-ionised water</b>	<b>2% (w/v) VP/VA copolymer solution</b>	<b>5% (w/v) VP/VA copolymer solution</b>
Surface tension [mN/m]*	72.8	56.2 ± 1.1	53.5 ± 0.7
Viscosity [mPa.s]^	1.1	1.5	3.9
Density [kg/m <sup>3</sup> ] <sup>#</sup>	998	998	998
*Surface tension measured using capillary rise method			
^Obtained from BASF handbook [1]			
<sup>#</sup> Density taken at room temperature. At approx 22 °C using Mettler Toledo densito 30PX			

### 3.2 Powder Characterisation - Hydrophobic Fumed Silica (Aerosil)

Hydrophobic fumed silica (Aerosil) was used as the hydrophobic coating powder for the investigation of liquid marble stability. Aerosil is the commercial name given to silica silylate and is commonly used in cosmetics [3, 4] and in research [5-9]. Aerosil was supplied by Evonik Degussa and is available in different grades [10]. The different grades of Aerosil differs in their surface area, carbon content and pH [10]. In general, fumed silica is produced by the hydrolysis of chlorosilanes in a high temperature process (the AEROSIL<sup>®</sup> process). The hydrophobic rendering of the resultant powder occurs via further chemical reaction with the silanol groups on the surface of the fumed silica [3]. AEROSIL<sup>®</sup> R974, which is the grade used throughout this thesis, results from fumed silica after treated with dimethyl-dichlorosilane (DDS) [11].



**Figure 3.3: a) Bulk Aerosil R974 powder and b) Aerosil particles at 100 times magnification**

Aerosil is used commonly in the cosmetics and pharmaceutical industry as an excipient to improve and maintain free flowing and anti-caking characteristics of powders. It is also used in the paint and adhesives as a rheology controller of complex liquid systems [11]. The general powder properties of Aerosil are shown in Table 3.2 [11].

**Table 3.2: Summary of powder properties of Aerosil R974**

<b>Powder property</b>	<b>Hydrophobic fumed silica (Aerosil®)</b>
<b>Wettability</b>	Hydrophobic
<b>Appearance</b>	Opaque, amorphous
<b>Melting point</b>	>1600°C
<b>Mean particle size</b>	12 nm
<b>Solubility in water</b>	Insoluble
<b>BET surface area</b>	150-190 m <sup>2</sup> /g
<b>Loss on drying (2 hours at 105°C)</b>	≤ 0.5%
<b>SiO<sub>2</sub> content</b>	≥ 99.8%

### 3.3 References

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# 4

## Characterisation of Liquid Marbles in Commercial Cosmetic Products

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This Chapter investigates cosmetic products containing liquid marbles which are currently available for sale from commercial outlets. A detailed comparison is undertaken for these products to gain a better understanding of why such products are able to have over two years shelf-life compared to laboratory made marbles which are only able to exist for a fraction of that time.



## 4 Introduction

Liquid marbles are droplets of up to 98% fluid, coated with a hydrophobic powder. Exhibiting both solid and liquid properties, they are able to roll like a solid but deform like a fluid. Their unique properties have resulted in the use of these particles in commercial cosmetic and hair care products [1, 2]. First attempts to use liquid marbles or “Dry Water” as they were also called goes back to the 1960’s [3]. This concept of using these particles commercially was then further extended on by Japanese cosmetic companies in the late 1990’s to early 2000’s [4-6]. Commercially produced products have been found to last over two years while laboratory made marbles survive for only a few seconds, or days at most. This conflicting information on the survival time of liquid marbles has not been previously investigated.

The first step towards understanding the fundamental science behind the extended stability of commercial liquid marbles is to characterise several foundation and hair products that are commercially available. For each product, we analyse the formulation ingredients, particle size distribution, moisture content, visual appearance and general stability of the product. We also generate liquid marbles based on a common but simpler formulation and investigate the marble stability in controlled laboratory experiments.

## 4.1 Experimental

### 4.1.1 Materials

A total of twelve commercially available products were identified for the study, as summarised in Table 4.1a and b. Images of the products are given in Figure 4.1.



Figure 4.1: Examples of Commercial products available and tested

Table 4.1a: Table of foundation products used in this study, where year of manufacture was determined using the serial/batch number on the product and the website <http://checkcosmetic.net>.

Company	Product Name	Product Description & Comments	Year of Manufacture (Batch ID)
Christian Dior	IOD Aqua Powder Aquatique	A matt make-up foundation designed to moisturise and reduce shine.	2011
Dermalogica®	MAP-15 regenerator™	A “powder-to-emulsion technology” which also delivers “high concentrations” of vitamin C to the skin.	~ 2013 (1E01)
Prescriptives	Magic Liquid Powder	A powder foundation to release pigmented liquid when applied to the skin. Light refracting powders are also included to give a matt finish on the skin.	2008
Physicians Formula	Aqua Powder	Powder foundation said to contain “high moisture content”.	~2010 (3012)

**Table 4.1b: Table of hair styling products used in this study where year of manufacture was determined using the serial/batch number on the product and the website <http://checkcosmetic.net>.**

Company	Product Name	Product Description & Comments	Year of Manufacture (Batch ID)
Schwarzkopf	OSIS Dust it Mattifying Powder	To apply, the product is rubbed between the hands to release the inner liquid to form a gel which is then applied to dry hair	2012
	Volume Powder	The product is rubbed to form a gel before applying to dry hair, where it then dries clear.	2011
	Got 2b powder'ful	Another product by Schwarzkopf with similar properties to Volume powder (above). Contains “weightless microparticles” designed to texturize hair and increase hair volume.	2012
Instant Rockstar	Stardust	Product is rubbed between the palms to release the inner liquid and form a gel and then applied to the hair to produce a matt finish and give a styled look.	~2013 (EU01)
L'Oreal	Tecniart Texture Dust	A powder which provides texture and definition. A relatively new product which only became commercially available in 2012-2013.	2012
	Tecniart Super dust	Similar to Texture Dust mentioned above.	2012
Nak	done.n.dusted	Provides hair with a matte finish and increases volume.	~2013 (20443)
Sexy hair concepts	Big sexy hair Powder	This product liquefies when applied and claims to be weightless, odourless & colourless on hair.	~2013 (10327E)

Since commercial products must list the ingredients in order from most to least, these products were initially identified as containing liquid marbles via the product information and ingredients list as “Aqua” (water - liquid phase) and “silica silylate” (hydrophobic powder phase) were listed as the first two ingredients. Silica silylate is also known as “Aerosil” and is commonly used in cosmetics [2, 7] and in research [8-12].

A detailed breakdown of the composition of each product is given in Table 4.2 and 4.3. The excipients/ingredients in Table 4.2 and 4.3 are listed in decreasing order. E.g. products contain

mostly water, then silica silylate, then VP/VA copolymer etc. VP/VA copolymer (film former) was a common ingredient in most of the commercial products samples. VP/VA copolymer, also known as “Copovidone” is a copolymer made from monomers of polyvinylpyrrolidone (VP) and vinyl acetate (VA) [13, 14]. Film formers such as VP/VA copolymer are chemicals that are surface active and create a barrier coating between two interfaces, often by forming a continuous but flexible matrix at the interface [14].

Table 4.3 shows the formulation breakdown of all the hair styling products tested. In all cases, water, silica silylate and a film former appear as the first three ingredients. Both VP/VA copolymer and Octylacriamide/Acrylates/ Butylaminoethyl methacrylate copolymer act as film formers, with Octylacriamide/Acrylates/ Butylaminoethyl methacrylate copolymer being used in the more recent formulations. Citric acid is commonly used as pH adjuster and all samples contained one or more preservative (sodium benzoate, potassium sorbate and phenethyl alcohol [15]).

**Table 4.2: Formulation breakdown of commercial hair styling products. Ingredients are listed in decreasing order.**

Excipients/ Ingredients	Water	Silica silylate	VP/VA copolymer	Octylacriamide/Acrylates/butylaminoethyl methacrylate copolymer	Citric acid	Sodium Benzoate	Potassium sorbate	Phenethyl alcohol	Glycerin	Other - fragrance	Other - occlusive	Other - binder	Other – appearance enhancers
OSIS+ dust it mattifying powder	✓	✓	✓			✓							
Nak done.n.dusted	✓	✓	✓		✓	✓				✓			
Tecniart texture dust	✓	✓			✓	✓	✓	✓	✓			✓	✓
Tecniart super dust	✓	✓	✓		✓	✓	✓		✓	✓			
Stardust	✓	✓	✓			✓			✓	✓			
Volume powder	✓	✓		✓	✓	✓							
Got 2b powder’ful	✓	✓		✓	✓	✓							
Big sexy hair powder play	✓	✓				✓				✓	✓		

Table 4.4 show the detailed formulation breakdown of commercial cosmetic foundation products. As a foundation product, all contain significantly more ingredients than the more

simple hair styling products. However, there are a few common attributes. Water and silica silylate all appeared as the first two products, except for MAP-15 regenerator, where silica replaced silica silylate as the second ranking ingredient. All the foundation products contained a one or more preservative (phenoxyethanol and parabens [15]). Based on the order of ingredients, preservatives were ranked higher in the foundation products compared to the hair styling products, which would indicate greater importance and higher relative concentration to other ingredients in the foundation products. As expected, colouring agents also hold significant importance in the foundation products. In the case of foundation products, only magic liquid powder contained a film former (sodium polyacrylate [15]). The use of a different film former to that found in the hair styling products (VP/VA copolymer) could stem from the different functions of the commercial products. For foundation products, the colouring and the skin feel of the product is of priority while for hair styling products, an easy to use powder delivery system is the priority. Sodium polyacrylate can also function as a skin-conditioning agent [15], which is desirable in foundation products but not in hair-styling. As such, that is possibly why sodium polyacrylate is used instead.

**Table 4.3: Formulation breakdown of commercial cosmetic foundation products. Ingredients are listed in decreasing order.**

Excipients/ Ingredients	Water	Silica silylate	Phenoxyethanol	Paraben (methyl/ethyl/butyl)	Colourants (iron oxides, titanium dioxide, mica)	Sodium Polyacrylate	Other – occlusive /humectant*	Other – skin appearance enhancers#	Other – preservative/ anti-microbial	Other - fragrance	Other – anti-caking agent	Other - binders	Other- bulking agent	Other- viscosity modifier	Other- pH adjuster
IOD aqua powder	✓	✓	✓	✓	✓				✓		✓				
Magic liquid powder	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓			
Aqua powder	✓	✓		✓	✓		✓	✓	✓		✓		✓		
MAP-15 regenerator	✓	✓*	✓		✓			✓	✓	✓	✓			✓	✓

\*In the case of MAP-15, silica silylate is present but expected to be in lower quantities compared to the other products due to location on ingredients list. For all other formulation products, water and silica silylate are the first two ingredients while for MAP-15, it ranks significantly lower.

### 4.1.2 Experimental Procedure

The physical appearance of each commercial sample was characterised by gently spreading the sample over a glass slide (without a coverslip) and examining the marbles using an optical microscope (Olympus BX-60, Spot imaging Solutions, US). The optical microscopy method minimises stress on the marbles and ensures the measured size of the liquid marbles is not compromised by shear forces which may cause marble rupture. The delicate nature of the liquid marbles means that once they are removed from the packaging, they are prone to rupture under shear (as required in their consumer application). It was somewhat difficult to obtain a thin layer of the powder on a glass slide without subjecting the sample to shear which could rupture the marbles. In some cases, even during the imaging of current samples, rupturing of the marbles can be observed. Images for each sample were taken using an external snake lighting system and Spot Insight QE camera with a resolution of 72 pixels/inch.

Particle sizing of the liquid marbles was determined through Image J analysis of a series of approximately 30 optical microscope images, with a minimum of 3000 liquid marbles being measured. Feret's diameter was used to characterise the liquid marble size distribution. Feret's diameter is distance between two tangents on opposite side of the particle [16]. This is equivalent to the diameter if the particle is a perfect sphere. For particles which are not exactly spherical, the projected diameter will be slightly different depending on which plane the tangents are taken. For the purposes of this study it was assumed that commercially produced liquid marbles will be close to perfect spheres and that the Feret's diameter is a relatively good measure of particle size. For all the samples,  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  values were determined from a cumulative frequency plot, where the diameter of particles is determined from image J and the cumulative frequency of particle sizes calculated in Microsoft Excel.

Some fine, loose excipient particles were visible in all the products. These were partially excluded by limiting the particle size range considered. In order to determine the liquid marble size, these fine loose particles were partially excluded by limiting the particle size range considered in the image analysis. Particles below 20  $\mu\text{m}$  can be excluded since most of the insoluble excipients have a particle size of less than this e.g. Aerosil has an average particle size of 16 nm [17]; iron oxides have an average particle size of 1- 20  $\mu\text{m}$  as they often exist as agglomerates [18]. Other components such as the preservatives (parabens and sodium benzoate), film formers (VP/VA co-polymer), pH adjuster (citric acid) are all highly soluble, and are therefore dissolved with the liquid marble and do not affect particle size analysis.

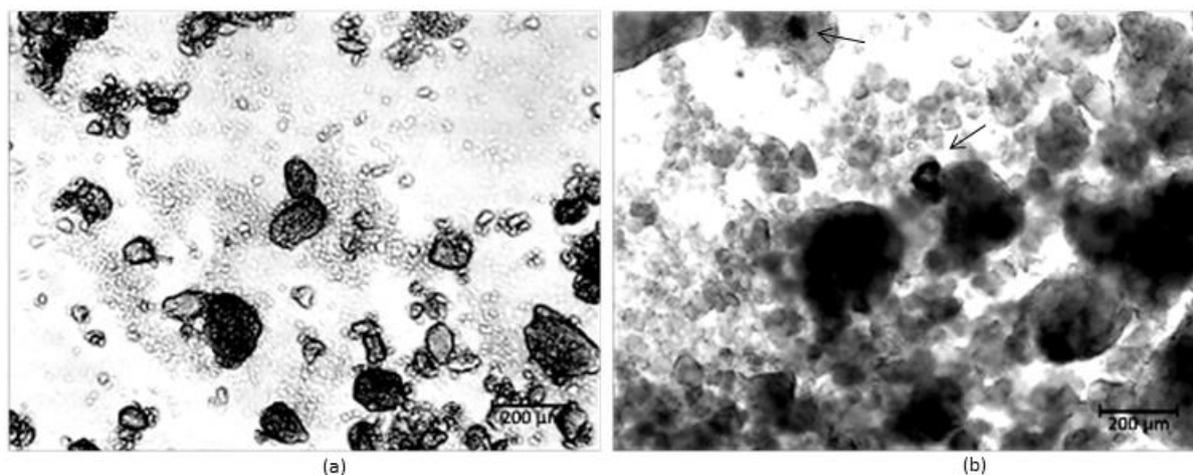
Formulation ingredients such as bulking agents (zinc oxide and tin oxide) vary significantly in particle size depending on the manufacturer, however, in recent years there has been a move to using microfine particles which tend to be in the nanometer to low micrometer range [19]. While excluding particles less than 20  $\mu\text{m}$  may affect the particle sizing data, it was assumed that most of the bulking agents and other fine excipients are incorporated within the powder shell of the liquid marbles.

The moisture content of the commercial liquid marble samples was determined by drying approximately 0.1 g samples at 105°C and weighing them every 24 hours until no significant change in weight could be observed, usually within  $\pm 0.001$  g. This weight loss is due only to water as the boiling point of fragrances and other liquid components in the products were above the drying temperature of 105°C [20]. It is assumed that majority of the liquid content is trapped inside the marbles, and that moisture loss due to humectants absorbing moisture from the atmosphere was negligible. The moisture content test was conducted in duplicates and error range calculated from the results.

## 4.2 Results

### 4.2.1 Appearance of Commercial Samples

Images of pure Aerosil and laboratory made liquid marbles (dyed) in a dish of Aerosil are shown in Figure 4.2, with liquid marbles indicated by arrows in Figure 4.1b.



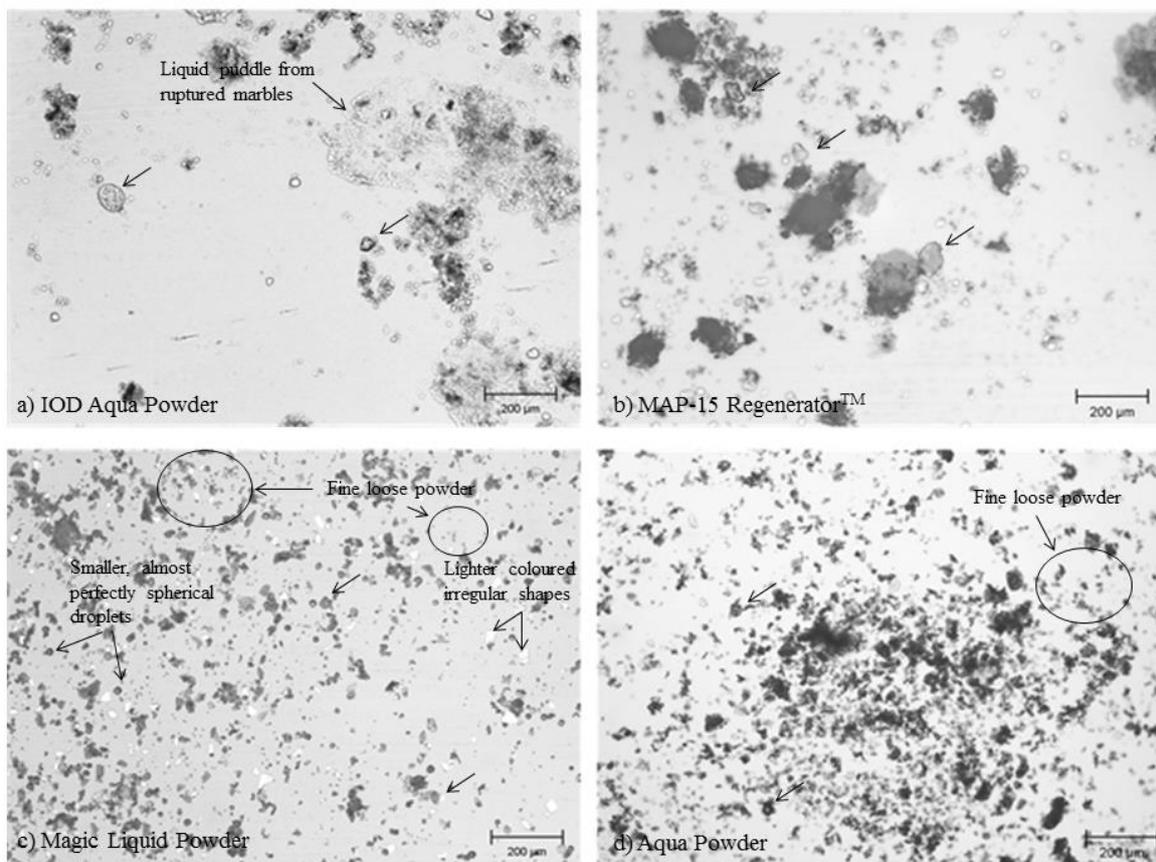
**Figure 4.2: Images of (a) pure Aerosil without liquid marbles and (b) Laboratory made liquid marbles using deionised water (with dye) in Aerosil powder. The liquid marbles are indicated by arrows.**

This provides a comparison between the highly agglomerated pure Aerosil R974 powder and what would be an expected image of liquid marble made from Aerosil R974. It is clear that pure Aerosil tends to form agglomerates and these agglomerates show the characteristic light center and dark outline which is also characteristic of a liquid marble. This makes it extremely difficult to identify the presence of liquid marble based on imaging alone in the absence of any identification markers on the liquid marbles. However, we can independently confirm that the majority of the structures observed in the images of the commercial samples must be liquid marbles, due to the high moisture content of the products, which was generally between 50 – 90% (Tables 4.4 and 4.5).

#### 4.2.1.1: Foundation Products

The visual appearance of the foundation products are shown in Figure 4.3. Additional example images are in Appendix B. Despite the difficulty in separating liquid marbles from silica silylate agglomerates, liquid marbles can still be identified in the images for two reasons. First, water is the main ingredient and will be in excess compared to the hydrophobic powder in the commercial samples (see Tables 4.2 and 4.3). Therefore, it is expected that most of the silica silylate will be incorporated into liquid marbles. Second, unlike the control images in Figure 4.2, the commercial samples contain other excipients which further decrease the possibility that

free silica silylate agglomerates are present due to the almost ‘sticky’ nature of this very low density powder.



**Figure 4.3: Typical images of liquid marble foundation products (a) IOD Aqua Powder by Christian Dior (b) MAP-15 regenerator™ by Dermalogica (c) Magic Liquid Powder by Prescriptives (d) Aqua Powder by Physicians Formula. Liquid marbles are indicated by arrows, unless specified.**

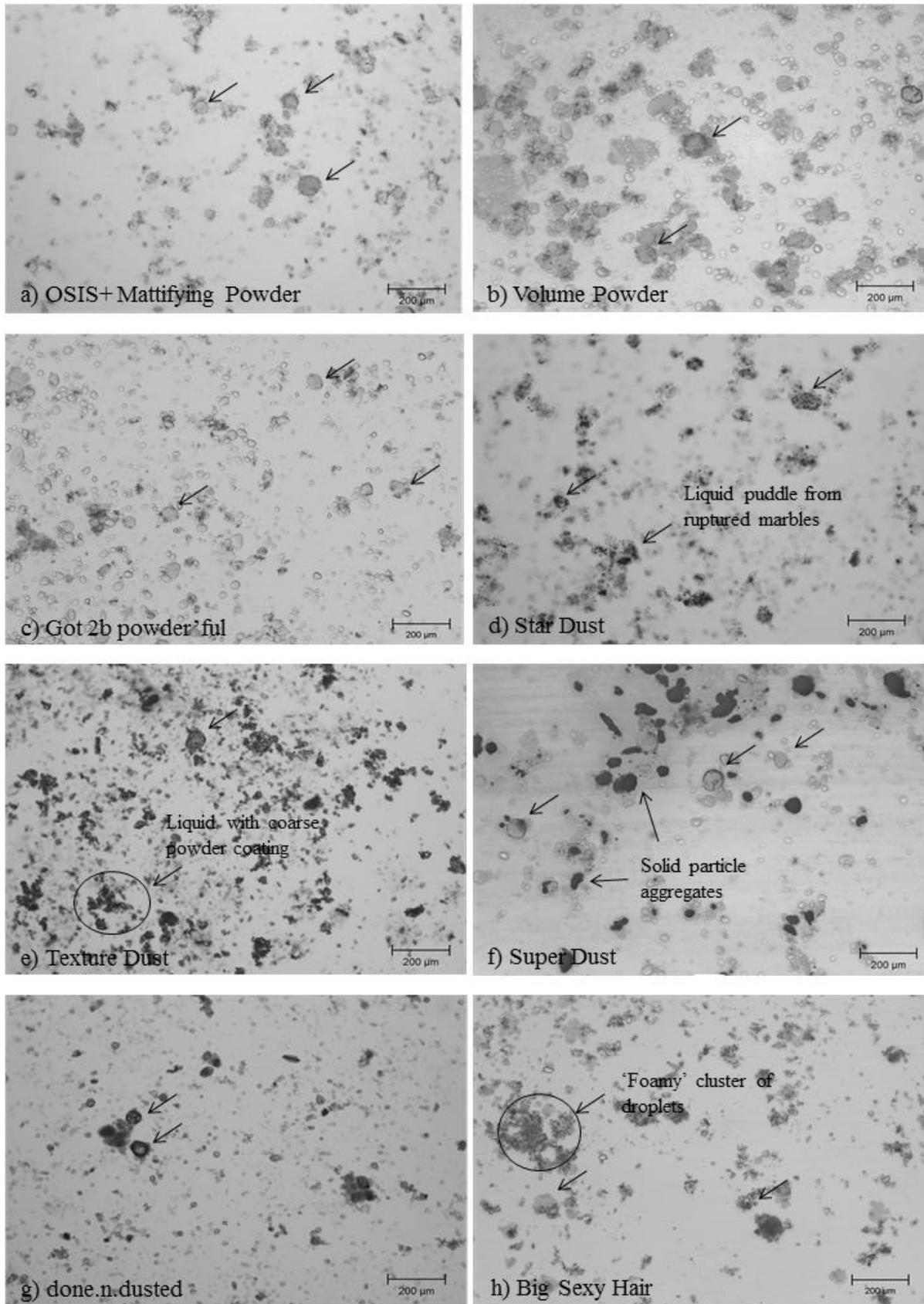
Images of *IOD Aqua Powder* and *MAP-15 regenerator™* (Figure 4.3a, b) both clearly show the presence of liquid marbles with the characteristic shell and transparent center. It is assumed that the center consists of all the liquid components which are made up of water and soluble excipients and the outer shell consists of hydrophobic powder. However, we are not able to confirm the exact composition of the liquid marbles. The *MAP-15 regenerator™* formulation is different from all the other foundation products in the ingredients listing. All other products have water and silica silylate as the two main ingredients, while for *MAP-15*; silica is the solid phase in abundance. Based on this, it is possible that for the *MAP-15* sample, the major component of the hydrophobic shell is silica as opposed to silica silylate which is expected to have hydrophobic shell covering consisting of mostly silica silylate.

*Magic Liquid Powder* by Prescriptives (Figure 4.3c) contains a significant amount of excipients in addition to liquid marbles, as shown by the large numbers of irregularly shaped and reflective particles and its low moisture content compared to the other foundation products (Table 4.4). These irregularly shaped particles are most likely excipients such as colouring agents (iron oxides, titanium dioxide and mica particles) which are also present in images from *Aqua Powder* (Figure 4.3d). The presence of large amounts of colouring agents is expected given that both products are used as foundations. While liquid marbles are present in the *Aqua Powder* sample, it is not clear whether some of the smaller spherical shapes observed are excipients or small marbles from the images alone. Although all four of the foundation product samples contain colouring agents, it is believed that the excipients are more prominent in the *Magic Liquid Powder* and *Aqua Powder* samples due to their low moisture content (Table 4.4), which means given the same amount of powder, less excipients would become incorporated as part of liquid marbles in the sample. This seems to be supported by the greater amount of free loose components in Figures 4.3c and 4.3d, compared to the bigger agglomerates in Figures 4.3a and 4.3b, which have higher moisture content and better defined liquid marbles in comparison.

One very clear difference between all the foundation samples is liquid marble shape. In the Dior powder all of the liquid marbles had quite non-uniform spherical shapes whereas *Magic Liquid Powder* consisted of liquid marbles which were almost perfectly spherical. This is most likely due to the ingredients used in the formulation. Different grades of silica silylate with varying degrees of hydrophobicity may have been used [21], which would also impact on the appearance of the sample. Increasing hydrophobicity of the powders will promote formation of liquid marbles, while decreased hydrophobicity will result in formation of foams and irregular shaped marbles [22]. Unfortunately, none of the products specify the exact grade of silica silylate used.

#### **4.2.1.2: Hair Styling Products**

Images of commercially available hair styling products are shown in Figure 4.4 and additional images are in Appendix B.



**Figure 4.4: Typical images of liquid marble hair-styling products (a) OSIS+ Mattifying powder by Schwarzkopf (b) Volume powder by Schwarzkopf (c) Got 2b powder'ful by Schwarzkopf (d) Star Dust by Instant Rockstar (e) Texture dust by L'Oreal (f) Super dust by L'Oreal (g) done.n.dusted by NAK (h) Big Sexy Hair by Powder Play. Liquid marbles are indicated by arrows unless otherwise specified**

The Schwarzkopf samples (*OSIS+ Mattifying powder*, *Volume powder* and *Got 2b powder'ful*) all show the characteristic shell and transparent centre which is assumed to be liquid. The three samples are very similar in appearance which is expected as they have essentially the same formulation and are most likely produced via a similar production methodology. *Osis+* is the earlier version contains VP/VA copolymer, while the later versions contain Octylacriamide/Acrylates/ Butylaminoethyl methacrylate copolymer as film former instead. The later products also includes citric acid which is used as a pH adjuster [15] While the liquid marbles in the Schwarzkopf samples are quite distinct, the sizes of the marbles seem to vary significantly (Figure 4.4a–c).

Comparison of the Schwarzkopf products with other products containing similar formulation such as Stardust by *Instant Rockstar* (Figure 4.3d) and *done.n.dusted* by NAK (Figure 4.4g) suggests that the manufacturing procedure may be a major contributor to product difference. These products look quite different to the Schwarzkopf samples despite all having the same key ingredients and only varying very slightly in excipients such as the presence or absence of fragrances or humectants.

The two L'Oreal samples, *Tecniart Texture dust* and *Tecniart Super dust* differ only slightly in the formulation. However, differences in concentration of components have caused quite significant changes in the particle shape and uniformity as seen from Figure 4.4e and 4.4f. While *Super dust* has more distinct liquid marbles, there are also solid particles of similar particle size, as seen by the completely black 'blobs' in Figure 4.4f. *Texture dust* has less distinct marbles and small puddles of liquid with a powder coating were present in the images, which may indicate ruptured marbles. This may stem from the difference in water to silica silylate ratio present. A combination of the presence of solid particles in the *Super dust* sample and the lower moisture content (Table 4.5) compared to *Texture dust* seem to indicate that *Super dust* has lower water to silica silylate ratio in comparison.

The other three products - *Star dust* by Instant Rockstar (Figure 4.4d), *done.n.dusted* by NAK (Figure 4.4g) and *Big Sexy Hair* by Powder Play (Figure 4.4h), also show varying numbers of liquid marbles in the images taken. *Star dust* showed liquid marbles with similar appearance to the *Texture dust* sample by L'Oreal, where the liquid droplets seemed to be covered by more coarse particles. *done.n.dusted* seemed to contain the least amount of observable liquid marbles with the majority of particles observed to be either agglomerates of fine particles which may indicate the rupture of actual liquid marbles during transport or manufacture. The last sample,

*Big Sexy Hair* also contained limited individual liquid marbles, with images showing agglomerates of small liquid droplets, which is observed as an almost ‘foamy’ cluster of semi-transparent droplets in Figure 4.4h.

#### 4.2.2: Moisture Content and Particle Size of Commercial Products

Table 4.4 and Table 4.5 provide the moisture content as a percentage weight of powder for foundation and hair styling products respectively. Both tables also provide the  $d_{50}$  and  $d_{90}$  data for the respective products.

**Table 4.4: Moisture content of foundation products (% weight) and error interval with corresponding particle size measurement ( $d_{50}$  and  $d_{90}$ ).**

Foundation Product	Moisture Content (% weight)	$d_{50}$ ( $\mu\text{m}$ )	$d_{90}$ ( $\mu\text{m}$ )
IOD Aqua Powder Aquatique by <i>Christian Dior</i>	$94.8 \pm 13.6$	43	66
MAP-15 regenerator <sup>TM</sup> by <i>Dermalogica</i> <sup>®</sup>	$81.2 \pm 0.6$	43	65
Magic Liquid Powder by <i>Prescriptives</i> *	$61.8 \pm 0.6$	43	66
Aqua Powder by Physicians Formula	$28.0 \pm 1.2$	45	91

\* Denotes moisture content data measured in 2010 at 60°C as part of an earlier unpublished study. The other samples were all tested in 2013.

**Table 4.5: Moisture content of hair styling products (% weight) and error interval with corresponding particle size measurement ( $d_{50}$  and  $d_{90}$ ).**

Hairstyling Product	Moisture Content (% weight)	$d_{50}$ ( $\mu\text{m}$ )	$d_{90}$ ( $\mu\text{m}$ )
OSIS Dust it Mattifying Powder by <i>Schwarzkopf</i>	$77.5 \pm 0.4$	44	89
Stardust by Instant <i>Rockstar</i>	$80.2 \pm 10.2$	46	95
Volume Powder by <i>Schwarzkopf</i>	$78.0 \pm 10.0$	47	118
Tecniart Texture Dust by <i>L’Oreal</i>	$98.1 \pm 2.0$	44	82
Tecniart Super dust by <i>L’Oreal</i>	$60.0 \pm 3.2$	45	94
done.n.dusted by <i>NAK</i>	$47.7 \pm 19.2$	46	97

The moisture content varied significantly between the tested commercial products. Moisture content of foundation products ranges from 95% to 28% and for hairstyling products, 98% to 48% water by weight. The moisture content measured here does not take into account previous water loss due to evaporation during transport from the manufacturing location to Australia or

during storage. The time between production and moisture content analysis is between 1-3 years (see Table 4.1 for sample manufacturing years), and the moisture content may have decreased during storage. Although, the measured data above may not be representative of marbles at the time of manufacture, it is still a useful indicator of typical ranges.

*Aqua Powder* had the lowest measured moisture content of 28% by weight. It is not clear whether this product has a higher rate of moisture loss compared to the others or if it exited the manufacturing stage with lower initial moisture content. Some of the commercial products also contain humectants at unknown concentrations, which may impact on how much moisture is retained.

The particle size analysis shows that all the commercial products tested had a very narrow range of  $d_{50}$  sizes between 43 – 47  $\mu\text{m}$ . The  $d_{90}$  of the samples did vary between the foundation and hair styling products. The three foundation products (*IOD Aqua Powder*, *MAP-15 regenerator<sup>TM</sup>*, *Magic Liquid Powder*) consist of liquid marbles with a  $d_{90}$  of 66  $\mu\text{m}$ . The hair styling products in general have a variable upper limit with 90% of the particles being less than 82 – 118  $\mu\text{m}$ .

The two Schwarzkopf samples analysed (*OSIS+ Dust it Mattifying Powder and Volume Powder*) were not similar in their upper range which was unexpected given similar appearance and moisture content (Figure 4.4 and Table 4.5). None of the samples analysed contained mono-dispersed liquid marbles given all of them had large particle size range. The difference in the upper limit of liquid marble sizes in the products may be due to agglomeration of some of the particles, although where possible this effect has been minimised by manually adjusting parameters on Image J. Overall, majority of particles fell within the range of 20– 100  $\mu\text{m}$  regardless of whether it was a foundation or hair styling product. It is interesting to note that the liquid marble size in all products tested was almost identical. It is not clear whether they were all manufactured to be this size for a particular reason or if the marbles contract to this size over time.

The data in Table 4.4 and 4.5 shows that larger particle size (implying a potentially larger liquid volume size) does not necessarily result in average higher moisture content. For example, *Volume Powder* which contains the largest spread of particles with  $d_{90}$  of 118  $\mu\text{m}$  has a moisture content of  $78.0 \pm 10.0\%$  by weight compared to *Tecniart Texture dust* which has a  $d_{90}$  of 82  $\mu\text{m}$  and a moisture content of  $98.1 \pm 2.0\%$ . This data implies that larger marbles will lose

liquid content more easily, and that smaller  $d_{90}$  sizes may be better for overall liquid marble stability.

### 4.3 Conclusion

Commercial products containing liquid marbles was investigated to obtain a better understanding of liquid marbles and identify clues to their long- term stability which has been achieved in commercial products. Their appearance, formulation, particle size and moisture content were analysed. Analysis of appearance using optical microscopy shows the presence of liquid marbles in these commercial products by their characteristic shell and transparent centre. The optical images show that the shape and uniformity of liquid marbles varies between products which may be due to the different formulations, grade of silica silylate used and production methodology. Cosmetic formulations tend to contain more excipients and the shape and uniformity of liquid marbles in such formulations tend to vary significantly. However, even products with similar formulation do not always have a similar appearance, which suggest that manufacturing methodology influences the appearance in addition to the formulation.

There seems to be an ideal particle size range for both foundation and hair styling products, of around 45  $\mu\text{m}$ . However, this data is not completely indicative of the size of the liquid marbles as it does not account for the proportion of liquid marbles in the formulation, although where possible, manual adjustment and limits were set to try and account for the liquid marbles. In general, the particle size range for both foundation and hair styling products are remarkably similar, however, it is unclear whether this is due to the manufacturing and product design, or due to liquid marbles contracting to this size over time.

Moisture content of the liquid marbles tended to be higher for formulations with more uniform particle size and hair products in general. Hair products showed on average higher moisture content compared to the foundation products. It is possible that foundation products contained less water to begin with in the formulation due to extensive amount of colouring agents required. However, more ingredients do not necessarily mean lower moisture content.

Analysis of the formulations of products containing more distinct and stable liquid marbles showed the presence of a film former such as VP/VA copolymer. As film formers such as VP/VA copolymer create a barrier coating between two interfaces, it is expected that addition of film formers function to enhance liquid marble stability by changing surface properties such as the evaporation rate of the liquid from the marble. The effect of VP/VA copolymer and its

influence on the gradual deformation and eventual collapse of liquid marbles will be investigated in further detail in Chapter 5.

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# 5

## Effect of Film Formers on Liquid Marble Stability

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This section examines the effect of film formers on liquid marble stability and the impact on their drying. A hypothesis on drying mechanism is also provided in this chapter.



## 5 Introduction

This chapter will focus on the use of VP/VA copolymer (a film former) on the stability of liquid marbles. While a lot of research has been conducted on various uses of liquid marbles from micro-reactors, gas sensing to magnetic marbles [1-6], there is only a rudimentary understanding on their stability. Currently, there is conflicting data between the shelf-life of commercial products which lasts over two years compared to laboratory made liquid marbles which survive for seconds [7], hours [8] or days [2]. As such, it is important to further study the possible parameters which influence liquid marble stability. Previous research in Chapter 4 showed that 60% of all the commercial formulations studied contained a film former. Image analysis conducted in Chapter 4 showed that products containing film formers contained relatively consistent looking liquid marbles compared to products that did not contain film formers. This is expected as film formers are chemicals that are surface active and create a barrier coating between two interfaces. In the case of liquid marbles, the formation of this protective layer by the film former will provide a more defined interface at which the powder and liquid interacts. The film former of choice used in this chapter is VP/VA copolymer or Kollidon VA64, which is same as that used in 60% of the commercial formulations containing film former investigated in Chapter 4. VP/VA copolymer is also an ideal film former for study as it is used as an excipient in many cosmetic and pharmaceutical formulations.

This chapter will explore in more detail how the film former affects the drying of the liquid marble in terms of their shape and survival time. A hypothesis on the different drying mechanisms which occur with the addition of film former as a result of different interactions between the shell and the liquid is established in this chapter as well. This is correlated with established dimensionless numbers, the Bond number and the Ohnesorge number which have been previously linked to describing the shape of liquid marbles through interactions between different forces which exist as the liquid marble forms.

### 5.1 Experimental

Liquid marbles containing liquid volumes of approximately 15  $\mu\text{L}$ , 30  $\mu\text{L}$  and 50  $\mu\text{L}$  were made by releasing droplets onto an aerosil bed using a 1 mL syringe with an 18 g needle forming marbles with diameters of approximately 4 mm and 4.6 mm being made respectively. The powder bed was gently agitated by lightly moving the petri dish to ensure complete powder coverage of the marble. Table 5.1 provides a summary of the liquid marbles produced

and their corresponding liquid and powder phase materials. Properties of VP/VA copolymer were given in Chapter 3, Table 3.1.

**Table 5.1: Summary of liquid marbles produced.**

Reference Name	Liquid Phase	Powder Phase	Marble Volumes ( $\mu\text{L}$ )	No. Repeats
Control	Pure de-ionised water	None	15, 30, 50	2
0% VP/VA copolymer	Pure de-ionised water	Aerosil R974	15, 30, 50	3
2% VP/VA copolymer	2% (w/v) VP/VA copolymer solution	Aerosil R974	15, 30, 50	3
5% VP/VA copolymer	5% (w/v) VP/VA copolymer solution	Aerosil R974	15, 30, 50	3

The liquid marbles were left to dry and collapse at standard laboratory conditions with temperatures ranging between 22 – 25 °C. The drying process of liquid marbles created with and without VP/VA copolymer was recorded via a series of images taken using a SMZ stereo microscope with a 2 MP Motic moticam camera at 10 minute intervals. Height and width profiles were measured using Image J, with results for height and width as a function of time represented graphically. Drying time was identified as the last time point at which the marble showed no subsequent changes in height and width.

The Ohnesorge number was used to describe the shape and rebound phenomenon of a drop impact on solid surface [9, 10]. It relates the viscous forces to the inertial and surface tension forces of the droplet and is described by equation 5.1.

$$Oh = \frac{\mu}{(\rho\gamma_{LV}R)^{0.5}} \quad (\text{eq 5.1})$$

Where  $\rho$  = density of liquid

$\gamma_{LV}$  = surface tension at liquid vapour interface

R = drop radius

$\mu$  = viscosity

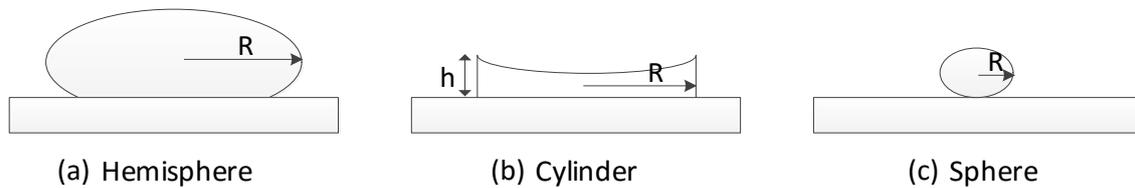
A transition value of  $Oh = 0.05$  is proposed for two different drop retraction regimes. When  $Oh < 0.05$  the “capillary – inertial” regime dominates and when  $Oh > 0.05$ , the capillary – viscous regime is present [11]. Droplets are more likely to rebound without splitting into smaller droplets when in the “capillary – viscous” regime. This chapter will explore whether

the transition value of  $Oh = 0.05$  also applies to the changing shape of liquid marbles during drying and can be extended to describe rebound phenomenon across an extended time frame.

To calculate the Ohnesorge number, the concentration of the marbles was required in order to extrapolate viscosity of the marbles throughout drying. Viscosity to concentration data was taken from Kollidon VA64 (VP/VA copolymer) handbook [12]. An example of how viscosity is calculated and an example calculation of the Ohnesorge number is given in Appendix F. Concentration of the copolymer solution could not be directly measured throughout the experiment; hence, it was derived using the concentration-volume law:

$$C_1V_1 = C_2V_2 \quad (eq\ 5.2)$$

Marble volume could not be measured directly due to the constantly changing shape during drying. Therefore basic estimations of liquid volume were obtained by modelling the marbles as three different shapes throughout the drying process. The three basic shapes of the marbles at various stages of drying and their corresponding shape for modelling are shown in Figure 5.1.



**Figure 5.1: Diagram of general drying shapes and their corresponding shape for modelling (a) hemisphere (b) cylinder (c) sphere**

As such, the volumes of the marbles were estimated using the following calculations.

For the hemisphere stage, the volume is estimated by equation 5.3. The hemisphere is mostly used to model the volume of medium and large marbles at the beginning of the drying process when the contact length with the powder surface is relatively long compared to height.

$$V_{Hemisphere} = \frac{1}{2} \left( \frac{4}{3} \pi R^3 \right) \quad (eq\ 5.3)$$

Where  $R$  = radius of the marble measured from side to side of the liquid marble.

Although, modelling the liquid marble shape described in Figure 5.1a as a hemisphere is a bit simplistic, comparison of volumes between the model and the actual volume showed less than 10% difference.

During some experiments, the contact line remains pinned and the marble collapses from the top resulting in a puddle like structure (see Figure 5.1b). This structure is estimated by equation 5.4 below.

$$V_{cylinder} = \pi R^2 h \quad (eq\ 5.4)$$

Where R = radius of the cylinder/ marble.

h = height

For small marbles which maintained a spherical structure and in cases where the marble rebounded back to a spherical structure; the marble volume was estimated using the equation 5.5.

$$V_{sphere} = \left(\frac{4}{3}\right) \pi R^3 \quad (eq\ 5.5)$$

Where R = radius of the marble

In this case, the radius is taken as the half width for consistency, as the height to width ratio should be close to one.

## 5.2 Results

### 5.2.1 Drying Time of Liquid Marble

The time taken for liquid marbles to dry and the 95% confidence interval with the presence of different concentration of film former are shown in Table 5.2.

**Table 5.2: Drying time (min) of laboratory made liquid marbles with and without film former**

	≈ 15 μL Marble	≈ 30 μL Marble	≈ 50 μL Marble
<b>Control (Pure water droplet)</b>	150 ± 10	197 ± 31	335 ± 35
<b>0% VP/VA copolymer</b>	190 ± 20	230 ± 10	343 ± 35
<b>2% VP/VA copolymer</b>	190 ± 10	337 ± 75	413 ± 55
<b>5% VP/VA copolymer</b>	197 ± 15	303 ± 40	383 ± 42

An increase in drying time is observed due to both the presence of Aerosil powder coating and the addition of film former. The effect due to addition of just the Aerosil shell is seen through the comparison between the control (pure water droplet) and the 0% VP/VA

copolymer liquid marble. The results show that for marbles of all volumes, the drying time was extended in the case where Aerosil is present. This is expected given that a multilayer powder coating will slow down the vapour diffusion rate at the interface [13]. The extent of the increase is likely to be impacted by the thickness of the powder shell. Although, the experimental procedure has been kept constant, the shell thickness cannot be directly controlled. During the rolling of the marble, complete coverage of the marble can be ensured, but the exact layer thickness of Aerosil at the surface could not be controlled. The difference in shell thickness may be a contributing factor to the variation in time observed.

The addition of 2% VP/VA copolymer seemed to increase the drying time significantly, especially for the larger 30 and 50  $\mu\text{L}$  marbles. This is expected as film former is a surface active agent which forms a barrier coating at the interface. The formation of a film should further decrease the vapour diffusion rate from the surface, thereby extending drying time. It is also possible that the film former may interact with the Aerosil, resulting in a stronger shell layer which may also contribute to the extended drying time.

Interestingly, increasing VP/VA copolymer concentration to 5% (w/v) did not extend the drying time of liquid marble compared to the 2% copolymer solution liquid marble. In some cases, especially as the marbles increased in size, the marble actually destabilises and drying time decreases compared to the 2% liquid marble. This is likely due to two aspects. Firstly, surface area is only dependent on marble volume, hence, for the same marble volume, it is possible that the surface is saturated with film former at the 2% concentration. Secondly, from Figure 5.7 and 5.8d, the large 50  $\mu\text{L}$  marble was not always able to rebound back into a sphere. The ‘rebound’ phenomenon will be discussed in further detail in section 5.2.2. As spheres have the least surface area to volume ratio, the destabilisation of the liquid marble and maintenance of the ‘puddle’ structure at the higher copolymer concentration means higher surface area and therefore faster drying time.

From Table 5.2, it can also be seen that increasing marble size resulted in longer survival time for marbles made from the same liquid phase. This is expected as the film former should only affect vapour diffusion rate. At a constant film former concentration, the vapour diffusion rate from the surface should be constant and the total time required for the liquid marble to dry will be affected only by surface area. Change in surface area is not linear with respect to changing volume, with surface area per unit volume decreasing at a slower extent with increasing volume. This means that drying time will show a slower rate of increase with

increasing marble volume. Experimental observation supports this as increasing volume from 15  $\mu\text{L}$  to 30  $\mu\text{L}$  showed a greater change in drying time, while increasing the volume from 30  $\mu\text{L}$  to 50  $\mu\text{L}$  did not increase drying time as significantly in comparison.

### **5.2.2 Height Profiles of Liquid Marbles During Drying**

Figure 5.2 shows a 50  $\mu\text{L}$  Aerosil and pure-deionised water marble drying over 370 minutes, progressing from a hemisphere structure to a flat puddle as it dries. Figure 5.3 shows the characteristic lengths of the marble over time from the images taken. The physical changes are similar for all marble sizes but varied in the time taken to reach each stage. Additional profiles of replicate marbles for the different marble volumes are given in Appendix E.

Figure 5.3 shows the height and width profiles of 15, 30 and 50  $\mu\text{L}$  pure de-ionised water marbles (no film former) with Aerosil coating over time as it dries. Initially the liquid marbles are a hemisphere (Figure 5.2a) and b)) and a relatively stable decline occurs in height (Figure 5.3). As the marble progresses towards the final stages of drying, the top collapses down to lose the rounded dome (Figure 5.2c). This correlates to the more rapid height loss in the height profiles (Figure 5.3 left), while the width stays relatively constant (Figure 5.3 right). Eventually, the liquid marble dries as a flat puddle (Figure 5.2d) with minimal height and relatively large width in comparison (Figure 5.3). This is expected for a pure water marble; once all the liquid evaporates there is nothing to support the shell to maintain its spherical structure. The shell collapses with the removal of liquid, resulting in a flat disk of the dyed powder.

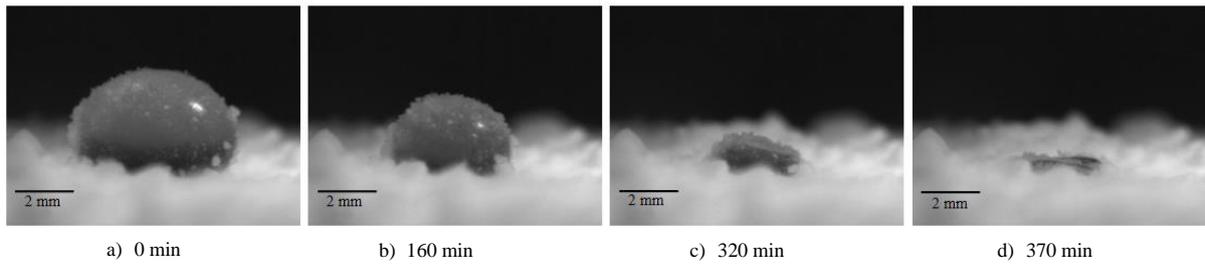


Figure 5.2: Images of a 50  $\mu\text{L}$  aerosil and water marble at various stages during drying

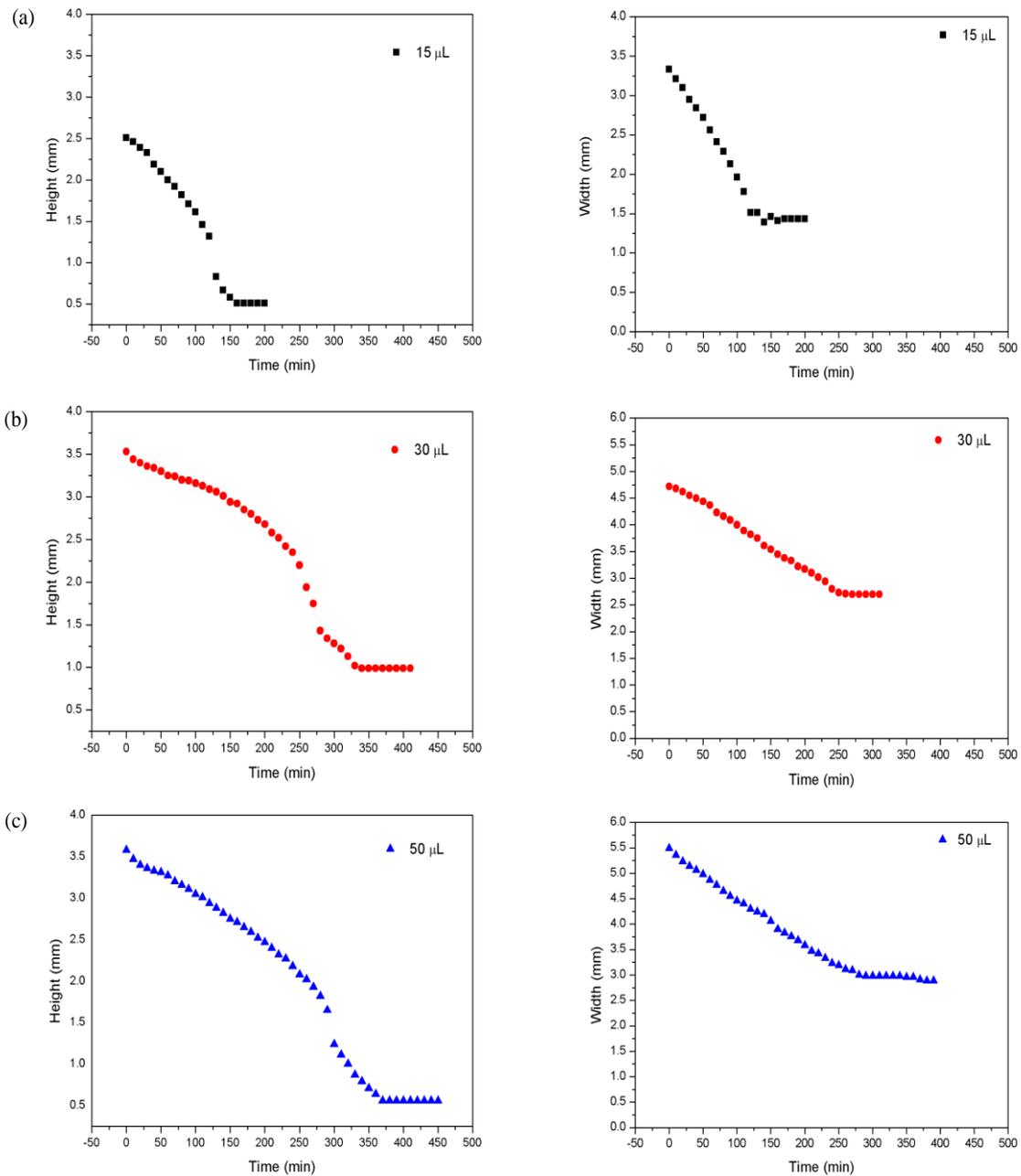


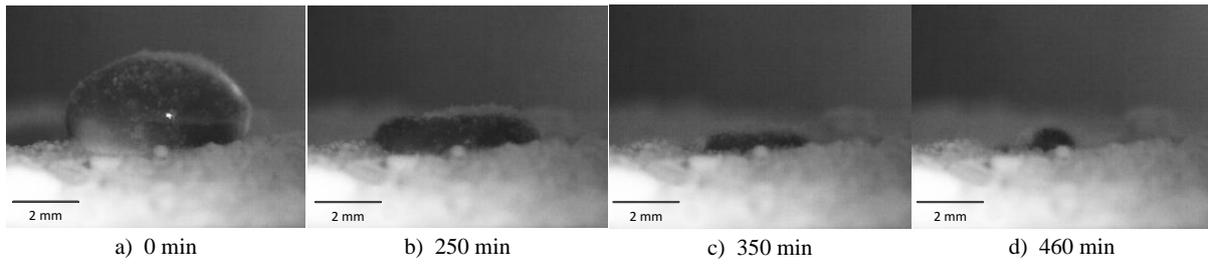
Figure 5.3: Height and width profiles of drying aerosil & water marbles over time of a) 15  $\mu\text{L}$  marble, b) 30  $\mu\text{L}$  marble and c) 50  $\mu\text{L}$  marble

Figure 5.4 shows the characteristic drying profiles of a 50  $\mu\text{L}$  2% VP/VA copolymer liquid marble and Figure 5.5 shows the height and width profiles of the 15, 30 and 50  $\mu\text{L}$  liquid marbles. Images of the 15 and 30  $\mu\text{L}$  marbles are given in Appendix E, which show a similar overall drying pattern to that observed in Figure 5.4 but at different time points.

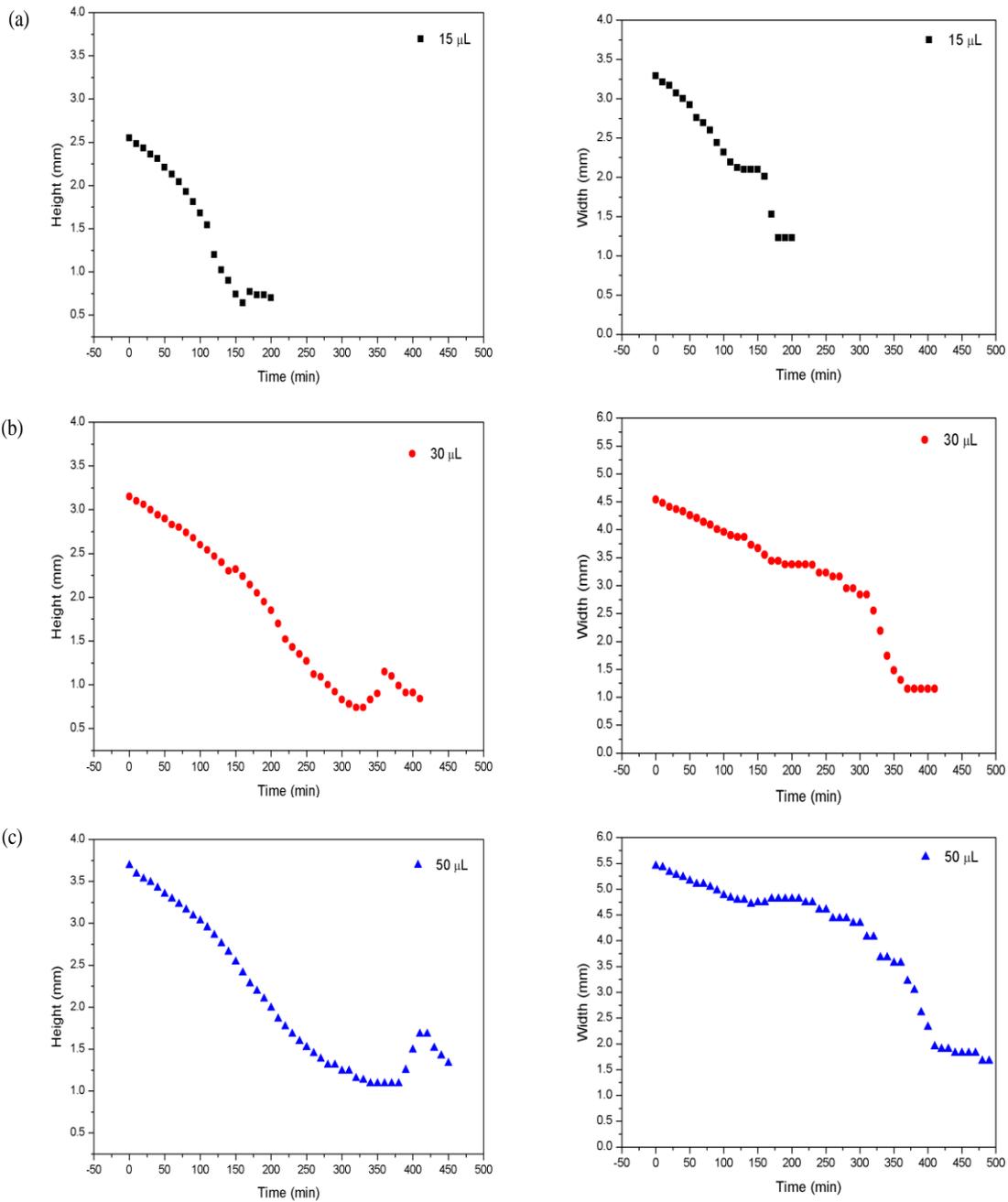
The inclusion of film former changed the drying profiles of the liquid marble with major differences in the end structure and overall drying time.

When no film former is present (Figure 5.2 and Figure 5.3), the marbles have a tendency to collapse into a puddle. However, in the case of 2% copolymer (Figure 5.4 and Figure 5.5), the marble regained its spherical shape in a type of ‘rebound’ effect. Initially the shrinking of the liquid marble and the collapse of the rounded dome (Figure 5.4a,b) is similar to that observed in Figure 5.2a-c. However, as the 2% VP/VA copolymer liquid marble starts to dry as a puddle with both height and width decreasing (Figure 5.4b,c), it reaches a point just before complete drying, where the width undergoes a steep decrease and height increases (Figure 5.5) to reform a spherical droplet (Figure 5.4d).

Addition of 2% VP/VA copolymer increased drying time of the liquid marble compared to a 0% VP/VA copolymer liquid marble. As mentioned in Section 5.2.1, film formers function by forming a coating at the interface and are expected to strengthen the shell and decrease vapour diffusion. Therefore, increased drying time is expected with the addition of film former.



**Figure 5.4:** Images of a 50  $\mu\text{L}$  2% copolymer marble at various stages during drying, including rebound into a sphere between (c) and (d).

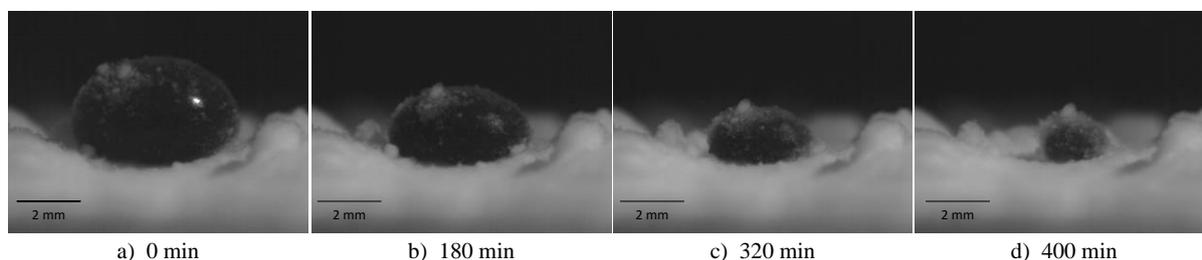


**Figure 5.5:** Height and width profiles of drying 2% film former marbles over time of a) 15  $\mu\text{L}$  marble, b) 30  $\mu\text{L}$  marble and c) 50  $\mu\text{L}$  marble

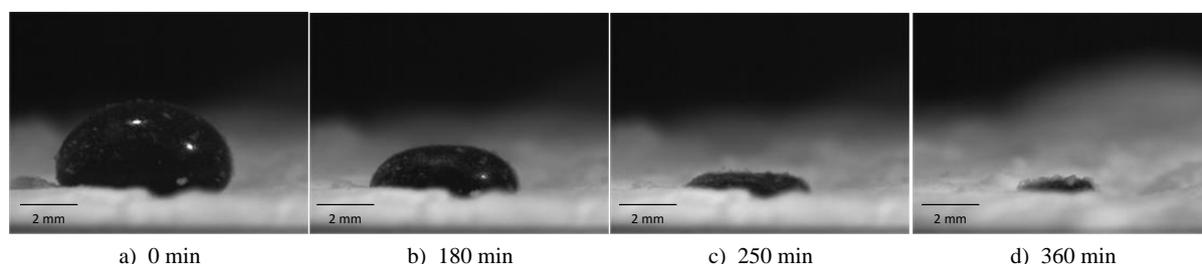
Figures 5.6 show the drying pattern of a large 5% VP/VA copolymer liquid marble with the ‘rebound’ effect that is also characteristic in the smaller sized marbles. Additional images of the drying of the smaller 5% liquid marbles are given in Appendix E.

Similar observations are seen between the 2% VP/VA copolymer results and the 5% VP/VA copolymer results. The ‘rebound’ phenomenon which was characterised by a sudden increase in height and steep decrease in width is also observed in Figures 5.7 and 5.8b,c. However, slight deviation from this is seen in the small 15  $\mu\text{L}$  liquid marble where the height increase and corresponding width drop is clearly observed. From Figure 5.8a (top two images), it can be seen that the height and width declined at similar rates, indicating that the liquid marble maintained its spherical shape throughout the entire drying process.

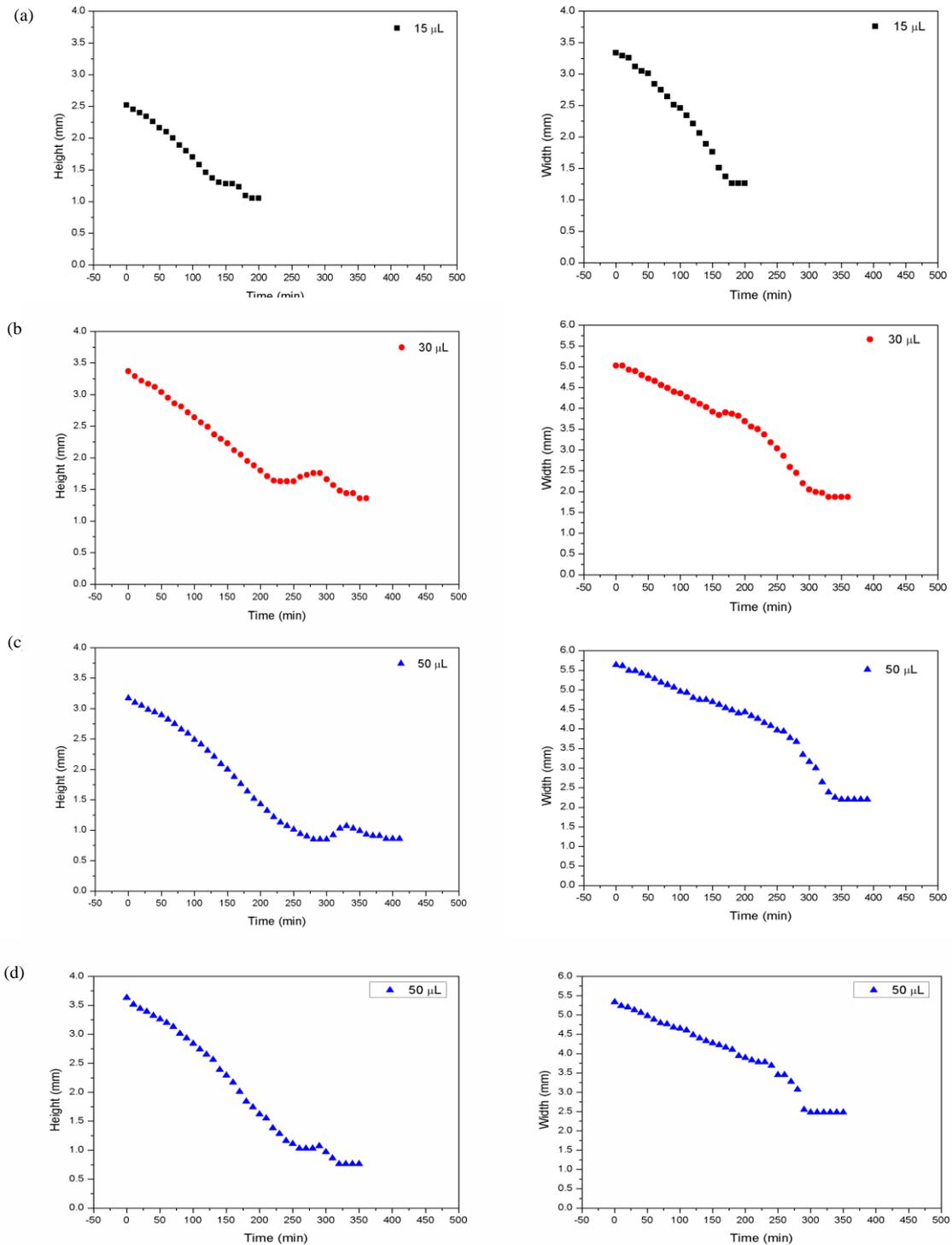
In conjunction, the 50  $\mu\text{L}$  liquid marble also deviated from the typical ‘rebound’ phenomenon where in some cases it maintained a ‘puddle’ structure and the final ‘rebound’ step did not occur (Figure 5.7 and Figure 5.8d). In such cases, the drying time is also slightly shorter than for those that did ‘rebound’ into a sphere (Figure 5.7 compared to Figure 5.6). It can also be observed that the width of the drying marble does not decline as fast as in those that show rebound and the characteristic jump in height is missing (Figures 5.8c ,d).



**Figure 5.6: Images of a 50  $\mu\text{L}$  5% copolymer marble at various stages during drying where the final marble has ‘rebounded’ back into a sphere.**



**Figure 5.7: Images of a 50  $\mu\text{L}$  5% copolymer marble at various stages during drying where the final marble has not ‘rebounded’ back into a sphere.**



**Figure 5.8: Height and width profiles of drying 5% VP/VA copolymer marbles over time a) 15  $\mu\text{L}$  marble, b) 30  $\mu\text{L}$  marble, c) 50  $\mu\text{L}$  marble with rebound phenomenon, d) 50  $\mu\text{L}$  marble with no rebound phenomenon**

Table 5.3 summarises the rebound time observed during the drying of the 2% and 5% VP/VA copolymer marbles, which correlate to the time at which the height suddenly increases in Figures 5.5 and 5.8

**Table 5.3: Time period during which the ‘rebound’ phenomenon occurred in minutes from the start of drying for the 2% and 5% VP/VA copolymer liquid marbles.**

	Time ‘rebound’ phenomenon occurred (min)		
	15 $\mu\text{L}$	30 $\mu\text{L}$	50 $\mu\text{L}$
<b>2% VP/VA copolymer</b>	140-160	320-340	380-410
<b>5% VP/VA copolymer</b>	150-160	240-260	290-310

It is possible that this ‘rebound’ effect is part of the reason why commercial samples seen in Chapter 4 seem to have a longer survival time of over two years compared to laboratory made marbles. In Chapter 4, spherical liquid marbles are assumed to have been stable and maintained their shape throughout their shelf-life. As drying liquid marbles are able to re-obtain their spherical shape over time, it is possible that these ‘rebounded’ spherical marbles are observed and hence, attributed to have prolonged survival time.

### 5.2.2 Rebound Effect and Ohnesorge Number Correlation

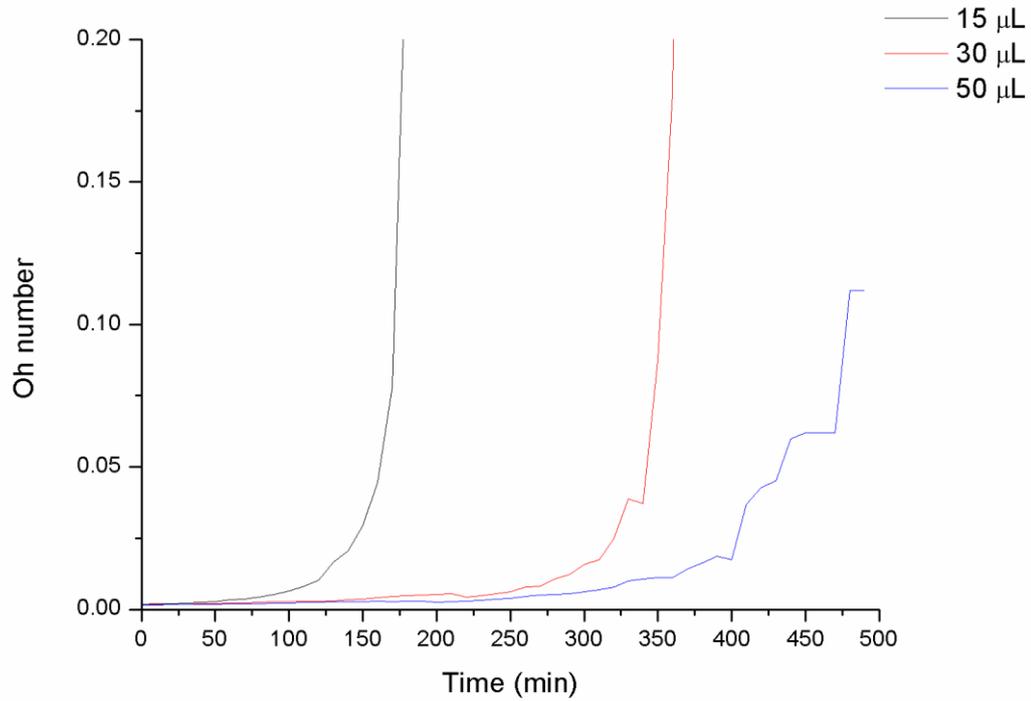
The Ohnesorge number ( $Oh$ ) was investigated for its use in determining whether the ‘rebound’ effect can be estimated using this value. The Ohnesorge number has previously been used to describe the shape and rebound phenomenon of a drop impact on solid surface [9, 10]. It is hypothesized that during drying, the inertia caused by fluid movement during drying will mean the Ohnesorge equation still applies. As such, a study into whether the Ohnesorge number is applicable to describe this ‘rebound’ situation was also conducted.

The Ohnesorge number is made up of four different variables: viscosity ( $\mu$ ), density ( $\rho$ ), surface tension ( $\gamma_{LV}$ ) and radius ( $R$ ) (eq 5.1). Density and surface tension was determined previously (Chapter 3) for the film former solutions at different concentrations. Surface tension was assumed to be constant for calculation purposes as increasing film former concentration did not show significant decrease in surface tension.

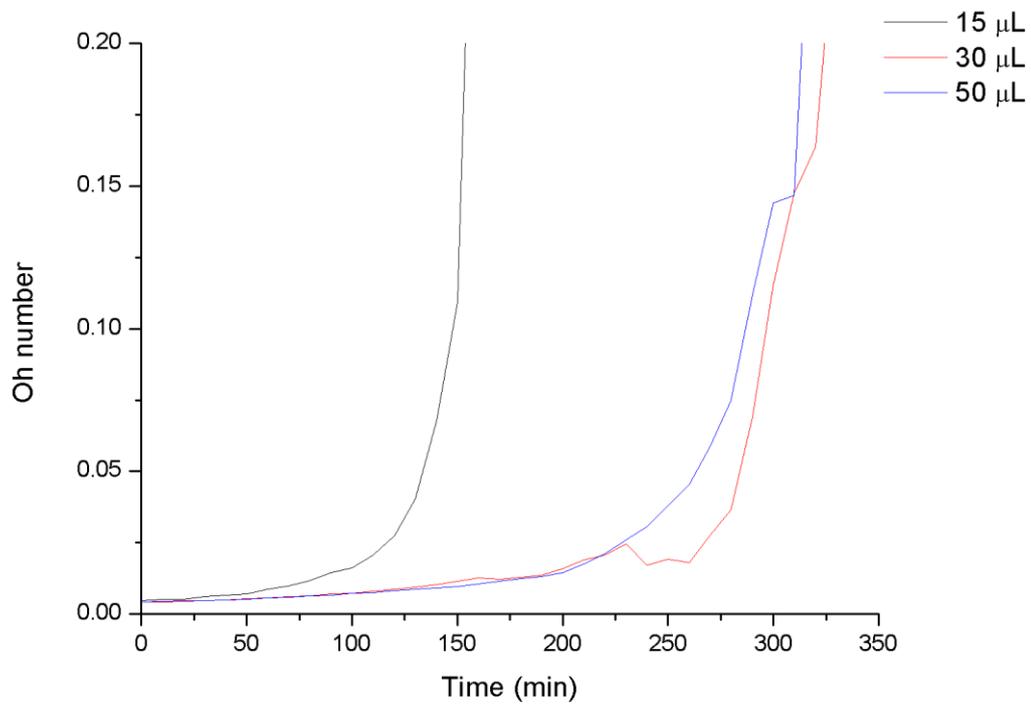
The height and width data of the liquid marble of interest is obtained through image analysis using Image J. Radius is defined as either half of the height or the width. An adjusted concentration is calculated based on a concentration volume correlation (eq 5.2), with volume estimates based on marble shape (eq 5.3 –5.5). Using the adjusted concentration, the adjusted viscosity is obtained using the concentration – viscosity graph or extrapolated using the polynomial trend line established from the BASF Kollidon VA64 (VP/VA copolymer)

handbook [12]. A more detailed explanation and an example of how the Ohnesorge number was calculated is given in Appendix F.

a)



b)



**Figure 5.9: Calculated Ohnesorge number using height as radius as a function of time for a) 2% VP/VA copolymer solution liquid marbles b) 5% VP/VA copolymer solution liquid marbles**

**Table 5.4: Time point at which the calculated Ohnesorge number is 0.05 in minutes from the start of drying for the 2% and 5% VP/VA copolymer liquid marbles.**

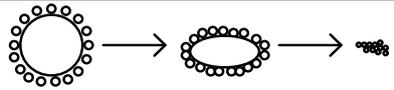
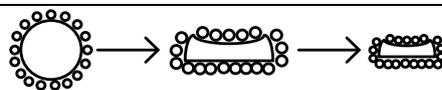
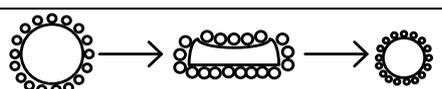
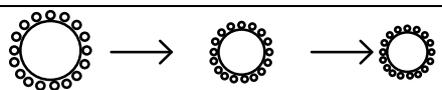
	<b>Time at which calculated Ohnesorge number = 0.05 (min)</b>		
	<b>15 <math>\mu\text{L}</math></b>	<b>30 <math>\mu\text{L}</math></b>	<b>50 <math>\mu\text{L}</math></b>
<b>2% VP/VA copolymer</b>	160	330	420
<b>5% VP/VA copolymer</b>	140	260	280

Figure 5.9 and Table 5.4 shows the calculated Ohnesorge number corresponding to the drying displayed in Figures 5.5 and 5.8 for the 2% VP/VA copolymer marbles and the 5% VP/VA copolymer marbles respectively. It is observed that the point of inflection in the calculated Ohnesorge number graphs corresponds to the time-point at which the ‘rebound’ of the marble occurs (Table 5.3 and 5.4). As the Ohnesorge number is calculated using the the height of the marbles as the basis of the radius value in the equation (eq 5.1), it is possible that correlation is coincidental. However, due to the difficulty in measuring the changing viscosity, the Ohnesorge number cannot be accurately calculated though measured values. As a result, only a rudimentary correlation between the rebound effect and the Ohnesorge number change can be established at this point. Supplementary data with calculated Ohnesorge number for repeats is given in Appendix F.

### 5.3 Discussion

The results from the drying profiles of liquid marbles containing 0%, 2% or 5% VP/VA copolymer solution (Figures 5.3, 5.5 and 5.8) showed four different potential behaviours which are summarised in Table 5.5.

Table 5.5: Summary of different drying behaviours

Schematic of Drying Behaviour	Conditions
	<ul style="list-style-type: none"> <li>0% VP/VA copolymer droplets</li> </ul>
	<ul style="list-style-type: none"> <li>50 <math>\mu</math>L 5% VP/VA copolymer marble</li> <li>No rebound observed</li> </ul>
	<ul style="list-style-type: none"> <li>2% VP/VA copolymer marbles and 5% VP/VA copolymer marbles</li> <li>Rebound observed</li> </ul>
	<ul style="list-style-type: none"> <li>15 <math>\mu</math>L 5% VP/VA copolymer marble</li> <li>Maintained spherical shape</li> </ul>

A potential hypothesis to describe why liquid marbles dry in different ways and what the parameters which influence their drying behaviour was developed and outlined in Figure 5.10. The flow diagram shows the steps which leads to the four different drying outcomes. It can be seen there are several aspects of drying which will ultimately determine which type of dried marble will result.

Firstly, the liquid marble must be fully covered by powder to prevent wetting of the powder surface. If wetting occurs, the marble will become ‘stuck’ to the powder bed and the contact line becomes pinned. When this occurs the drying marble will not be able to undergo the ‘rebound’ process, resulting in a dried, pancake - like structure at the end, where the top has collapsed.

The next aspect to consider is the type of contact line. A pinned contact line will mean that the two contact ends of the marbles cannot move and the marble will again be ‘stuck’

resulting in the gradual flattening of the marble during drying and ultimately drying into a flat disk. As such, a non-pinned contact line is crucial for the later potential ‘rebound’ process. While a constant non-pinned contact line would be ideal, it is possible for the marble to change between pinned and non-pinned. This phenomenon has also been documented in literature as a stick-slip mechanism [14]. Pinning of the contact line can be observed in Figures 5.3, 5.5 and 5.8 where the width stays consistent while height of the drying marble decreases. Ultimately, in order for the ‘rebound’ to occur, a non-pinned contact line or a “slip stick event” is required, else the sudden decrease in width to allow for the height increase could not occur.

In conjunction with the two steps outlined above, the strength and type of interactions present between the powder, liquid and shell will determine the final dried marble structure. In general, the different types of outcomes are outlined in the following section.

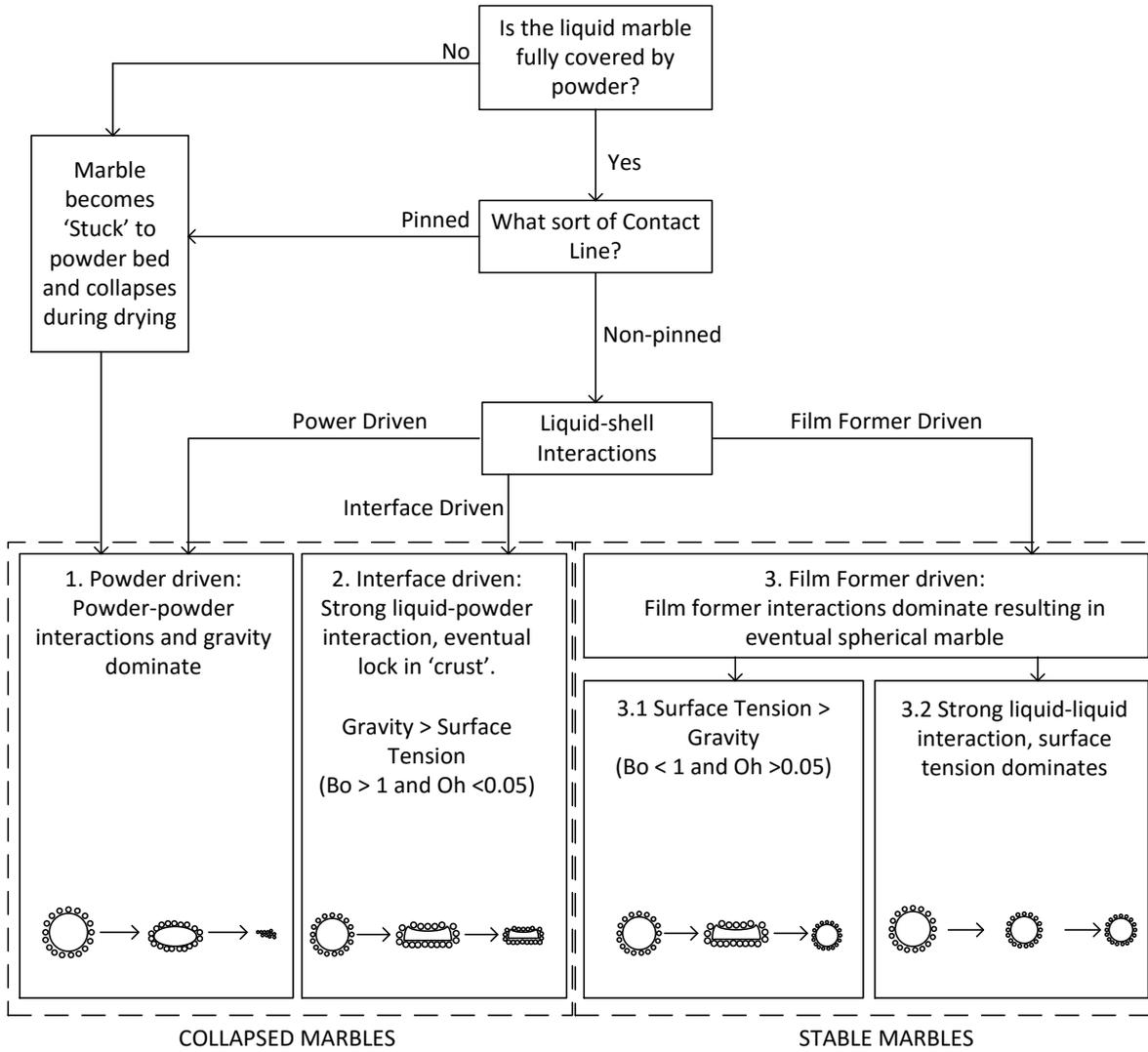


Figure 5.10: Flow diagram showing hypothesised liquid marble drying mechanism

### 5.3.1 Collapsed Marbles

#### 5.3.1.1 Powder driven drying

Powder driven drying is believed to be promoted by strong powder-powder interaction and lack of shell strength. This is seen when a pure water liquid marble is dried (i.e. when no-film former is added to the liquid solution), as seen in Figure 5.2 and 5.3. In such case, the droplet will undergo three main stages during drying and is similar to that observed for most liquid marbles researched previously [15, 16].

1. Marble starts to shrink as liquid center evaporates.
2. Powder on the droplet becomes denser as liquid surface area decreases, causing powder build up on the top of the droplet. Gravitational forces acting on both powder and the liquid overcome surface tension, causing the top of the droplet to collapse.
3. Liquid completely evaporates.

#### 5.3.1.2 Interface driven drying (Solid-Liquid Interface)

Interface driven drying is hypothesized to result in a collapsed marble as a result of liquid – powder interaction at the interface and the time taken for a ‘crust’ to form and lock into shape. Two main factors, the surface tension to gravity force ratio, which is described by the Bond number as well as the forces described by the Ohnesorge number helps to determine the final shape of the marble.

Interface driven drying is likely to result when the interface is not strong enough to support the spherical droplet and gravitational force on the powder on the top of the droplet, causes the top to collapse, resulting in the formation of a ‘puddle’. This will be more likely to occur when surface tension is dropping from increasing film former concentration. This is supported by the fact that a ‘puddle’ is more likely in the large 5% film former marbles. This ratio of forces is summarised by the Bond number. A Bond number of less than 1 will result in a spherical drop, while a Bond number greater than 1 will result in gravity dominating and a puddle being formed [17].

### 5.3.2 Stable Marbles

#### 5.3.2.1 Film Former driven drying

We hypothesize that film former driven drying occurs when the addition of film former causes significant impact on the interaction between the liquid and powder phase, which results in a stable spherical liquid marble. The spherical shape of the liquid marble can be obtained through two different methods:

1. A ‘rebound’ effect. This phenomenon is observed when the film former interaction with the powder is strong enough to support the resultant droplet and maintain the spherical shape as surface tension becomes greater than gravity over time, which is represented by a Bond number of less than 1.

In such cases, it was also observed that calculated Ohnesorge number using extrapolated viscosity values, showed a point of inflection, which is usually close to 0.05 (Figure 5.9). This transition correlated with the time at which the ‘rebound’ occurs. This correlates well to previous work in literature, where an Ohnesorge number of 0.05 has been observed to be an important transition boundary value between two different drop retraction regimes [11]. An Ohnesorge number of less than 0.05 correlates to the capillary-inertial regime and inertial forces oppose retraction of liquid droplets. When Ohnesorge number is greater than 0.05, the capillary – viscous regime dominate and is commonly associated with the droplet regaining shape without breaking [11].

2. Spherical marble maintained throughout drying. This is expected to occur when the combination of surface tension and film former interaction with powder creates a stronger external shell that is continuously able to withstand gravity. As a result, the droplet dries while maintaining its spherical shape. This is seen in the high concentration film former with small to medium droplet size (Figure 5.8a). Higher film former concentration will result in greater interface interaction and potentially help lock the shell into its shape at a faster rate. This hypothesis also explains why the 5% VP/VA copolymer larger marbles are sometimes unable to rebound back into a sphere as the shell has already started locking before the rebound phenomenon can occur (Figure 5.8d).

## 5.4 Conclusion

The impact on liquid marble stability via addition of VP/VA copolymer was investigated following previous work from Chapter 4 which showed that most commercial formulations with extended longevity of liquid marbles included a film former component. Incorporation of 2-5% film former into a basic Aerosil and water liquid marble showed increased drying time of the liquid marbles compared to the control of a pure de-ionised water marble with Aerosil coating. Although addition of film former resulted in lower surface tension compared to pure water; the interaction between the copolymer and powder at the interface, resulted in an observed ‘rebound’ phenomenon, or in some cases allowed the droplet shell to be strong enough to maintain a spherical shape throughout drying. This may aid in providing a potential explanation as to why commercial samples containing liquid marbles are able to survive significantly longer compared to laboratory made marbles. It is expected that the evaporation rate of the liquid from the marble is crucial in the gradual deformation and eventual collapse of the liquid marble. As such quantification of this phenomenon should be investigated further to allow for design of ‘rebounded’ spherical liquid marbles in other powder-liquid combinations. However, before that it may be of interest to observe whether this drying phenomenon is observed only in air drying or whether other methods of drying will yield the same results. This aspect will form the foundation of research in Chapter 6.

## 5.5 References

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# 6

## Drying of Liquid Marbles

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This Chapter looks into potential methods to dry liquid marbles and the resultant structures. In conjunction, it shows for the first time that freeze-drying is a potential drying method of liquid marbles to create a porous and highly stable structure.



## 6 Drying of Liquid Marbles

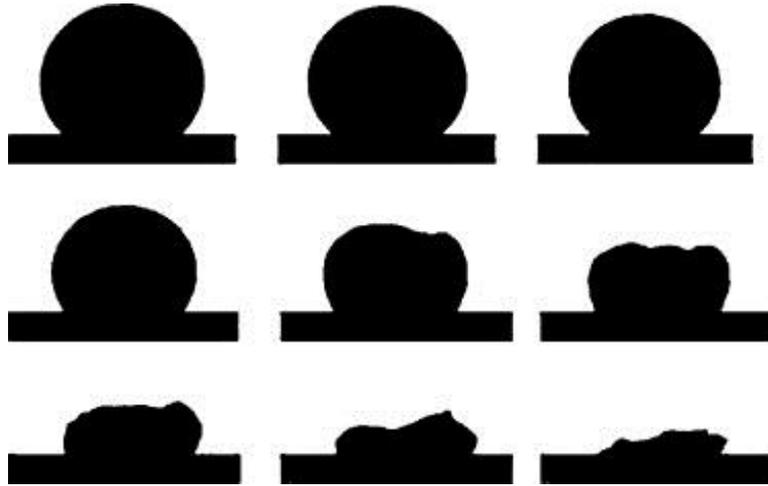
Drying of liquid marbles to date has not been studied in much detail despite being a common element in many production processes. In general large scale manufacturing of particulate products use air drying, spray drying and freeze drying as three of the most common drying methods. To date, conflicting data exists on how long liquid marbles can exist for and the effect of the powder shell on the drying speed of the liquid marble.

In all studies of liquid marble drying so far, only air drying of liquid marbles on a stationary surface has been investigated. This chapter will look at two other commonly used industrial drying methods (freeze drying and single droplet drying as a small scale simulation of spray drying) and compare their effectiveness in maintaining the shape and size of the original liquid marble.

### 6.1 Types of Drying

#### 6.1.1 Air Drying

Air drying of liquid marbles has commonly been the default due to its ease and low cost. Previous work by Bhosale et al. tried to determine the effect of the particle coating on liquid marbles compared to a pure droplet and the effect of different powder size on evaporation rate [1]. Bhosale et al. created water – based marbles made from microsize poly(tetrafluoroethylene) powder (approx. 7-12 microns) and 200-500 nm fumed silica powder aggregates, which were coated with either hexamethyldisilazane (HMDS) or dimethyldichlorosilane (DMDCS) to render the silica hydrophobic. The marbles created using HMDS-treated fumed silica was observed to have the highest resistance to diffusion, with the authors speculating that this was due to limited aggregation of the fumed silica compared to the DCMS treated marbles [1]. The liquid evaporation rates from PTFE – and graphite – shelled liquid marbles was investigated by Tosun and Erbil [2] and Dandan and Erbil [3] respectively. Encapsulating the fluid with PTFE micro powder reduced evaporation rate of the liquid marble compared to a pure water droplet by 25% to 45% as relative humidity increased and a longer time before the marble crumpled and collapsed was observed [2]. Profiles of PTFE liquid marbles drying is shown in Figure 6.1, which is also representative of pure water marble drying over time. A graphite coating almost doubled the lifetime of the liquid marble compared to a normal water droplet [4].



**Figure 6.1: Profiles of PTFE liquid marble drying over time [2]**

Droplets naturally drying on a powder bed have been observed to self-coat and form liquid marbles [5]. McHale et al. showed that a droplet will try to minimize its surface area and if there is no powder resistance (ie. cohesion) in the powder bed, evaporation of the liquid will result in a skirt of particles rising around the droplet and creating a self-coating effect. However, eventual buckling of the marble will result as the droplet evaporates completely [5].

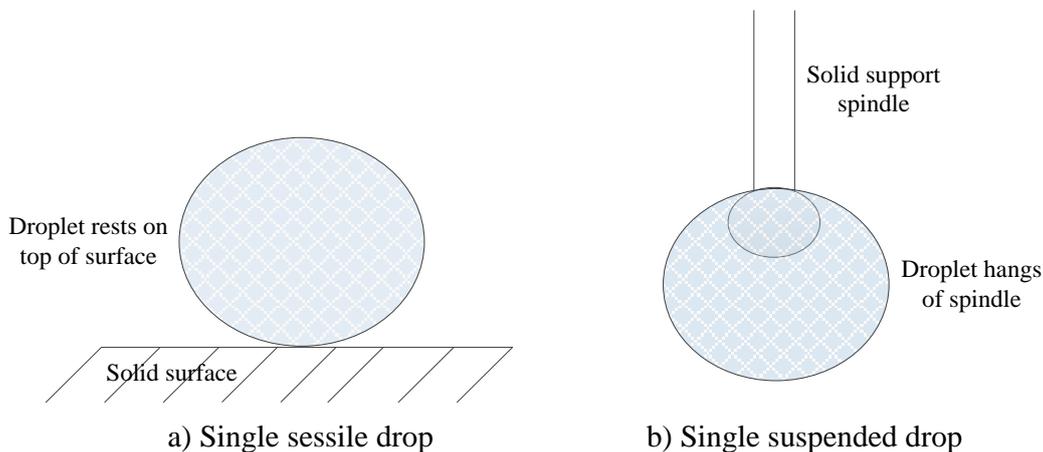
Complete drying of the inner liquid droplet of liquid marbles resulting in the formation of completely empty hollow spherical shells has also been observed [6-8]. Hapgood et al., demonstrated that stable hollow granules can be successfully formed in a granulator using a combination of sub-micron milled crystalline hydrophobic powder and water [8]. Further research into the formation of designer hollow granules has been conducted through study on formation of liquid marbles as a preliminary step [6]. Hapgood and Khanmohammadi studied liquid marbles made from water, glycerol and PEG with outer shell created from hydrophobic glass beads and hydrophobic drug powders such as salicylic acid and 2-ethoxybenzamide [6]. It was observed that water and glycerol which had the two highest surface tensions of the fluid tested were able to form liquid marbles with almost all of the powders [6]. Later work by Eshtiaghi et al., looked at hollow granules formed from liquid marbles created using PVP (poly-vinyl pyrrolidone), HPMC (hydroxyl propyl methyl cellulose) and HPC (hydroxyl propyl cellulose) solutions as their liquid phase and PTFE and fumed silica as the solid phase [7, 9]. Eshtiaghi et al. found that higher drying temperature, smaller or nano-sized particles and higher binder concentration tended to promote the formation of perfect hollow granules [7].

In recent times, Laborie et al, tried to quantitatively describe drying as a function of shell thickness. Their study looked at the effect of the powder particles on evaporation rate and

subsequent drying of water droplets [10]. They observed that liquid marbles coated with a monolayer of hydrophobic particles actually dried faster than a pure water droplet, while liquid marbles covered with a multilayer of particles will dry slower than a bare liquid droplet depending on the thickness of the coating [10]. This difference in drying rate was explained by the decrease in vapour diffusion rate through a porous media formed by the layering of particles at the interface compared to a monolayer of particles [10].

### 6.1.2 Single Droplet Drying

A common way to study droplet drying in a controlled environment is through the study of a single droplet. Glass filament single droplet drying, which is used in this chapter is the process where an isolated droplet is generated, hung on a glass filament and placed in a controlled environment (Figure 6.2b). The droplet drying behaviour and morphological changes is continuously monitored usually through use of a video camera [11]. The main difference between the drying of a usual droplet of liquid to ‘single droplet drying’ is the configuration and the droplet support system. The difference is highlighted in Figure 6.2. In the case of traditional drying of a single liquid droplet (in air drying and freeze drying) the droplet of liquid rests on a solid surface or powder bed (Figure 6.2a). However, in single droplet drying as mentioned in the rest of the chapter the droplet of liquid is suspended from a solid glass spindle (Figure 6.2b).



**Figure 6.2: Diagram highlighting the difference between a) a single sessile droplet sitting on a solid surface b) single suspended droplet hanging from a support spindle**

The data generated from single droplet drying provide fundamental information on the drying kinetics and droplet behaviour in given conditions. It has been used previously as a small scale experimental simulation of conventional spray drying for droplets containing dissolved solids

[12-15]. Walton and Mumford used the single droplet drying technique under controlled air temperature, humidity and velocity similar to that of a spray dryer. They demonstrated that the chemical and physical nature of the material affects the nature of the crust formed in the final structure [12]. Droplets containing polymeric materials tended to form thin-walled hollow particles on drying and increasing solute concentration resulted in a more permanent and stable crust [12].

The drying kinetics and evaporation of water droplets suspended by glass-filament has been investigated by many researchers. One of the main limitations of this method compared to droplets drying on a surface is the lack of free rotation and absence of inner flow [11, 16, 17]. Therefore, evaporation using the single droplet drying method is controlled by diffusion only at ambient conditions and absence of supplied air flow [18].

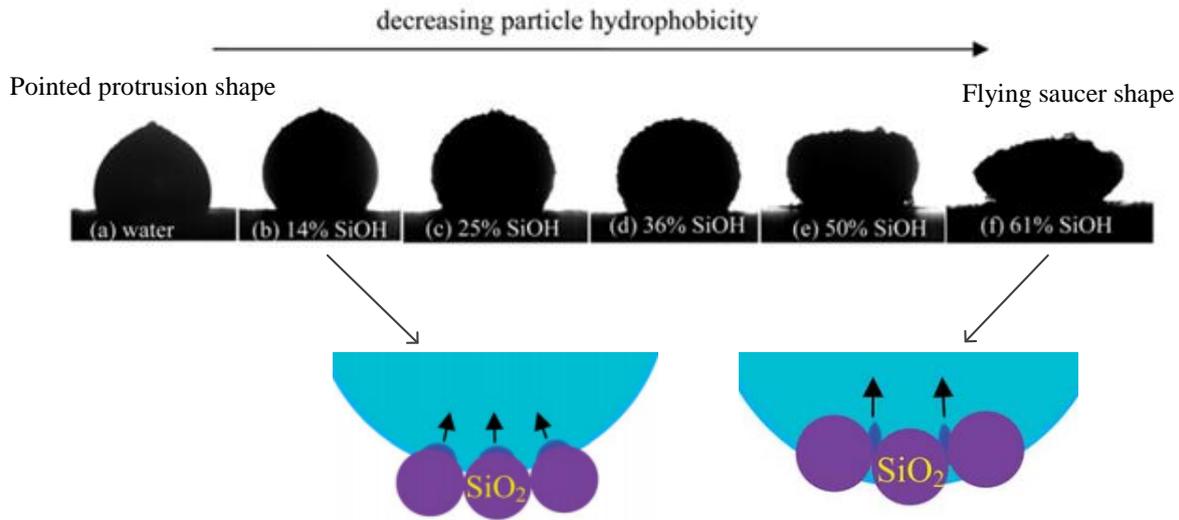
At the time of writing, no research group has investigated the use of single droplet drying as a method to maintain the shape of liquid marbles during drying.

### **6.1.3 Freeze Drying**

To date, there have been limited studies conducted on the effect of freezing liquid marbles. In a study by Hashmi et al. [19] liquid marbles made from de-ionised water and lycopodium particles are cooled on a thermo-electric cooler. Compared to a water droplet freezing on a superhydrophobic surface; liquid marbles undergo a gradual deformation and a ‘flying saucer-shaped’ ice marble results [19]. The observed deformation of liquid marbles was explained by Hashmi et al. by the principles of Marangoni convection and preferred nucleation [19]. It is proposed that the particles coating the liquid marble acts as an icing inhibitor, resulting in liquid flow of the water around the ice core as the marble freezes [19].

Slightly later work by Zang et al. [13] looked at the effect of hydrophobicity of silica powder coating on the ultimate shape of the liquid marble on freezing. They found that coatings using more hydrophobic powder resulted in an elongated marble with a pointed protrusion on top, while marbles coated with a low hydrophobic powder adopted a flying saucer shaped morphology similar to that observed by Hashmi et al. [13, 19]. Zang et al. attributed this difference to the different nucleation site present depending on where the particles sit at the air-liquid interface. That is, for very hydrophobic particle coatings, ice crystals grows on the convex surface of the particles, while for less hydrophobic particle coatings, the ice nucleation site is in the concave cavities between particles. The growth of ice crystals between the particle cavities then extends into the liquid droplet, causing lateral stretching of the surface shell

network, resulting in a flying saucer shaped frozen marble. Figure 6.3 shows the resultant structure from the two different ice nucleation sites.



**Figure 6.3: Effect of ice nucleation site on resultant frozen marble structure. Dark blue represents ice crystals and arrows show the direction of ice-growth. Adapted from Zang et al. [13]**

The previous work has all looked at freezing liquid marbles [13, 19] without removing the internal fluid. To date only Eshtiaghi et al., have tried to freeze dry liquid marbles [7]. Eshtiaghi et al. attempted to freeze dry liquid marbles made with 5% poly vinyl pyrrolidone (PVP), Hydroxyl Propyl Methyl Cellulose (HPMC) or Hydroxyl Propyl Cellulose (HPC) coated with either hydrophobic glass ballotini balls or Aerosil R974 [7]. The liquid was not first frozen before being put into the freeze dryer to dry at  $-50\text{ }^{\circ}\text{C}$  and 300 mmHg. In all combinations, Eshtiaghi et al. observed collapsed liquid marbles [7].

## 6.2 Experimental

Different drying methods were used to dry liquid marbles, with the aim to maintain shape integrity and long term stability of the resultant dried marble. Three drying methods, air drying, single droplet drying and freeze drying was investigated. Although both methods use air as the drying media, air drying and single droplet drying can be differentiated by the resting conditions of the liquid marble droplet. In the case of air drying, the liquid marble is dried at ambient condition or oven dried at higher temperatures, with the liquid marble resting on a powder bed (Figure 6.2a). Single droplet drying is used to describe the process when the liquid marble is hung from a spindle and allowed to dry at ambient conditions (Figure 6.2b).

### 6.2.1 Materials

Liquid marbles was created from the following solutions, where Kollidon<sup>®</sup> VA 64 is the commercial product name of VP/VA copolymer:

- Control: 0% VP/VA copolymer, with no Aerosil shell
- Liquid marble: 0% VP/VA with Aerosil shell (Ie. Liquid with Aerosil shell)
- Liquid marble: 2% VP/VA with Aerosil shell (Ie. Liquid with Aerosil shell)
- Liquid marble: 5% VP/VA with Aerosil shell (Ie. Liquid with Aerosil shell)

Properties of Aerosil and Kollidon<sup>®</sup> VA 64 (VP/VA copolymer) is given in section 3, Table 3.2.

### 6.2.2 Experimental Methods

#### 6.2.2.1 Oven drying at ambient conditions and higher temperatures

Liquid marbles of 30  $\mu$ L, with diameter around 4 mm were created by releasing droplets onto an aerosil bed using a 1 mL syringe with an 18 g needle. Solutions of 0%, 2% and 5% (w/v) VP/VA copolymer were used to make the marbles.

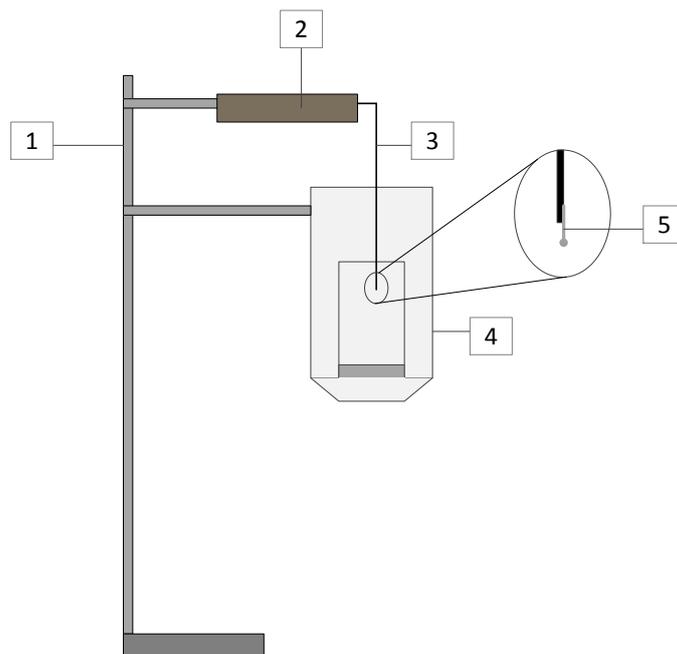
As a control, marbles were dried at room temperature (22-25 °C) in an enclosed cupboard to minimise disruption to the marbles on drying. To test the effect of drying the marbles at higher temperatures and the ability of the marbles to maintain shape integrity, drying in both convective and non-convective conditions were carried out at the following temperatures of 30 °C, 60 °C and 80 °C. Convective drying was carried out in a S.E.M. (SA) Pty. Ltd. fan-forced 60 L laboratory oven for 24 h. Non-convective drying was carried out in a S.E.M. (SA) Pty. Ltd. gravity convection 150 L drying oven for 24 h. Images of the final dried marbles were taken by a 16 MP Samsung Galaxy S5 phone camera.

In all cases, the initial marble diameter was around 4 mm compared to the final dried marble diameter of around 1 - 1.5 mm for the rebounded spherical marbles and 2 – 2.5 mm for the flat marbles.

#### 6.2.2.2 Single droplet drying

Single droplet drying was used to test whether a liquid marble suspended in air will maintain the shape integrity of the dried marble and whether a similar drying pattern can be observed compared to a liquid marble sitting on a powder bed.

Liquid Marbles of 2  $\mu\text{L}$  were created by releasing droplets onto an aerosil bed using a micro-syringe. The liquid marbles were then transferred using a glass filament to a glass hanging spindle. The drying process was recorded using a video camera fitted with a magnification lens. The video data is transferred into Sony PMB (Picture Motion Browser) software and images of the drying process captured at two minute intervals. The drop diameter is measured using Image J and images are manipulated using Microsoft Visio. A schematic diagram of the single drop drying apparatus used is given in Figure 6.4.



**Figure 6.4: Diagram of single droplet drying chamber: 1. Clamp and stand, 2. Wood block held by clamp with support pin, 3. Support pin, 4. Glass drying chamber, 5. Glass needle/filament**

### 6.2.2.3 Freeze drying

A two stage process was developed to freeze dry liquid marbles. The first stage is to freeze the marble (without drying it). The frozen marble is then transferred to a freeze dryer, and the liquid is removed in this second stage to produce a dry granule.

For the initial freezing stage, two different freezing methods were tried.

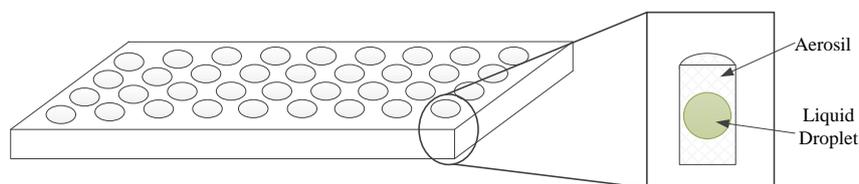
1. Snap freezing via liquid nitrogen immersion
2. Slow freezing using a freezer

### 6.2.2.3.1 Snap freezing via liquid nitrogen immersion

Droplets of 15, 30 and 50  $\mu\text{L}$  with VP/VA copolymer concentrations of 0%, 2% and 5% were dropped into a petri dish containing Aerosil. The dish was lightly agitated to ensure complete coverage of the droplet with Aerosil, resulting in liquid marbles. The Liquid marbles were then gently scooped up using a spatula and dropped into a small crucible containing liquid nitrogen. Once all the liquid nitrogen had evaporated, the snap frozen marbles were rolled out of the crucible.

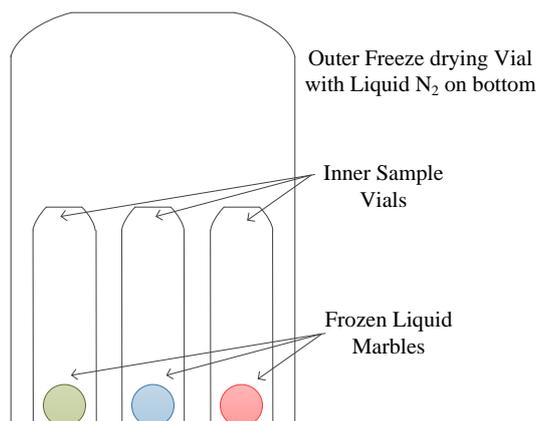
### 6.2.2.3.2 Slow freezing using a freezer

Liquid marbles of approximately 30  $\mu\text{L}$  were made by releasing droplets into the “wells” on a 96 well plate filled with Aerosil using a 1 mL syringe with an 18 g needle. The powder in the well was then lightly agitated to ensure complete powder coverage. To prevent the droplets from sticking to the sides of the “wells” it was important that the droplet is inserted into the middle of the powder by releasing the fluid in the center of the wells, allowing the powder to act as a natural barrier against the side and enabling the frozen droplets to slide out later. The natural fluid movement of the liquid as the droplet is injected into the wells also helps drag Aerosil particles across the surface of the droplets ensuring better powder coverage. Figure 6.5 shows a diagram of the wells and an enlarged cross section of a well, with droplet in middle of the well.



**Figure 6.5: Diagram of 96 well plate and cross section of a single well**

The plates of liquid marbles were frozen for 24 hours at  $-20\text{ }^{\circ}\text{C}$ . Given the nature of these marbles, which melt extremely quickly once removed from the cold environment and on contact with any ‘room- temperature’ items, all equipment required for transfer to freeze drying vials were kept in the fridge with the marbles. After 24 hours of freezing, the plate was inverted and the marbles rolled out from the wells, where they were then transferred to cold sample vials which were then immersed into 300 mL freeze drying containers containing liquid nitrogen for transport to the freeze dryer. A diagram of the different layers of sample vials is given in Figure 6.6.



**Figure 6.6: Diagram on configuration of sample vials for freeze drying**

The frozen liquid marbles were then loaded into a Christ Beta 1-8 LD plus freeze dryer, where they were left to dry for around 70 hours at  $-30\text{ }^{\circ}\text{C}$  and 0.37 mbar.

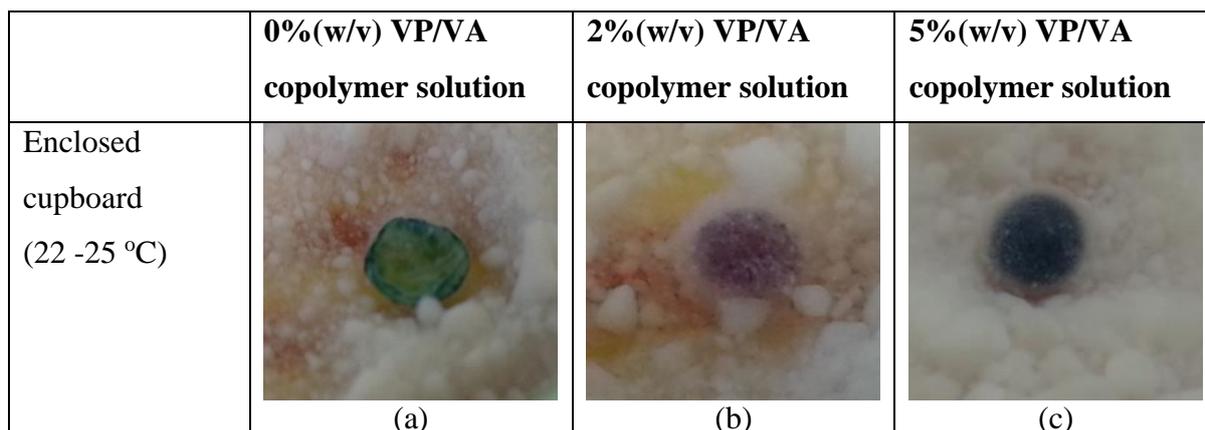
Images of the full size freeze dried liquid marble were taken by an SMZ stereo microscope with a 2 MP Motic moticam camera. To take images of the shell and center of the dried liquid marble, the marble was broken apart by a spatula. Close up images of the shell and center of the freeze dried liquid marble were taken by Moticam 352 camera attached to a Motic B1 series systems microscope. In each case, the liquid marble is around 4 mm diameter both before and after freeze drying.

## 6.3 Results

### 6.3.1 Air Drying in Ambient Conditions and Oven Drying

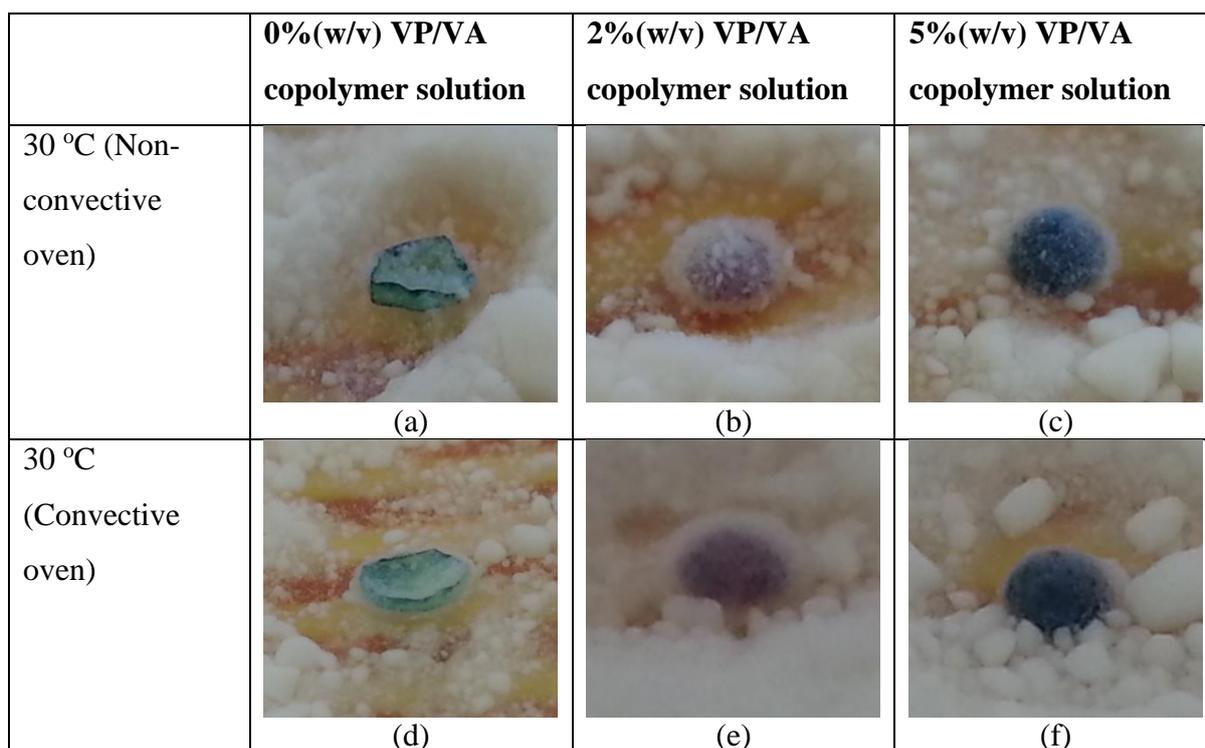
Figures 6.7 - 6.10 shows the final dried product of 30 $\mu\text{L}$  liquid marbles made from 0%, 2% and 5% (w/v) VP/VA copolymer solutions at different drying temperatures. When the liquid phase is 0% VP/VA copolymer (i.e. pure de-ionised water) droplet, the liquid marble dries as a very thin disk of dye and powder, regardless of the drying temperature (Figures 6.7 - 6.10 (a and d)). This is expected as the liquid marble is pure water with a powder coating. As the liquid phase shrinks during drying, the powder coating will stay at the interface and collapse with the marble, until all the liquid disappears and the powder is essentially resting on original powder bed.

At ambient conditions (Figure 6.7), both the 2% and 5% liquid marble regained their spherical shape. Although images of the overall drying process were not obtained in this case, from previous work conducted in Chapter 5, the marble was able to regain its spherical shape from a rebound phenomenon.



**Figure 6.7: Image of dried marbles at ambient conditions and changing VP/VA copolymer concentrations.**

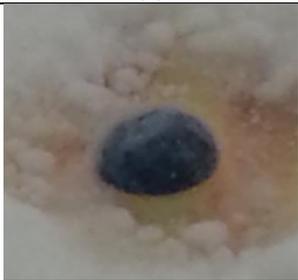
Figure 6.8b,c,e and f shows that at 30 °C, the resultant 2% and 5% VP/VA copolymer dried marbles are able to regain their spherical structure similar to that observed at ambient conditions and air flow does not affect the final structure.



**Figure 6.8: Image of dried marbles at 30 °C with liquid marbles made from 0%, 2% and 5% VP/VA copolymer solution dried in either a non - convective or convective oven.**

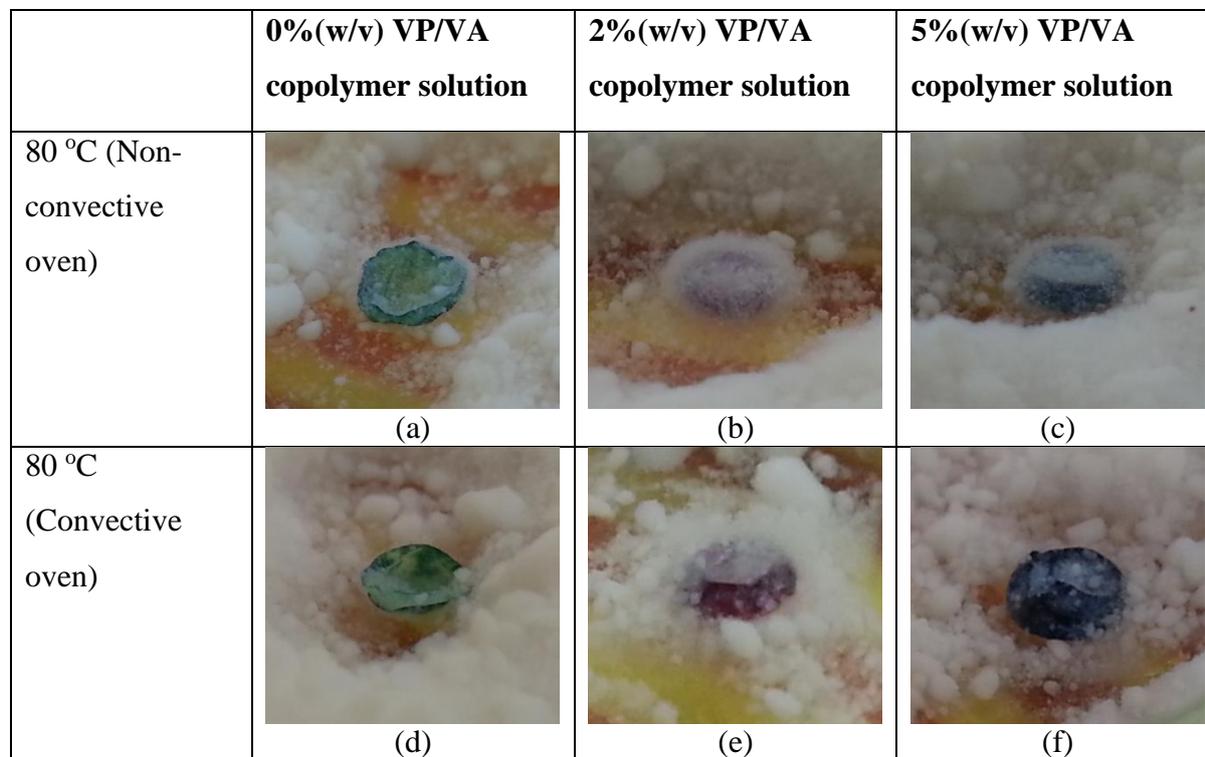
When the drying temperature increases to over 60 °C, the 2% and 5% VP/VA copolymer liquid marbles are unable to regain their spherical shape and air flow disturbances can be observed in dried products of liquid marbles dried in the fan - forced convection oven, compared to a gravity convection oven where forced air flow is present. When a gravity convection oven is

used, the marble dried as a flat puddle like structure (Figures 6.9b,c and Figures 6.9b,c) compared to liquid marbles dried in a fan-forced convection oven, which showed a more uneven ridge-like surface (Figures 6.9e,f and Figures 6.10e,f). The differences caused by fan – forced air flow across the surface supports the concept that a liquid marble shell is ‘fluid’ until it locks.

	<b>0%(w/v) VP/VA copolymer solution</b>	<b>2%(w/v) VP/VA copolymer solution</b>	<b>5%(w/v) VP/VA copolymer solution</b>
60 °C (Non-convective oven)	 (a)	 (b)	 (c)
60 °C (Convective oven)	 (d)	 (e)	 (f)

**Figure 6.9: Image of dried marbles at 60 °C with liquid marbles made from 0%, 2% and 5% VP/VA copolymer solution dried in either a non - convective or convective oven.**

Figure 6.10 shows that drying at 80 °C produces similar results to that observed when drying occurs at 60 °C (Figure 6.9), with the puddle shape of the gravity convection oven drying and the ridges seen in fan-forced convection drying more pronounced.



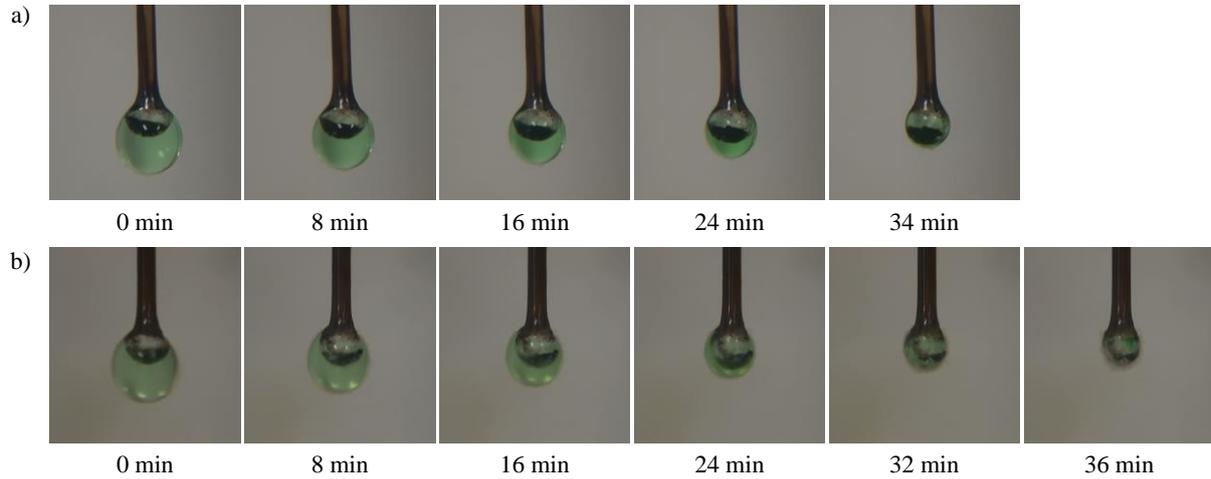
**Figure 6.10: Image of dried marbles at 80°C with liquid marbles made from 0%, 2% and 5% VP/VA copolymer solution dried in either a non - convective or convective oven.**

### 6.3.2 Single Droplet Drying

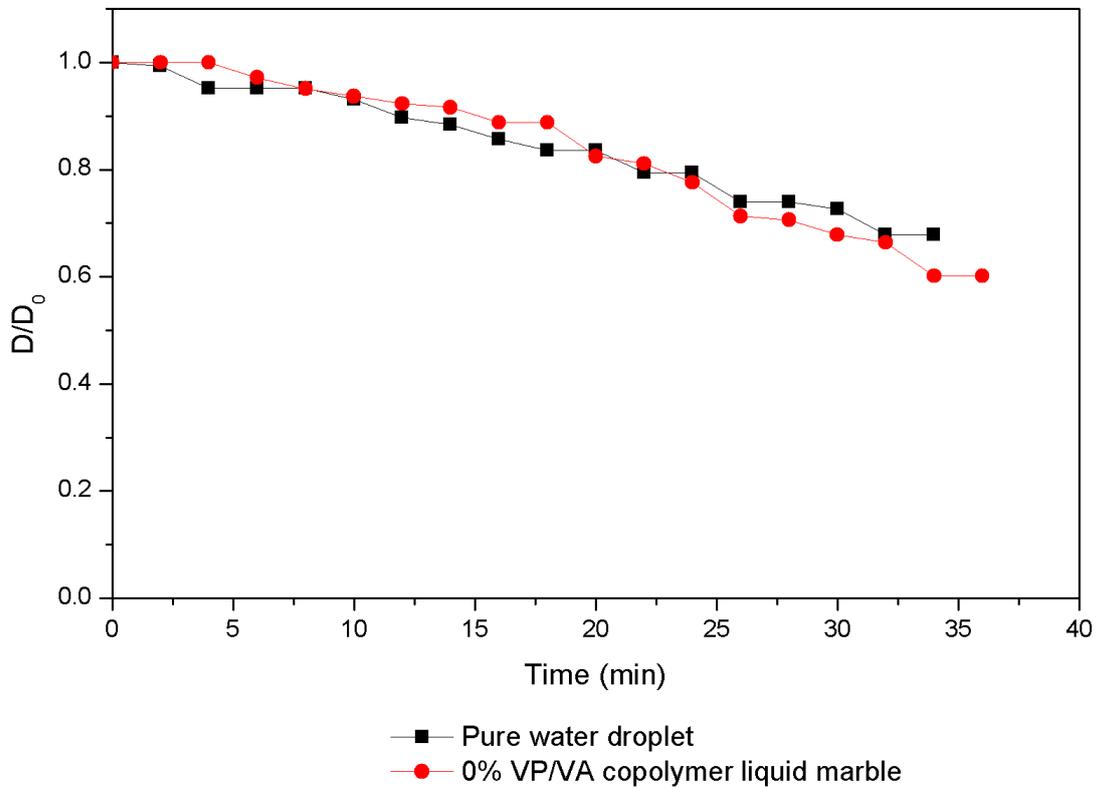
Figures 6.12, 6.14 and 6.16 show the change in diameter for liquid marbles produced from different copolymer solutions. The solid lines show the time it takes for complete drying of a droplet without aerosil coating (ie. a plain droplet), while the dotted line shows the time it takes for complete drying of a liquid marble made from same solution but with an aerosil coating (ie. a liquid marble). Figures 6.11, 6.13 and 6.15 show images of the drying droplet at different time points throughout the drying process. A more comprehensive set of images for the different liquid marbles and pure droplet solutions are given in Appendix G.

Figures 6.12, 6.14 and 6.16 show that addition of the aerosil coating does not increase the drying time of liquid marbles compared to the pure liquid droplet. Please note that the spindle bulb has a diameter of 0.9 mm, and hence, minimum  $D/D_0$  in the above figures is 0.6 on complete drying. A lack of increase in drying time between aerosol coated and pure liquid droplet may be due to the layers of powder on the marble surface. When a liquid marble is hung on the spindle, any powder which is not stuck to each other or the liquid droplet will fall

off the marble. Therefore, the liquid marbles on the spindle will most likely have a monolayer of powder in the coating compared to liquid marbles which sit on a flat surface, which is more likely to have multilayer powder coating. As the presence of a single layer of particles on the liquid surface does not significantly affect the drying rate [10], the lack of difference in drying time between a pure liquid droplet and a liquid marble is expected.

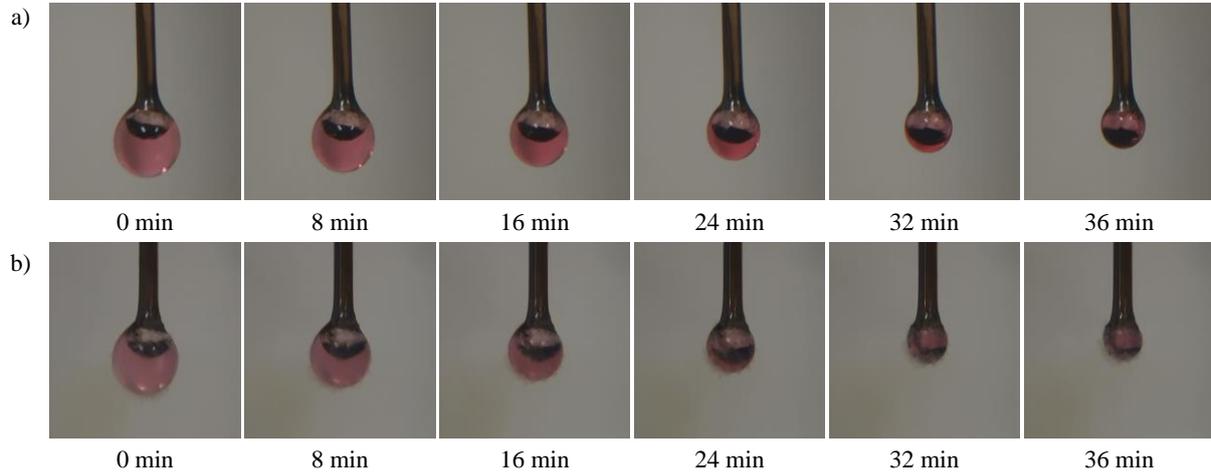


**Figure 6.11: Images of changing a) pure water droplet over time b) 0% VP/VA copolymer liquid marble over time. Spindle stem thickness of 0.5 mm**

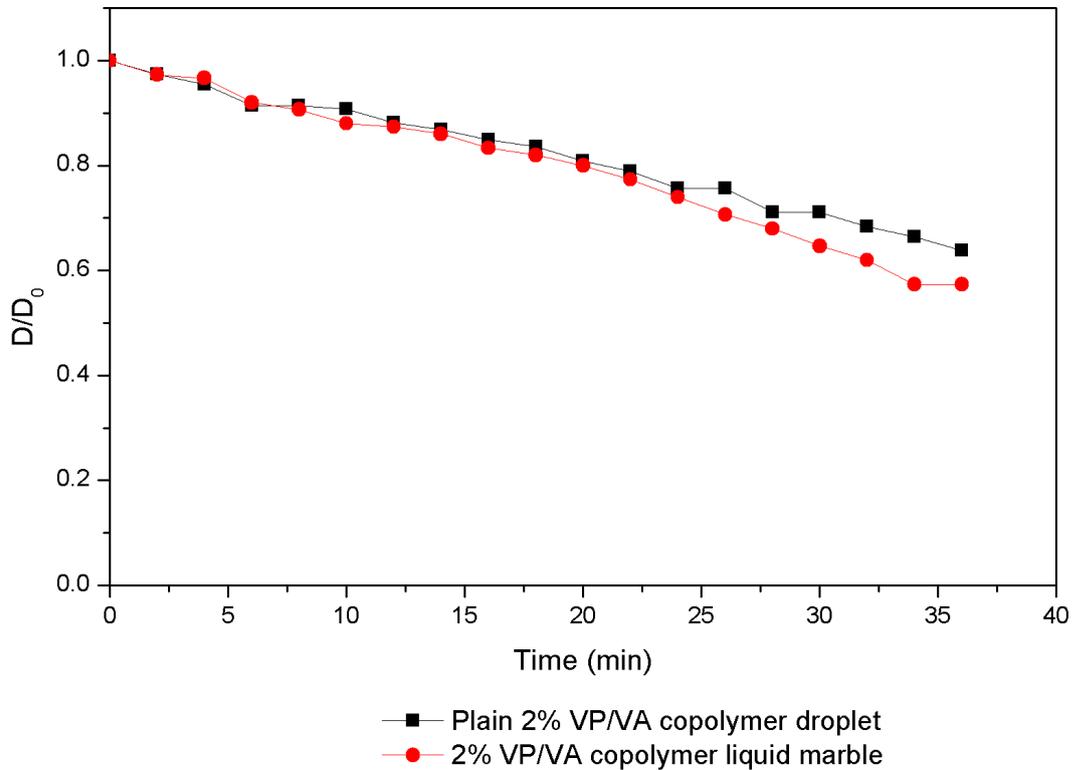


**Figure 6.12: Diameter compared to initial droplet diameter for control droplets (i.e. pure droplet with no Aerosil coating) and Aerosil coated liquid marble over time for 0% VP/VA copolymer droplets.**

Compared to a pure water droplet, the presence of VP/VA copolymer only slightly extends the drying time of a 2% copolymer liquid marble (Figure 6.14). As VP/VA copolymer is a film former, it will create a barrier at the interface between the liquid droplet and the powder shell. However, similar to a monolayer powder coating, it is not expected to retard the drying rate significantly to be able to result in a huge increase in drying time.

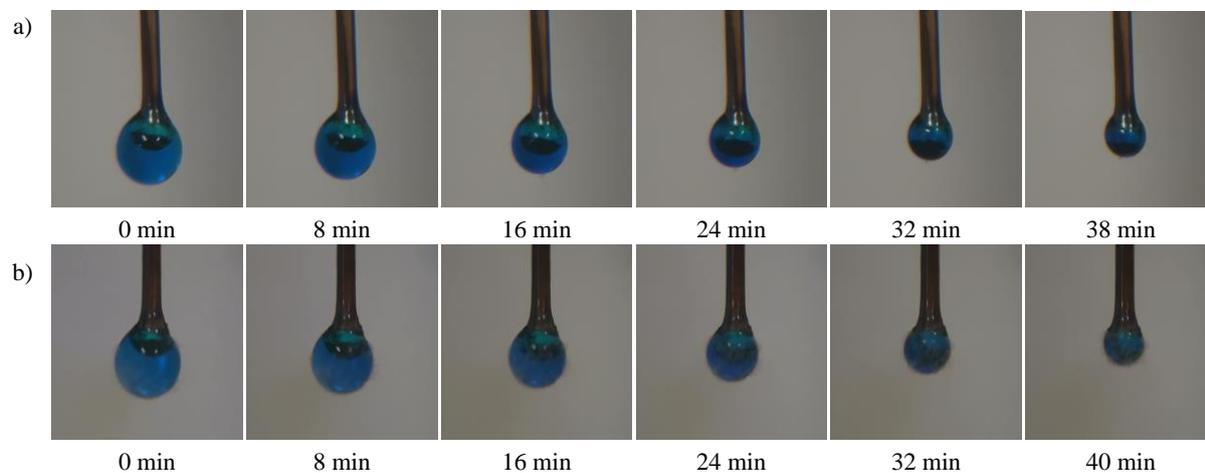


**Figure 6.13: Images of changing a) pure 2% VP/VA copolymer droplet over time b) 2% VP/VA copolymer liquid marble over time. Spindle stem thickness of 0.5 mm**

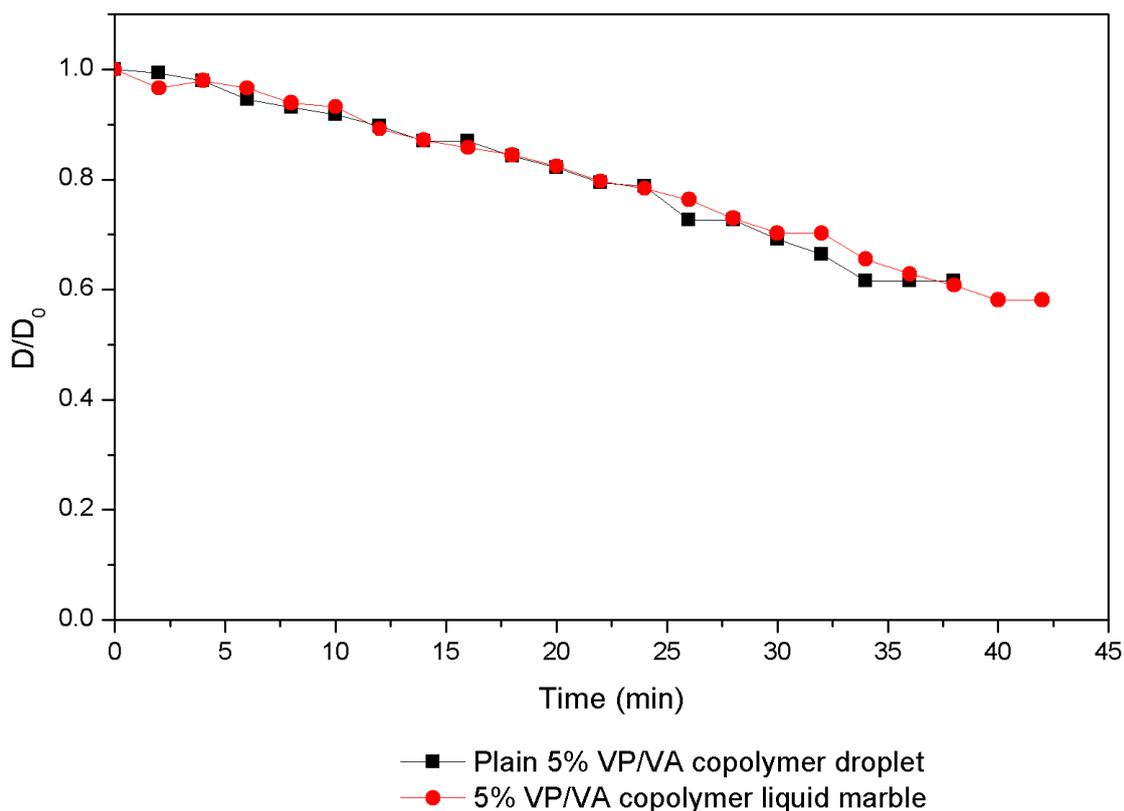


**Figure 6.14: Diameter compared to initial droplet diameter for control droplets (i.e. pure droplet with no Aerosil coating) and Aerosil coated liquid marble over time for 2% VP/VA copolymer droplets.**

The 5% copolymer liquid marble (Figure 6.16) shows similar results to that of the 2% copolymer liquid marble but with slightly longer drying time. This may be due to increased density of VP/VA copolymer at the interface.



**Figure 6.15: Images of changing a) pure 5% VP/VA copolymer droplet over time b) 5% VP/VA copolymer liquid marble over time. Spindle stem thickness of 0.5 mm**



**Figure 6.16: Diameter compared to initial droplet diameter for control droplets (i.e. pure droplet with no Aerosil coating) and Aerosil coated liquid marble over time for 5% VP/VA copolymer droplets.**

In all cases (the 0%, 2% and 5% (w/v) copolymer marbles) the collapsing of the marble and the rebound phenomenon which is seen in air dried marbles in the last section (Figure 6.7) and

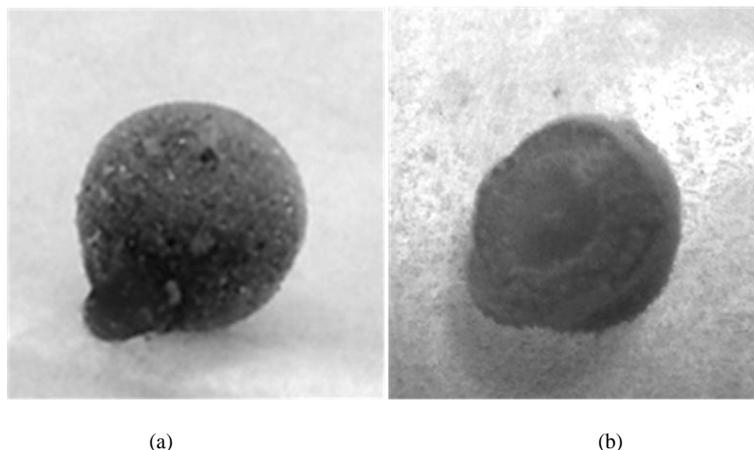
in Chapter 5 (Section 5.2) is not observed when single droplet drying is used. This is attributed to a pinned contact line when single droplet drying method is used. In order for the liquid marble to rebound back into its spherical structure, the contact area must be able to move and accommodate the sudden drop in width of the liquid marble as it changes from a puddle like structure back into the spherical marble shape (Section 5.2).

### **6.3.3 Freeze Drying**

Freeze drying in this study was a two-step process consisting of a freezing component and a drying component where the liquid is removed via sublimation. Although Eshtiaghi et al. previously attempted freeze drying of liquid marbles, the pre-freezing component was not undertaken and ‘wet’ liquid marbles underwent the freeze-drying stage directly [7]. Freezing of liquid marbles has been attempted previously by Hashmi et al and Zang et al [13, 19], but neither group created frozen liquid marbles which maintained their spherical shape. Two alternative freezing methods were tried to find a method of freezing which would enable the resultant liquid marble to maintain its spherical shape as a frozen marble. A second drying step was then undertaken in a freeze dryer to create a stable freeze dried liquid marble which has maintained its size and spherical structure.

#### **6.3.3.1: Freezing of liquid marbles via liquid nitrogen immersion**

Two types of frozen marbles resulted from this freezing method, as shown in Figure 6.17. The marbles were observed to freeze into either a bowl like shape or as a frozen droplet with a small protrusion, independent on the type of solution used. Assuming that the frozen shape forms the foundation of the final dried shape of the liquid marble, this methodology was not further investigated as the production of a stable marble which has retained the spherical shape and size of the original liquid marble is required. In addition, the frozen marbles were extremely delicate and melted on exposure to air almost straight away.



**Figure 6.17: Structures a) tip protrusion structure produced from snap freezing of liquid marbles using liquid nitrogen and b) ‘bowl’ like structure**

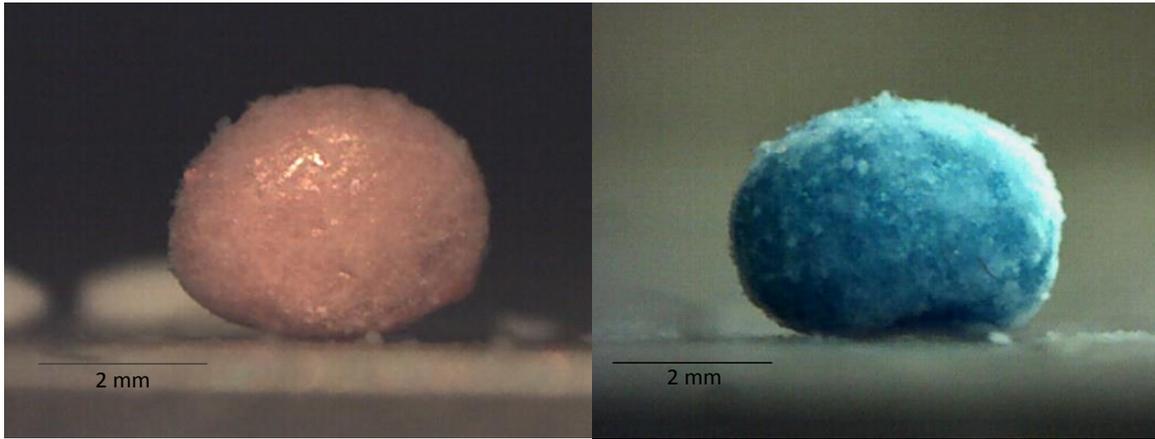
### **6.3.3.2: Slow freezing of marbles overnight at -20 °C.**

Freezing of liquid marbles overnight at -20 °C allowed for slower and more uniform freezing of the liquid component. As a result, the final frozen droplet retained its spherical structure. Unfortunately, images were not able to be taken due to the delicate nature of the resultant frozen marbles and the speed at which they defrosted. In conjunction, it was important to transfer the frozen marbles into the freeze dryer vials as soon as possible. The faster rate at which they defrosted compared to pure liquid droplets may be due to the presence of the powder, which acts as an icing inhibitor by providing thermal energy to the liquid molecules [8].

### **6.3.3.3: Drying of frozen liquid marbles**

Freeze drying works by causing all the water in the sample to sublime and the water vapour is then removed from the sample under vacuum. As this process occurs in an enclosed freeze dryer, the changes that the liquid marbles undergoes throughout this process could not be recorded. Therefore, only the final product can be imaged.

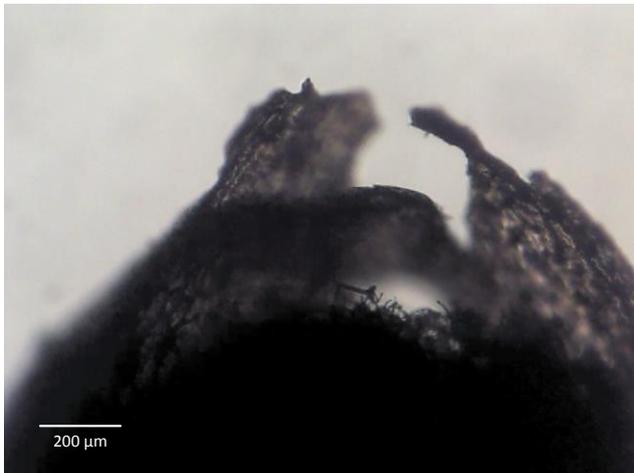
It was observed that the 0% VP/VA copolymer control marbles completely disappeared after drying, leaving only the powder behind. This is expected as the 0% VP/VA copolymer marbles are 100% water. Hence, when all the water vapour evaporates, only the powder is left, with the shell being too delicate to survive. Figures 6.18 shows that the 2% and 5% VP/VA copolymer liquid marbles were able to maintain their shape after freeze drying. Figure 6.19a show the crust and porous center of the resultant dried marble and the distinction between the shell and the almost ‘fluffy’ center of the marble.



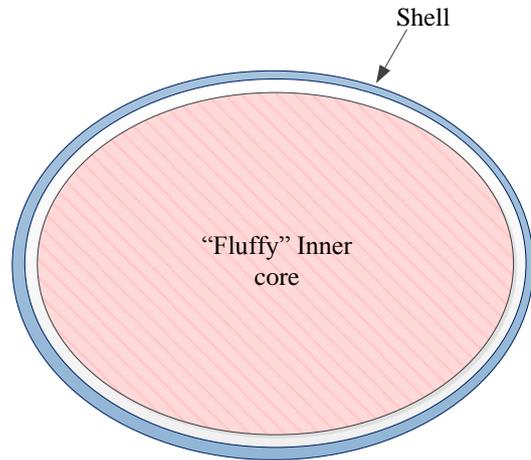
(a)

(b)

**Figure 6.18: Images of freeze dried liquid marbles made from a) 2% (w/v) VP/VA copolymer solution with Aerosil powder shell and b) 5% (w/v) VP/VA copolymer solution with Aerosil powder shell.**



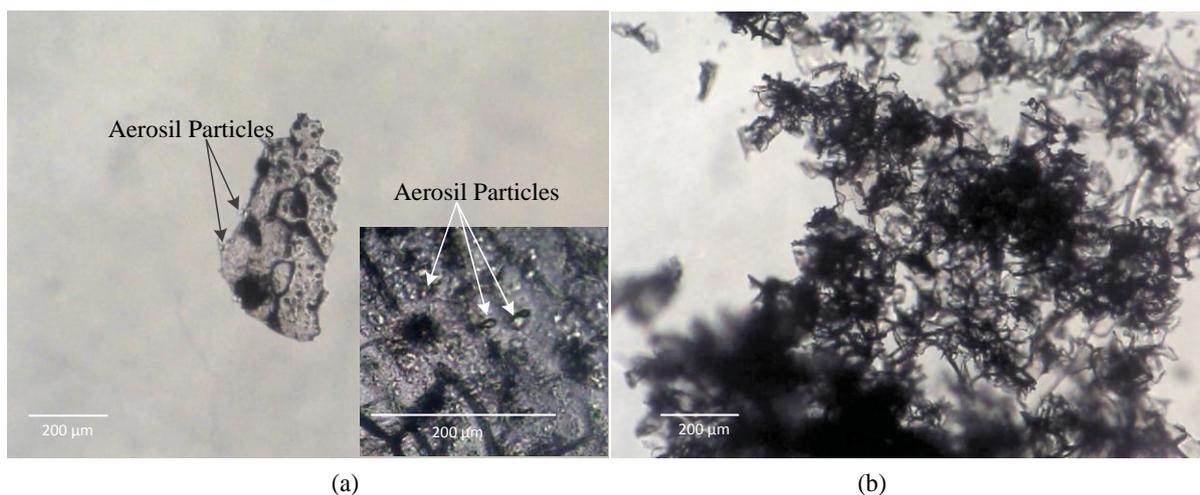
(a)



(b)

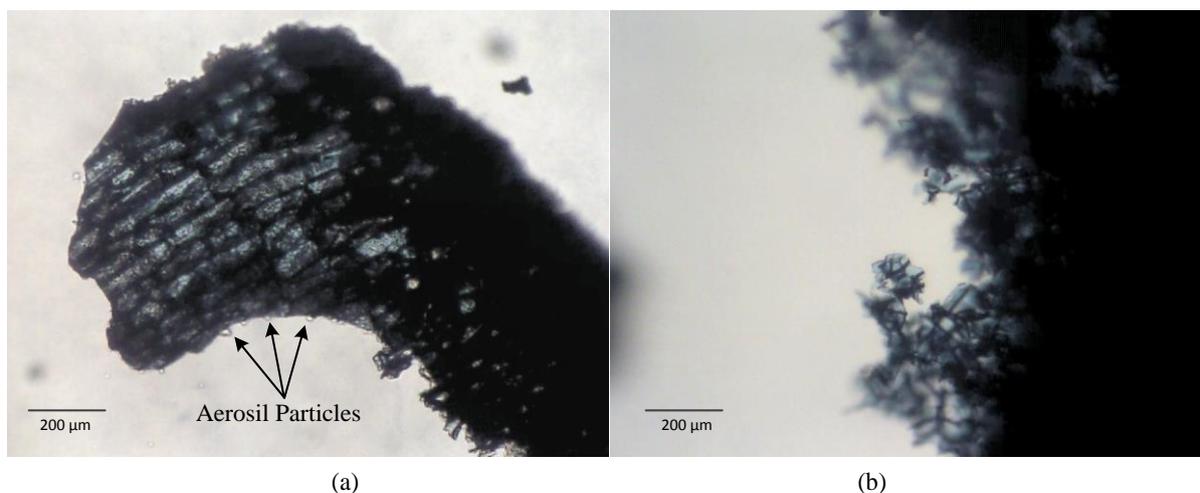
**Figure 6.19: a) Image of freeze dried liquid marble made from 2% (w/v) VP/VA copolymer solution with shell cracked for imaging and b) cross-section diagram freeze dried liquid marble if uncracked.**

Figure 6.20 shows in greater detail the shell fragments and the ‘fluffy’ inner material of the freeze dried 2% VP/VA copolymer liquid marble. The external shell has an almost ‘glassy’ look with the VP/VA copolymer chains forming a lattice which traps the aerosil on its surface. Figures 6.20a shows the tiny Aerosil particles, which are seen as the hollow spherical particles on the surface and ingrained in the shell.



**Figure 6.20: Images of the 2% (w/v) VP/VA copolymer solution liquid marble a) Shell fragment with the insert showing a magnified image b) Crushed inner material.**

The freeze dried 5% VP/VA copolymer liquid marbles show similar features to the 2% VP/VA copolymer liquid marbles. However, the shell matrix is more ordered and a denser concentration of polymer chains for the 5% (Figure 6.21a) compared to the 2% (Figure 6.20a) marble. This is expected due to the higher copolymer concentration of the 5% solution.



**Figure 6.21: Images of the 5% (w/v) VP/VA copolymer solution liquid marble a) Shell fragment and b) 'Fluffy' inner structure which has been broken off central core and not crushed.**

During imaging, it was observed that the shell and porous center had quite different properties. While the shell was generally quite un-reactive, the inner porous material was quite 'sticky' and had a tendency to stick to each other or the spatula transferring them to the slide for imaging. The inner material appears to be quite electrostatic.

## 6.4 Discussion

The drying methodology has a significant impact on the final shape integrity and the size of the liquid marble. The advantages and disadvantages of the different drying methods are summarised in table 6.1.

**Table 6.1: Summary of the different drying methods and the impact on final marble shape**

<b>Drying Procedure</b>	<b>Maintain Shape Integrity?</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Air Drying</b>	Maybe (depends on conditions)	- Easy - Not much equipment required	- The marble shrinks and doesn't maintain size.
<b>Single Droplet Drying</b>	No	- Potential to upscale to spray drying - Relatively easy to do	- Require specialised equipment - Difficulty hanging marbles - Doesn't maintain shape or size of marble
<b>Freeze Drying</b>	Yes	- Maintains shape and size of the marble - Formation of porous matrix means potential future applications in drug delivery or trapping of biomolecules or gases - Very consistent and resultant structure is very stable	- Difficult to conduct as require special equipment and two stage process. - Intermittent frozen marbles melt very quickly and transition between the two stages need occur quickly

A more detailed discussion of the different methods and the resultant marble shape and structures are given in more detail in the following sections.

### 6.4.1 Air Drying

Drying conditions will strongly influence the final shape of the dried marble. At ambient conditions or low temperatures, in the presence of film former, the marble will either dry spherically or 'rebound' to a spherical shape, depending on the concentration of film former and the initial size of the marble. The ultimate shape of the marble is dependent on the interactions within the powder shell, at the solid-liquid interface and within the liquid core. In conjunction, the rate of drying is shown to affect the resultant dried marbles. At ambient conditions and low temperatures, where the mass diffusion rate is low, the powder and film former are given enough time to interact and a hard shell can be created, resulting in a stable spherical dried marble. At higher temperature of over 60 °C, the mass diffusion rate would be

higher and the shell will not have enough time to stabilise and as the density of the powder thickens with rapid decline in surface area, gravity will dominate and create a ‘puddle’ or ‘disk’ on drying. The observance of air flow disturbances where a convective oven is used further supports the hypothesis that the shell is ‘fluid’ until it locks and solidifies.

#### **6.4.2 Single Droplet Drying**

Single droplet drying differs to the other methods in three main ways:

1. The droplet is hung on the support spindle and drying opposes gravity.
2. The contact line between the droplet, powder and the support spindle is pinned so that the drop cannot form a hemisphere.
3. With the support spindle, another solid – liquid interface exists within the liquid center compared to the other liquid marbles.

A combination of these three factors result in the drying droplet shrinking onto the spindle and showing little difference between the control where no aerosil is present and where an aerosil shell is present.

#### **6.4.3. Freeze Drying**

Of the three methods (air drying, single droplet drying and freeze drying), only freeze drying was able to maintain the original shape and size of the original marble. It is believed that this is due to two main factors:

1. The initial freezing step trapped the water molecules within the copolymer matrix as the entire solution interacts and solidifies over time in the freezer. The flexible nature of the powder shell meant that even with volume expansion as the water solidifies, the shell was able to accommodate this and prevent cracking of the shell.
2. Liquid marble shells are gas permeable [20], which means that during drying in the freeze-dryer, the gas vapour was able to escape without deforming the shape of the exterior marble shell.

### **6.5 Conclusion**

The effect on the shape and size of liquid marbles due to air drying, single droplet drying and freeze drying of liquid marbles made from deionised water, 2% and 5% VP/VA copolymer (Kollidon VA64), coated with Aerosil powder was studied in this chapter. Extending on previous work conducted in Chapter 5, where only air drying at room temperature was

conducted and the presence of the ‘rebound’ phenomenon was observed; this chapter aims to establish whether other drying methods would also maintain the shape and size of the liquid marble during drying.

Air drying of liquid marbles at different temperatures showed that higher temperatures resulted in ‘puddle’ like structures, which is likely to be due to higher mass diffusion rates, resulting in the marble top collapsing before it has time to stabilise or rebound back into its spherical shape.

Single droplet drying showed no difference between a liquid marble drying and a normal liquid droplet drying. This was attributed to three main possibilities; firstly, the contact line is pinned which means that the droplet cannot rebound; secondly, the droplet is hung and hence, compared to a droplet on a flat surface, gravity opposes collapse into the surface; and lastly, the spindle creates a second solid- liquid interface which dominates compared to the Aerosil solid-liquid interaction.

In this chapter, a successful two stage process was developed where the liquid marble is first frozen in a freeze overnight and then freeze dried. The freeze dried liquid marbles were able to maintain their shape and size to form a porous center with a crust. The process is achievable due to two key characteristics of liquid marbles. Firstly, the flexible nature of the powder shell accommodates liquid expansion during the freezing stage. The shell of liquid marbles is also gas permeable, which prevents shell cracking during the drying stage as water sublimates and is removed from the marble under vacuum. The development of this stable freeze dried liquid marble structure holds potential in future applications such as a biomolecule delivery system, where biomolecules are trapped in the porous matrix. This process may be further refined to create hollow granules, which may be used as long-lasting, highly stable structures with a high hydrophobic drug loading.

## 6.6 References

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# 7

## Conclusions and Recommendations for Future Work

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This section outlines the key findings from this thesis and also provides recommendations for potential future work in this area. Liquid marbles are remarkable particles and there is still much knowledge to be gained from continuous research.



## **7 Conclusions and recommendations for future work**

The work conducted for the writing of this thesis extends on our understanding of the fundamental structure of liquid marbles. Commercial products were studied to determine why commercial companies are able to obtain a shelf life significantly longer than those obtained in research laboratories. Insights gained from commercial products in Chapter 4 were then utilised in Chapter 5, where film former was added to a basic water and aerosil formulation. A unique drying pattern where a ‘rebound’ was observed in Chapter 5 and a potential drying hypothesis to explain the different types of drying phenomenon was constructed. Chapter 6 looked to identify other drying methods which were able to maintain the shape and structure of liquid marbles, leading to the establishment of freeze drying liquid marbles which has never before been attempted.

### **7.1 Conclusions**

The following key findings from each chapter of work are outlined below.

#### **Chapter 4:**

In this chapter twelve commercially available hair and foundation products believed to contain liquid marbles was compared in terms of their formulation, moisture content, appearance and particle size. The complexity of the formulations meant that it was often difficult to identify liquid marbles through appearance alone. However, a combination of generally higher moisture content; ingredient listing with water and silica silylate (Aerosil) being the two main components of the product; and the appearance of particles with a light center surrounded by a solid crust meant that we can assume with relative certainty the presence of liquid marbles in these products. The comparison of the commercial samples resulted in the finding that all of the products contained a film former such as VP/VA copolymer or something similar. As such, it was concluded that inclusion of a film former will contribute to the prolonged longevity of liquid marbles, potentially through forming a film at the solid-liquid interface, thereby retarding evaporation and slowing down drying which results in the loss of the shape of liquid marbles.

#### **Chapter 5:**

This chapter utilised the findings from Chapter 4 and VP/VA copolymer solution of 2% and 5% (w/v) concentration was used as the liquid phase. Images of how drying occurs over time was recorded to show some surprising results. It was observed that a ‘rebound’ phenomenon

occurs in marbles produced from 2% and 5% (w/v) VP/VA copolymer solutions. In conjunction, results showed a good correlation between the point of ‘rebound’ and the time at which the calculated Ohnesorge number showed a point of inflection. Previous literature has reported that the Ohnesorge number represents the point at which the capillary inertial regime transitions to the capillary viscous regime. The cross-over point is quantitatively defined at Oh number of 0.05. While this number was close in a lot of the cases, the correlation was not exact. It is possible that this is due to either calculation uncertainty as viscosity is extrapolated from concentration data calculated using measured height of the liquid marbles. A combination of the visual data and the calculations resulted in the construction of a drying hypothesis which identified three key drying mechanisms: powder driven, interface driven and shell driven drying.

It was hypothesised that powder driven drying is promoted by strong powder-powder interactions and lack of shell strength resulting in collapsed marbles as they dry. Interface driven drying can result in either collapsed or rebounded marbles depending on the balance of gravity and surface tension. If gravity dominates, the marble will collapse; while if surface tension dominates, the marble will rebound back into its spherical shape. Shell driven drying is expected to be characterised by strong liquid-liquid interaction and shell stability dominating throughout the drying process, resulting in the liquid marble retaining its spherical structure throughout.

## **Chapter 6:**

In order to further understand how different drying methods impact the shape and structure of liquid marbles, three common drying methods was explored. Extending on the air drying method used in Chapter 5, air drying at different temperatures was investigated and the effect on the final shape of the dried liquid marble. In Chapter 5, the addition of VP/VA copolymer and drying at room temperature often resulted in a final spherical marble which had rebounded from a puddle structure. However, it was found that as temperature increased, the ‘rebound’ effect became less common. It is expected that the higher temperature resulted in faster evaporation rate of liquid from the liquid marble, thereby decreasing the amount of time for the film former to react at the interface and the marble collapses before the shell has time to stabilise.

Single droplet drying, which is often used as the foundation to studying drying of droplets in a spray dryer was used to determine if spray drying of liquid marbles could help maintain the

shape integrity of a liquid marble or produce a hollow granule. The change in contact between a flat surface and those of a spindle with opposing forces meant that the drying marble did not have a surface to ‘rebound’ off and as a result retreated onto the spindle to dry as a coating.

Lastly freeze drying of liquid marbles was attempted. To date, freeze drying of liquid marbles has never been attempted, despite work having been conducted on freezing liquid marbles and the effect of freezing on its shape. However, freeze drying is a common drying methodology used to stabilise pharmaceutical products in industry and hence, was chosen to investigate what would happen to liquid marbles if they were freeze dried. Our research showed that freeze drying of liquid marbles made from VP/VA copolymer solution with an Aerosil shell resulted in perfectly spherical marble with a highly porous center.

## **7.2 Recommendations for Future Work**

This thesis concentrated on studying the effect of film formers on liquid marble stability and investigating liquid marble drying methodology on stability. While this is the first time that a comprehensive comparison of commercial samples containing liquid marbles has been conducted and the use of freeze drying as a potential drying methodology to maintain the stability of liquid marbles as a dried structure; further research is required on these remarkable particles. A more in depth study and further investigation is recommended in the following areas:

- New products are consistently being introduced to the market and even now, more products which potentially incorporate liquid marble technology are appearing on supermarket shelves. In conjunction, the delicate nature of liquid marbles means that it was difficult to accurately identify liquid marbles from the rest of the formulation via imaging alone. A better methodology of identifying liquid marbles from the rest of the formulation may be beneficial for future deconstruction of commercial samples and increasing our understanding of why they are able to achieve over two years shelf-life.
- While film formers was one of the main components present in the formulations with more obvious marbles, further studies on the effect of combinations of these formulation excipients could be interesting. In many cases, the commercial samples contained a combination of preservatives, surface agents, binders and film formers in conjunction to the water and silica silylate components. Further research on how the

combination of ingredients stabilises or de-stabilises the liquid marble shell may provide clues to their enhanced longevity.

- The effect of film former was studied using millimetre-sized marbles to ensure consistency of marble size and ability to manually move the liquid marbles. Further research into producing scalable micrometer marbles which are comparable in size to commercial samples will be beneficial to future work aimed at increasing our understanding of interactions within micrometer sized liquid marbles.
- Investigate the time scale of film formation by VP/VA copolymer compared to the time scale of drop evaporation may provide further information on how film formers increase liquid marble stability and how the polymer interacts with the solid particle phase of a liquid marble.
- Freeze drying of liquid marbles has been shown in this work to produce a porous spherical structure with a crust. However, the exact characteristics of these highly stable structures are unknown. Further work into characterisation of the properties of the shell and the inner structure may provide some insights into these new structures.
- Potentially, research into the pore size distribution of these freeze dried liquid marble structures may provide a novel use of dried liquid marbles as a drug delivery system where a higher hydrophobic drug loading is possible compared to conventional drug delivery systems.

A

Appendix A





## Appendix A: Formulations of Commercial Samples

Below are the formulations of the store-bought commercial products analysed in Chapter 4: Characterisation of commercial samples. The components are listed in the order they are listed on the packaging, which is done in decreasing order of prevalence. Uses of the component are taken from the Handbook of cosmetic and personal care additives by Ash and Ash [1].

### A.1 Foundation Products

<b>IOD Aqua Powder Aquatique by Christian Dior</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Seawater	Liquid phase
Silica Silylate	Hydrophobic powder phase used to form the shell of the liquid marble
Sorbic Acid	Preservative, or anti microbial agent
Methylparaben	Preservative.
Phenoxyethanol	Anti-microbial agent
Butylparaben	Preservative
Aluminium Myristates/ Palmitates	Anti caking agent.
Mica	Light refractor, adds sparkle or shine to the formulation. Colourant

<b>Magic liquid Powder by Prescriptives</b>	
<b>COMPONENTS</b>	<b>USE</b>
Water	Liquid phase
Polymethylsilsesquioxane	Film former.
HDI/ trimethylol Hexyllactone crosspolymer	Anti-caking agent
Silica Silylate	Hydrophobic powder phase
Dimethicone	Skin-conditioning agent- occlusive
Triethoxycaprylylsilane	Binder and emulsifier
Sodium Hyaluronate	Skin-conditioning agent - miscellaneous
Quaternium 15	Anti-microbial agent
Sodium Polyacrylate	Film former, skin- conditioning agent – emollient
Silica	Anti-caking agent
Sodium Dehydroacetate	Anti-microbial agent
Phenoxyethanol	Anti-microbial agent
Methylparaben	Preservative
Mica	Light refractor, adds sparkle or shine to the formulation. Colourant
Titanium Dioxide (CI77891)	Opacifying agent and colorant
Iron Oxides	Colouring agent

<b>Aqua Powder by Physicians Formula</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Talc	Anti-caking agent, bulking agent, opacifying agent
Glycerin	Skin-conditioning agent - humectant. Skin protectant
Silica Silylate	Bulking agent, skin conditioning agent-emollient. Hydrophobic powder to form marble shell
Mica	Colorant
Titanium Dioxide	Colorant, opacifying agent
Silica	Anticaking agent
Dimethicone	Skin-conditioning agent - occlusive
Methicone	Skin-conditioning agent - occlusive
Zinc Stearate	Anticaking agent, colourant
Nylon-12	Bulking agent, opacifying agent
Zinc Myristate	Anticaking agent
Zinc Oxide	Bulking agent, colourant
Lauroyl lysine	Skin conditioning agent - miscellaneous
Iron oxides	Colouring agent
Imidazolidinyl urea	Preservative
Methyl paraben	Preservative
Butyl paraben	Preservative
Propyl paraben	Preservative

<b>MAP-15 Regenerator by Dermalogica</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Solvent, liquid phase
Glycerin	Skin-conditioning agent- humectant
Silica	Anticaking agent, bulking agent, opacifying agent
Magnesium ascorbyl phosphate	Anti-oxidant, skin conditioning agent - miscellaneous
Hydrogenated lecithin	Skin-conditioning agent - miscellaneous, surfactant, suspending agent
C9-15 fluoroalcohol phosphate	Skin conditioning agent - miscellaneous
Phospholipids	Skin-conditioning agent - miscellaneous
Sodium hyaluronate	Skin-conditioning agent - miscellaneous
Glucosamine HCl	pH adjuster
Algae extract	Skin-conditioning agent - emollient, Skin-conditioning agent - miscellaneous
Yeast extract	No recorded use, although often used in cosmetics. Possible antioxidant properties
Saccharide isomerate	Skin-conditioning agent - humectant
Camellia sinensis leaf extract	Antimicrobial, light stabilizer, Skin-conditioning agent - miscellaneous, Skin-conditioning agent - humectant, Skin-conditioning agent - emollient
Nelumbo nucifera flower extract	Skin-conditioning agent - miscellaneous
Saccharide hydrolysate	Skin-conditioning agent - humectant
Magnesium aspartate	Skin-conditioning agent - miscellaneous
Glycine	Humectant
Alanine	Skin-conditioning agent - miscellaneous
Creatine	Skin-conditioning agent - miscellaneous
Polymethylsilsesquioxane	Opacifying agent
Silica dimethyl silylate	Anticaking agent, bulking agent, viscosity increasing agent-nonaqueous
Silica Silylate	Bulking agent, skin conditioning agent-emollient

Vinyl dimethicone/methicone silsequioxane	Viscosity increasing agent - nonaqueous
Dimethicone/vinyl dimethicone crosspolymer	Viscosity increasing agent - nonaqueous
Urea	Skin conditioning agent - humectant
Ethylhexylglycerin	Skin conditioning agent - miscellaneous
Hexylene glycol	Fragrance, solvent
Caprylyl glycol	Skin conditioning agent - emollient
Sorbic acid	Preservative
Potassium sorbate	Preservative
Propylene glycol	Skin conditioning agent - humectant, skin conditioning agent - miscellaneous
Sodium citrate	pH adjuster
Phenoxyethanol	Preservative

## A.2 Hair Styling Products

<b>OSIS Dust it Mattifying Powder by Schwarzkopf</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Silica Silylate	Hydrophobic powder phase
VP/ VA co polymer	Inhibit moisture absorption by formation of film, therefore maintain hair styling
Sodium Benzoate	Preservative

<b>Done.n.Dusted by NAK</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Silica Silylate	Bulking agent, Hydrophobic powder to form marble shell
PVP/VA copolymer	Binder and film former
Citric acid	Chelating agent, pH adjuster
Sodium benzoate	Preservative
Parfum	Fragrance
Limonene	Fragrance
Lilial	Fragrance
Coumarin	Fragrance

<b>Tecniart Texture Dust by L'Oreal</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Glycerin	humectant
Silica silylate	Bulking agent, Hydrophobic powder to form marble shell
Sodium benzoate	Preservative
Phenethyl alcohol	Preservative
Potassium sorbate	Preservative
Citric acid	Chelating agent, pH adjuster
Ethylhexylglycerin	Skin-conditioning agent – miscellaneous
PEG-90 glycerides	Binder, humectant
Maltodextrin	Binder, film former, hair conditioning agent
Gossypium Herbaceum/ Cotton extract	Skin-conditioning agent - miscellaneous

<b>Tecniart Super Dust by L'Oreal</b>	
<b>COMPONENT</b>	<b>USE</b>
Silica silylate	Bulking agent, Hydrophobic powder to form marble shell
Water	Liquid phase
Glycerin	humectant
Alcohol Denat.	Cosmetic astringent, fragrance
VP/VA copolymer	Binder and film former
Citric acid	Chelating agent, pH adjuster
Sodium Benzoate	Preservative
Potassium Sorbate	Preservative

<b>Stardust by Instant Rockstar</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Silica Silylate	Bulking agent, Hydrophobic powder to form marble shell
Alcohol	Antibacterial
Glycerin	humectant
VP/ VA co polymer	Inhibit moisture absorption by formation of film, therefore maintain hair styling
Sodium Benzoate	Preservative

<b>Volume Powder by Schwarzkopf</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Silica Silylate	Hydrophobic powder to form marble shell
Sodium Benzoate	Preservative
Citric acid	Chelating agent, pH adjuster
Octylacriamide/Acrylates/ Butylaminoethyl methacrylate copolymer	Film former, hair fixative

<b>Got 2b Powder'ful by Schwarzkopf</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Silica Silylate	Hydrophobic powder to form marble shell
Sodium Benzoate	Preservative
Citric acid	Chelating agent, pH adjuster
Octylacriamide/Acrylates/ Butylaminoethyl methacrylate copolymer	Film former, hair fixative

<b>Big sexy hair Powder Play by Sexy Hair Concepts</b>	
<b>COMPONENT</b>	<b>USE</b>
Water	Liquid phase
Propylene glycol	Fragrance, humectant, viscosity decreasing agent
Silica silylate	Hydrophobic powder to form marble shell
Euterpe oleracea pulp oil	Skin conditioning agent - occlusive
Oryza sativa (rice) bran oil	Anti-static agent, skin conditioning agent - miscellaneous and occlusive
Passiflora Edulis seed oil	Skin conditioning agent - emollient and occlusive
Sodium benzoate	Preservative

### **Nomenclature**

- Skin-conditioning agent – emollient: Ingredients that act as lubricant on the skin surface. These give the skin a soft and smooth appearance
- Skin-conditioning agent – miscellaneous: Ingredients that enhance the appearance of dry or damaged skin. Restores the suppleness of skin.
- Skin-conditioning agent – occlusive: Ingredient which slow loss of water from the skin by forming a barrier on the skin’s surface.
- Humectant: Slows the moisture loss from product
- Opacifying agent: Reduces the transparency of the product. Often used in foundations to hid flaws of the skin.

## References

1. Ash, M. and Ash, I., Handbook of cosmetic and personal care additives. 2nd ed. ed. Vol. 1. 2002, Endicott, NY: Synapse Information resources, Inc.

**B**

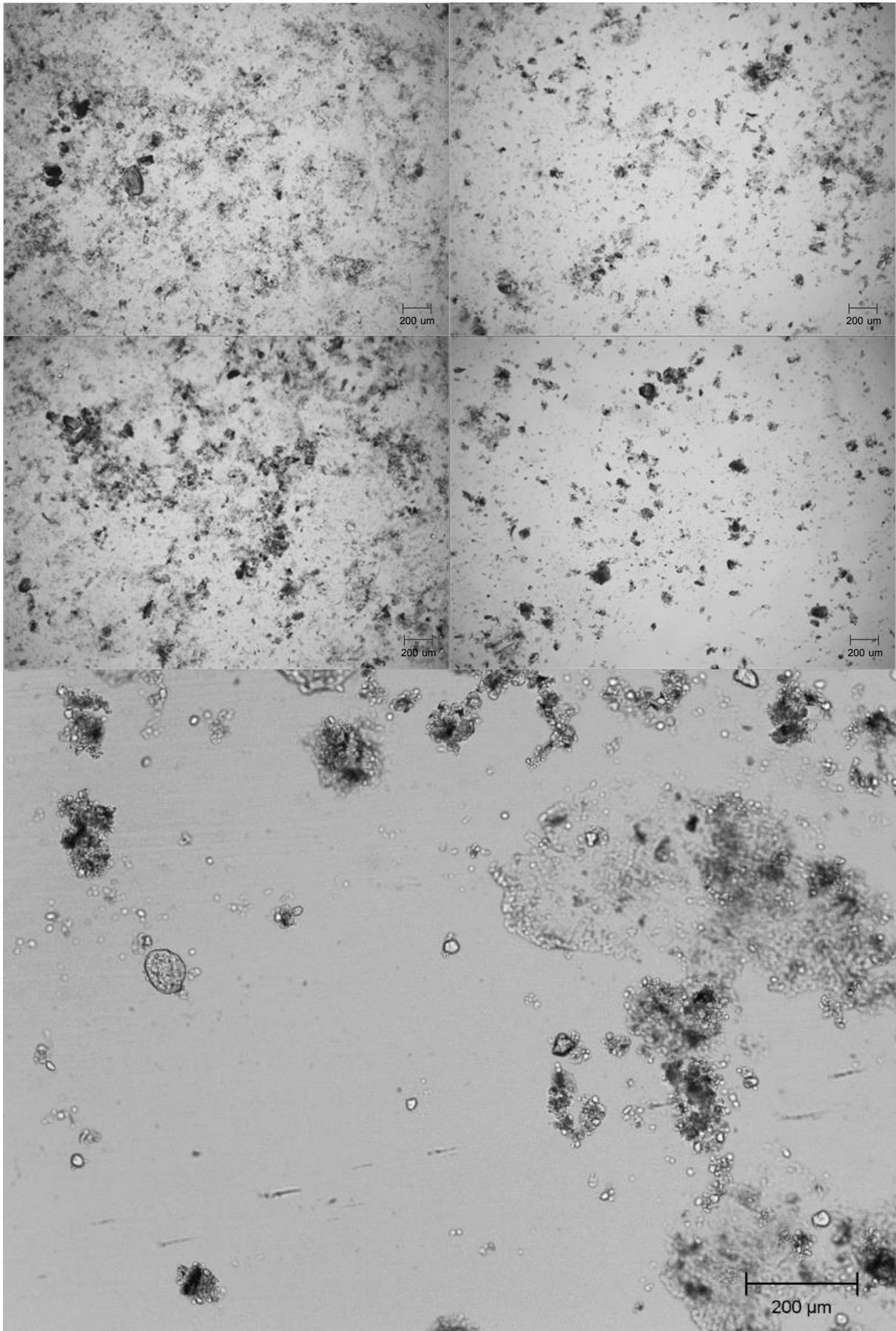
Appendix B



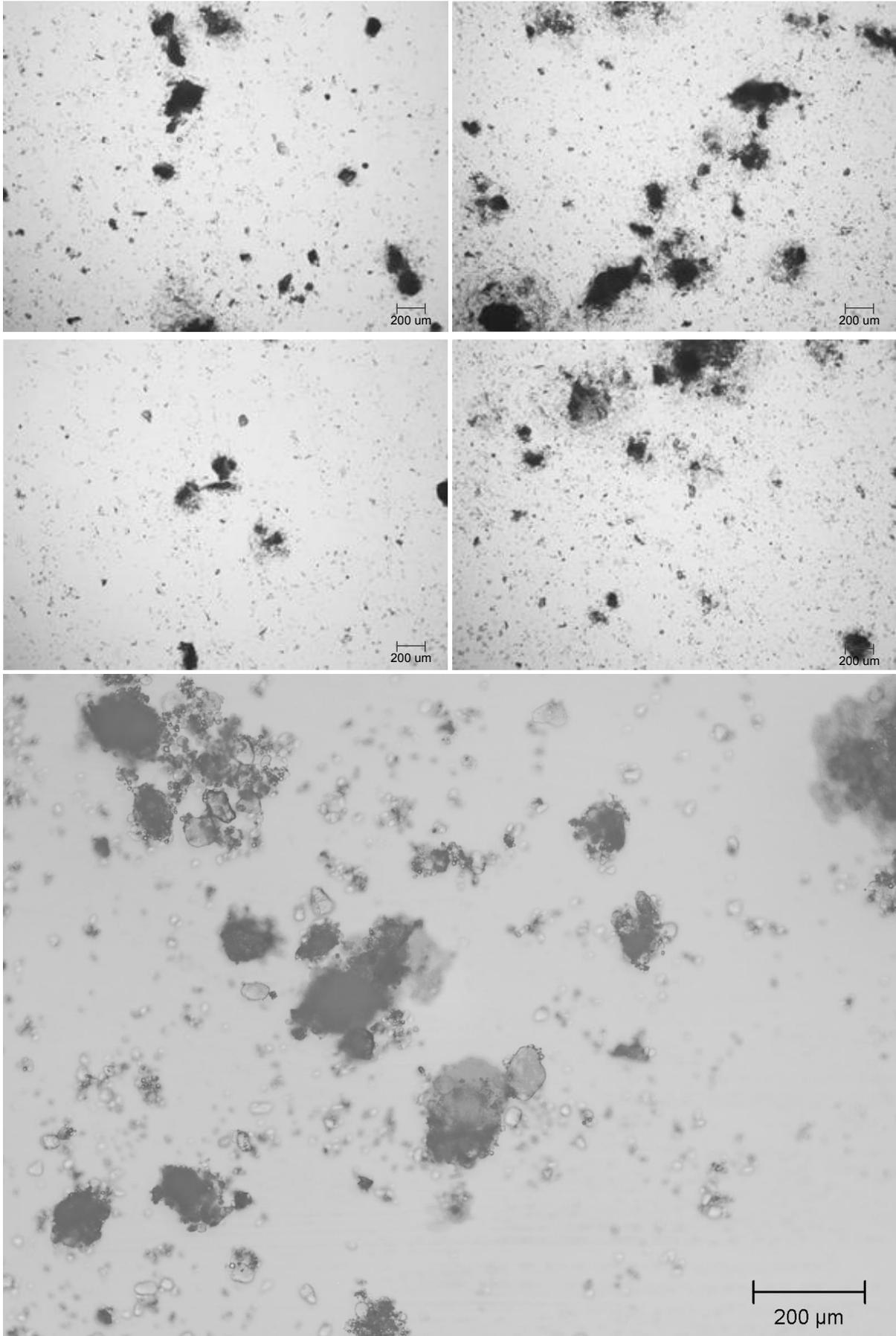
## **Appendix B: Raw Images of Commercial Product**

The appearance of the different samples were characterised using an optical microscope (Olympus BX-60, Spot imaging Solutions, US). Images for each sample were taken using an external snake lighting system and Spot Insight QE camera with a resolution of 72 pixels/inch.

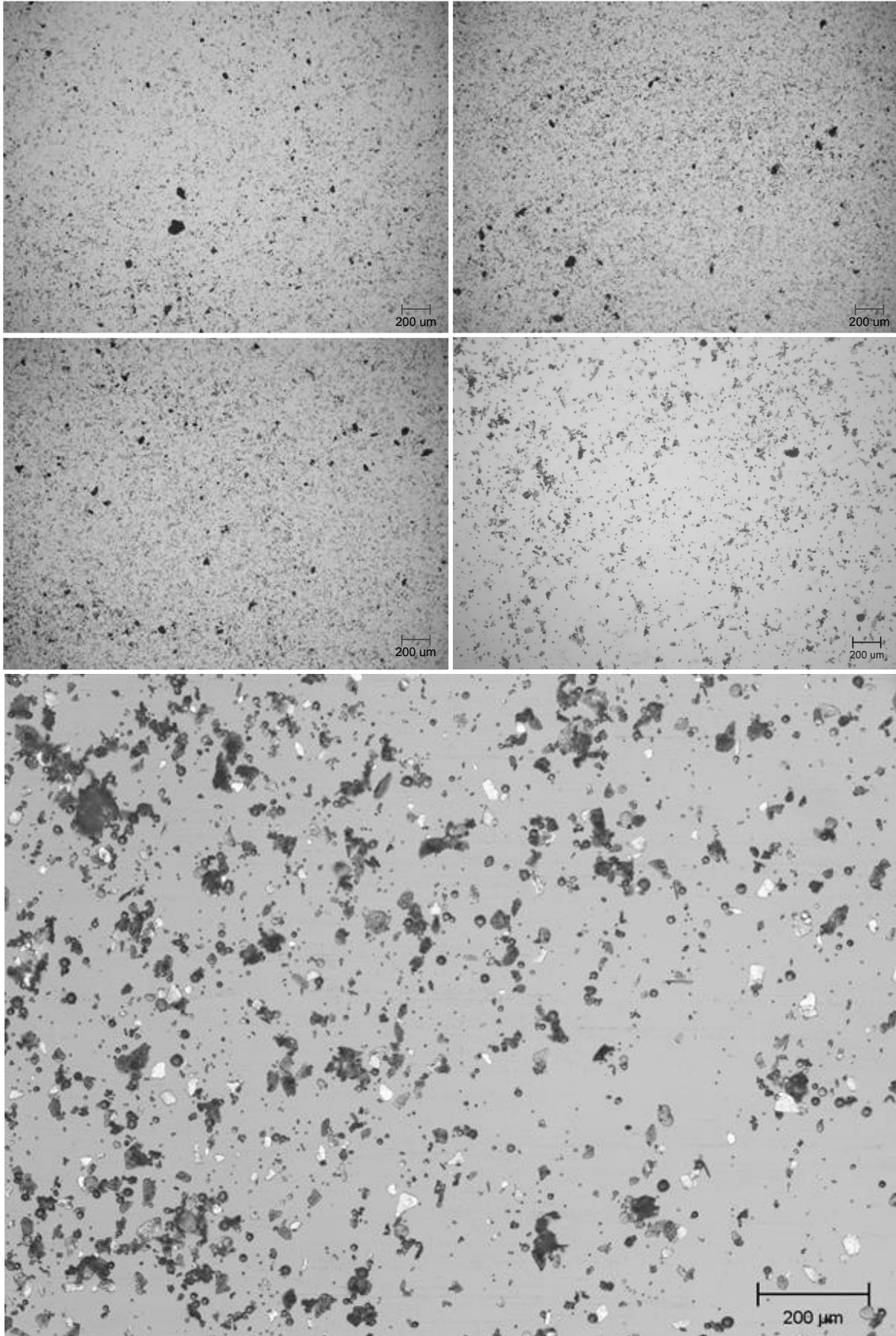
**Christian Dior IOD Aqua Powder Aquatique**



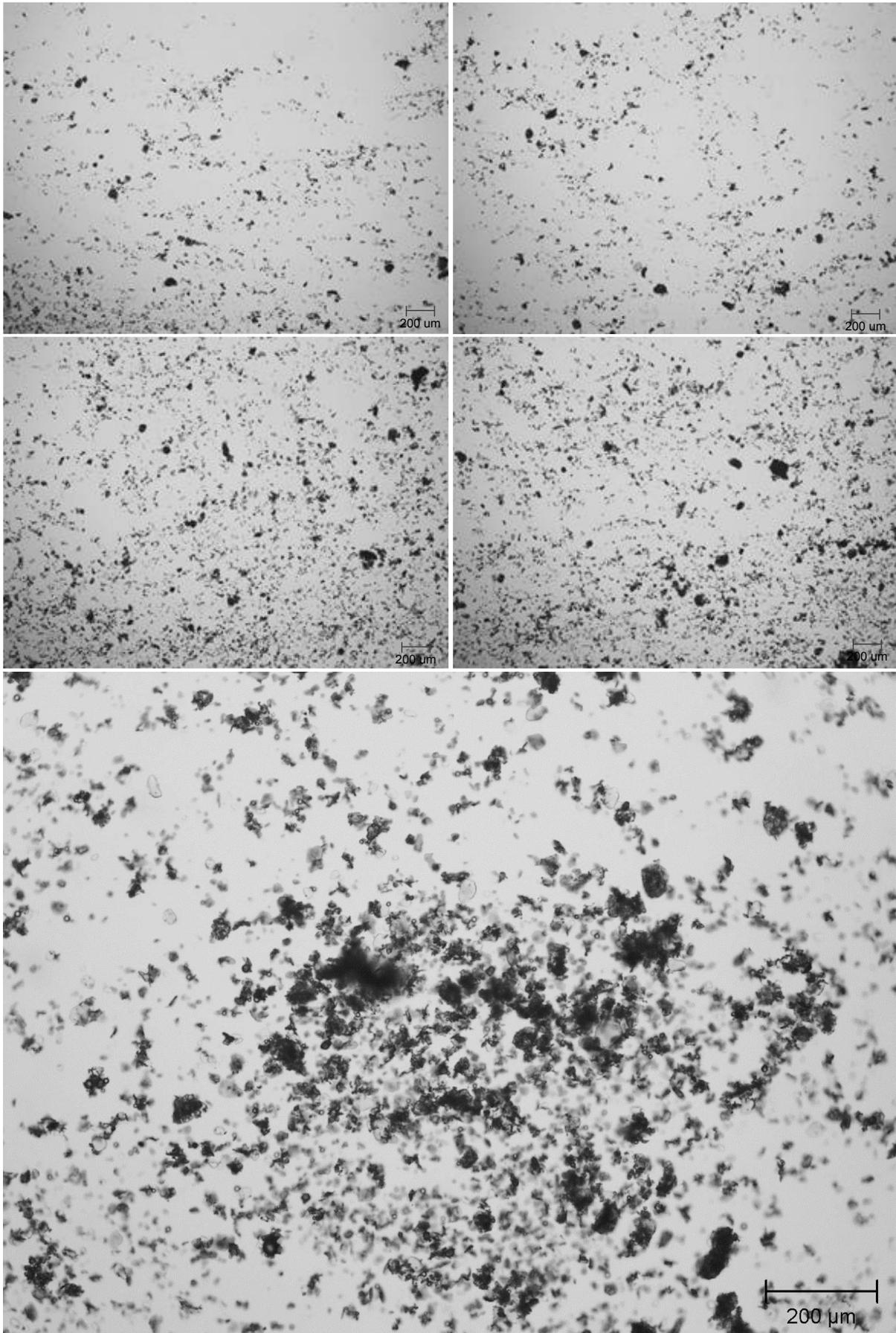
**Dermalogica® MAP-15 regenerator™**



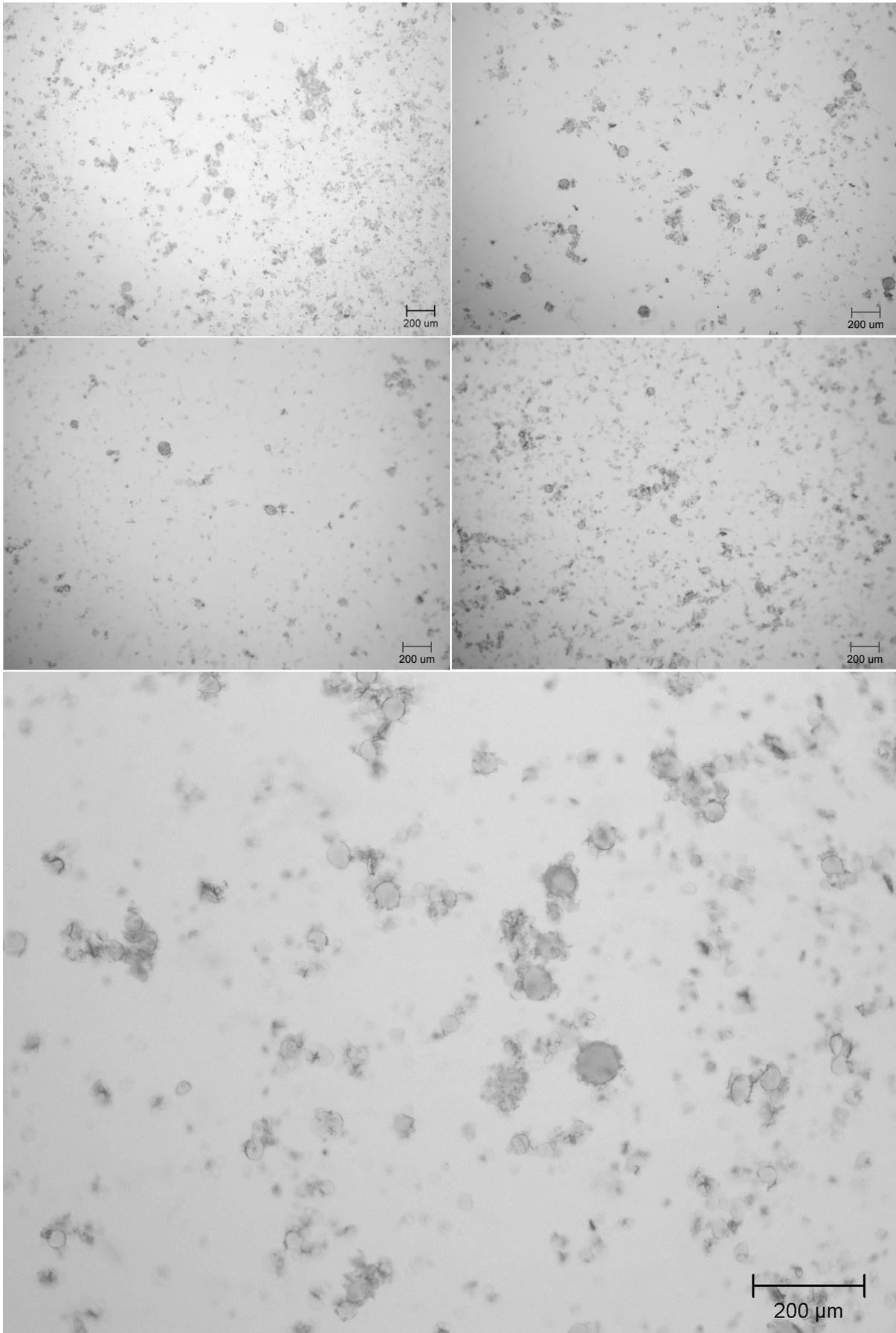
**Prescriptives Magic Liquid Powder**



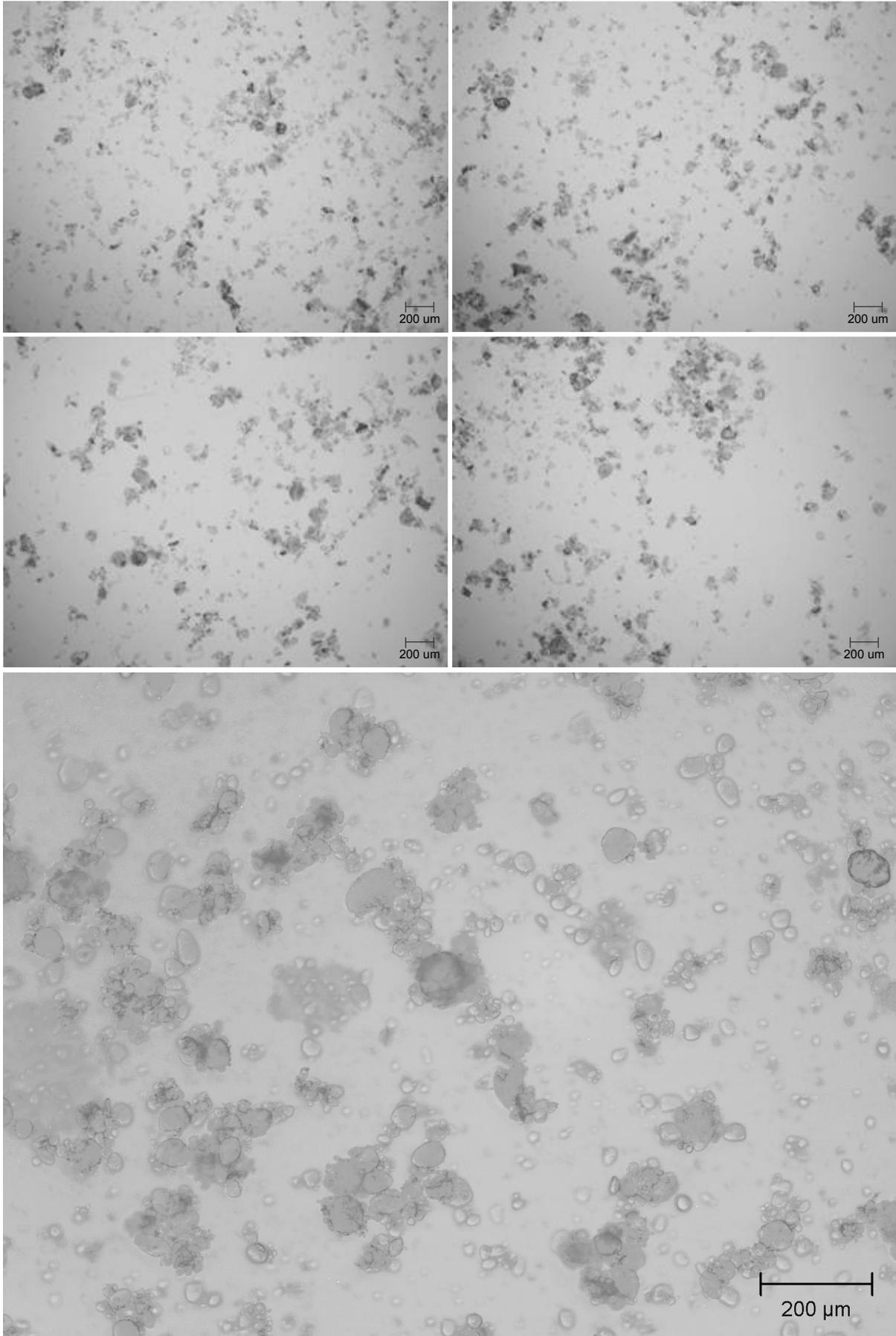
**Physicians Formula Aqua Powder**



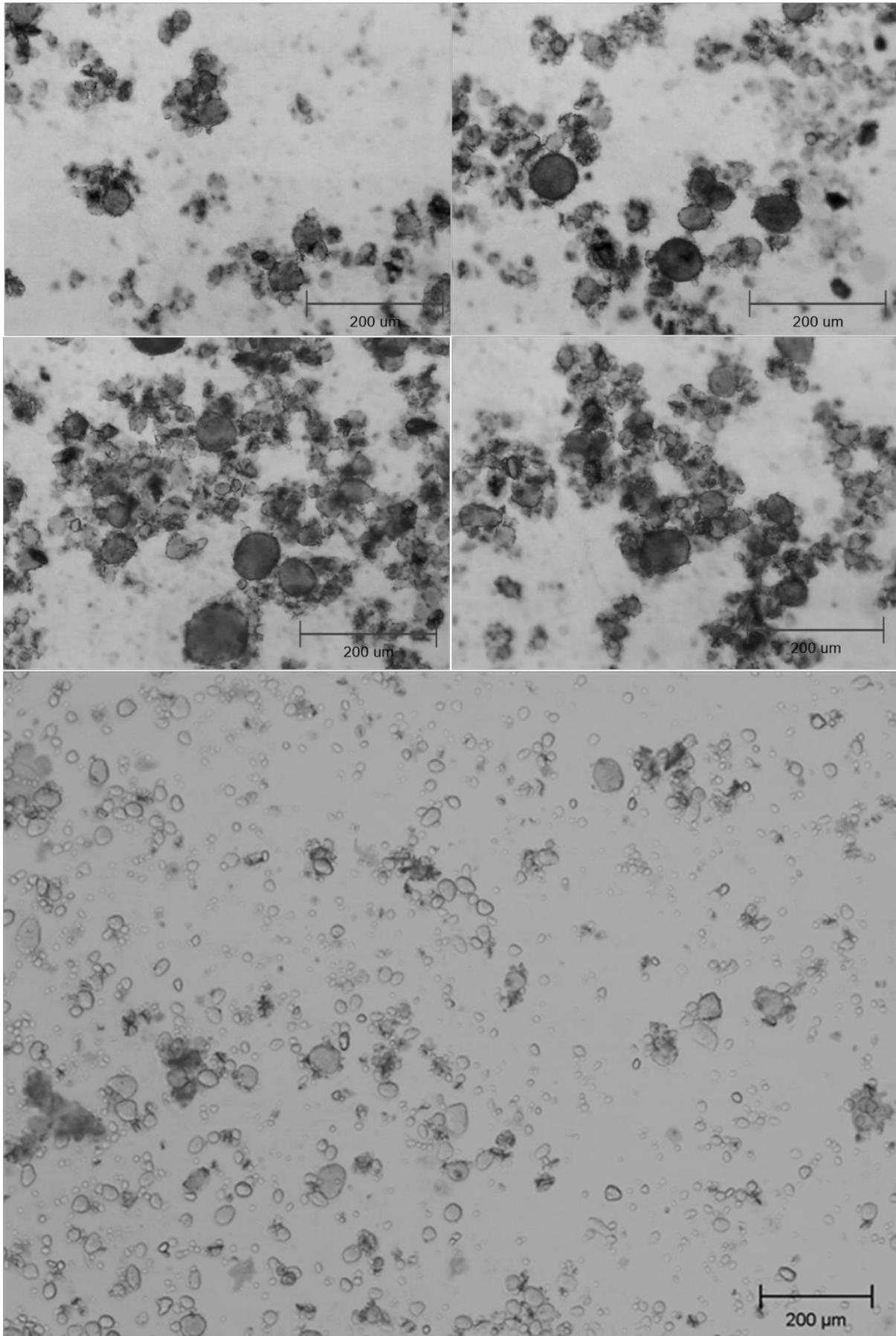
**Schwarzkopf OSIS+ Dust it Mattifying Powder**



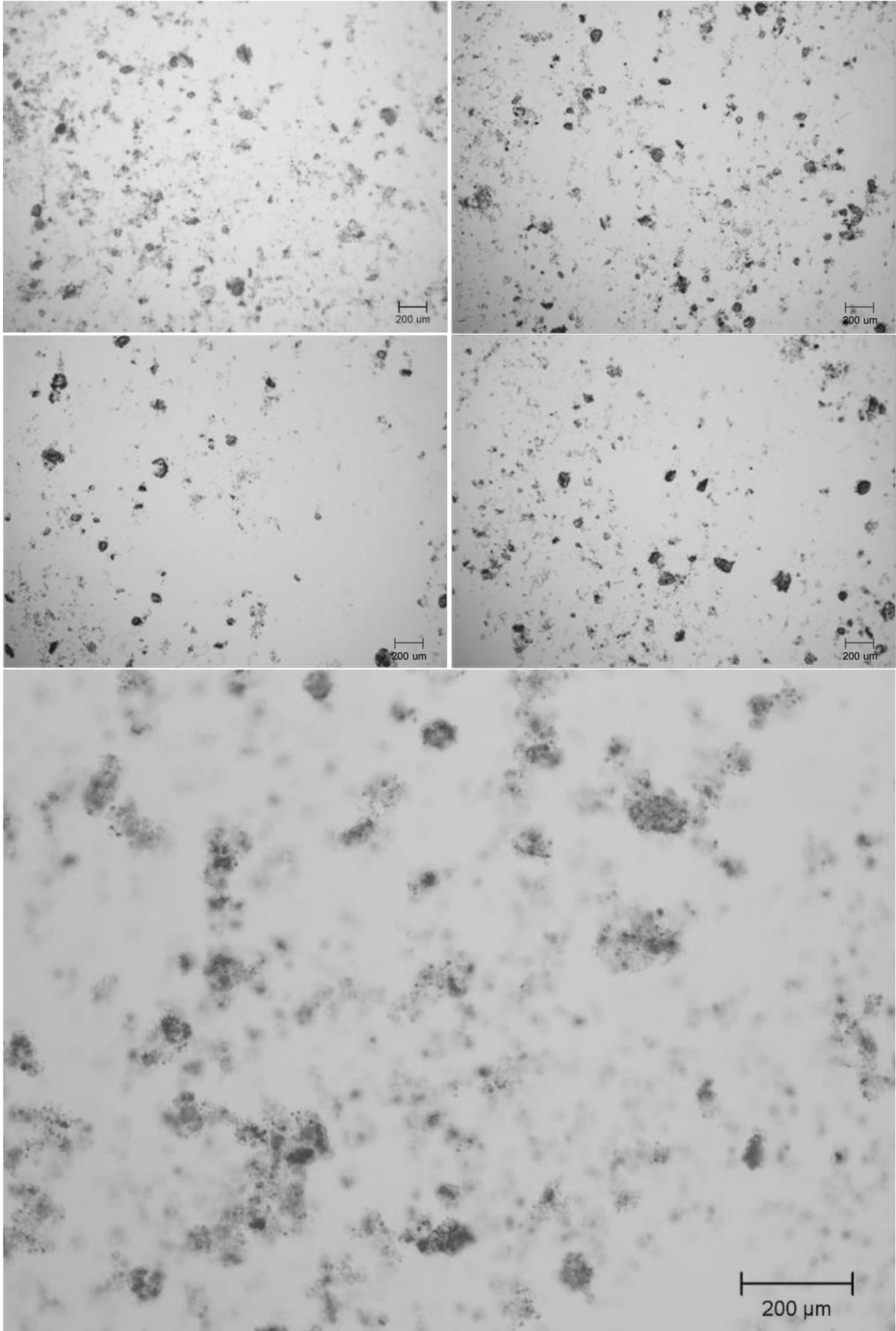
**Schwarzkopf Volume Powder**



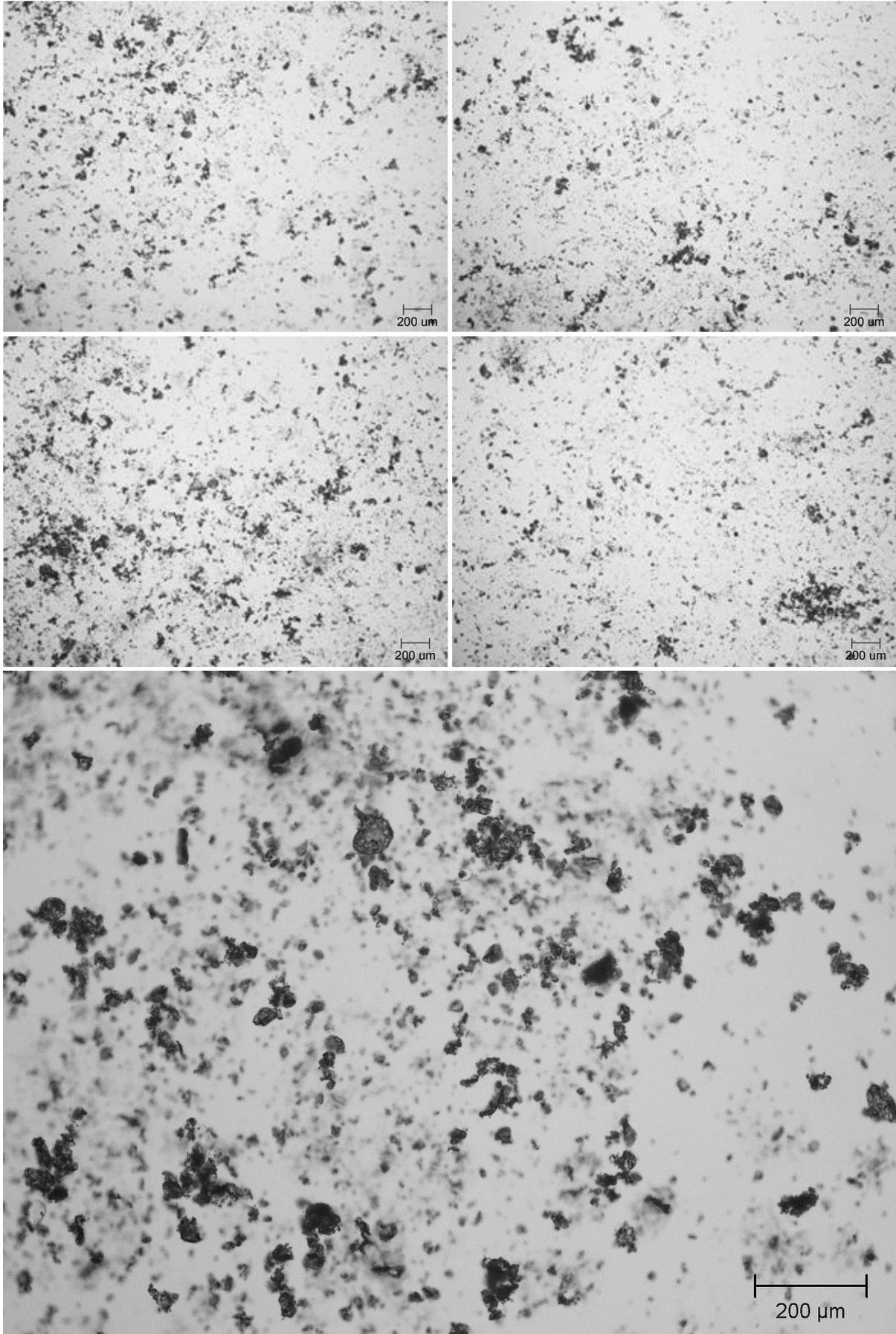
Schwarzkopf Got 2b powder'ful



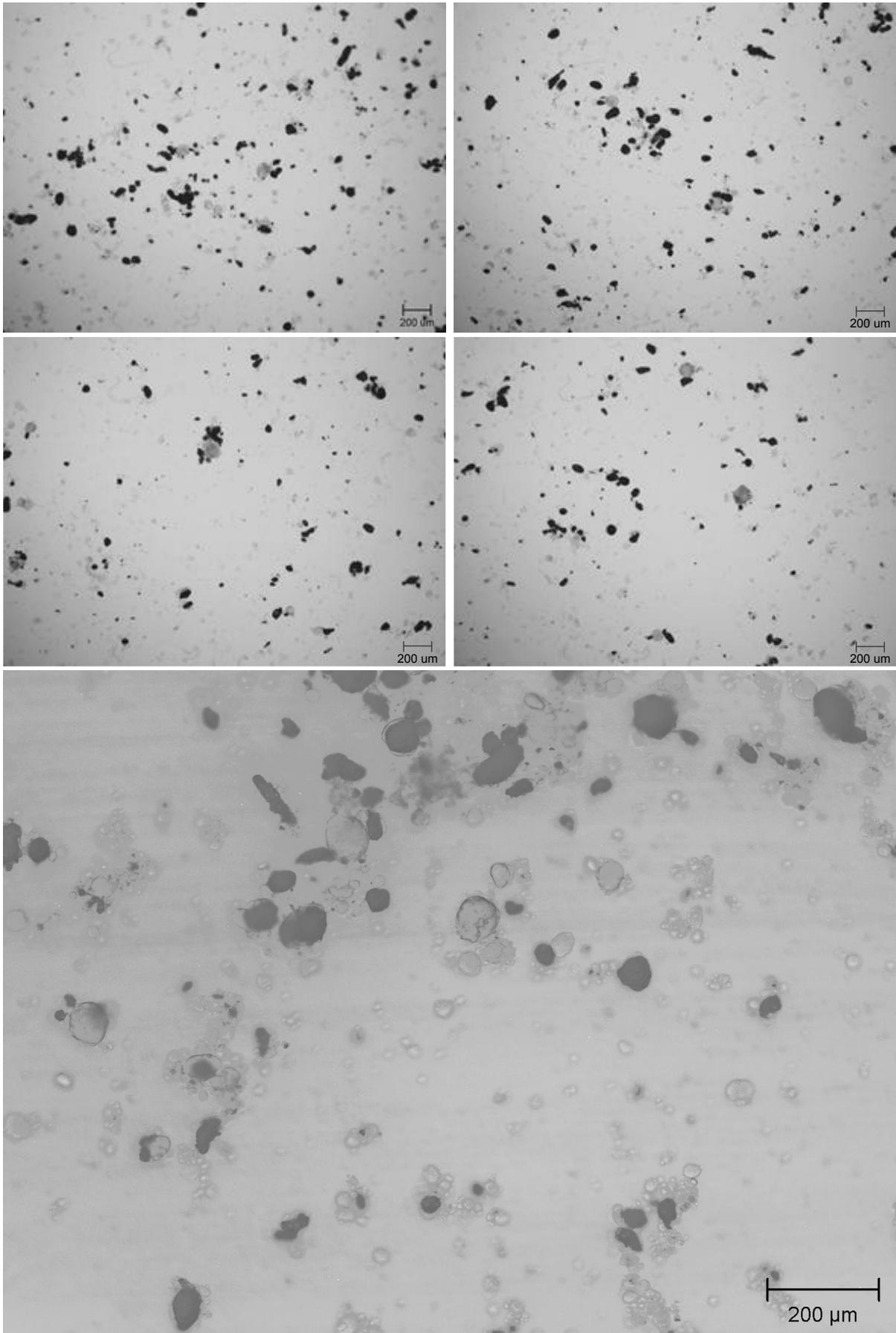
**Instant Rockstar Stardust**



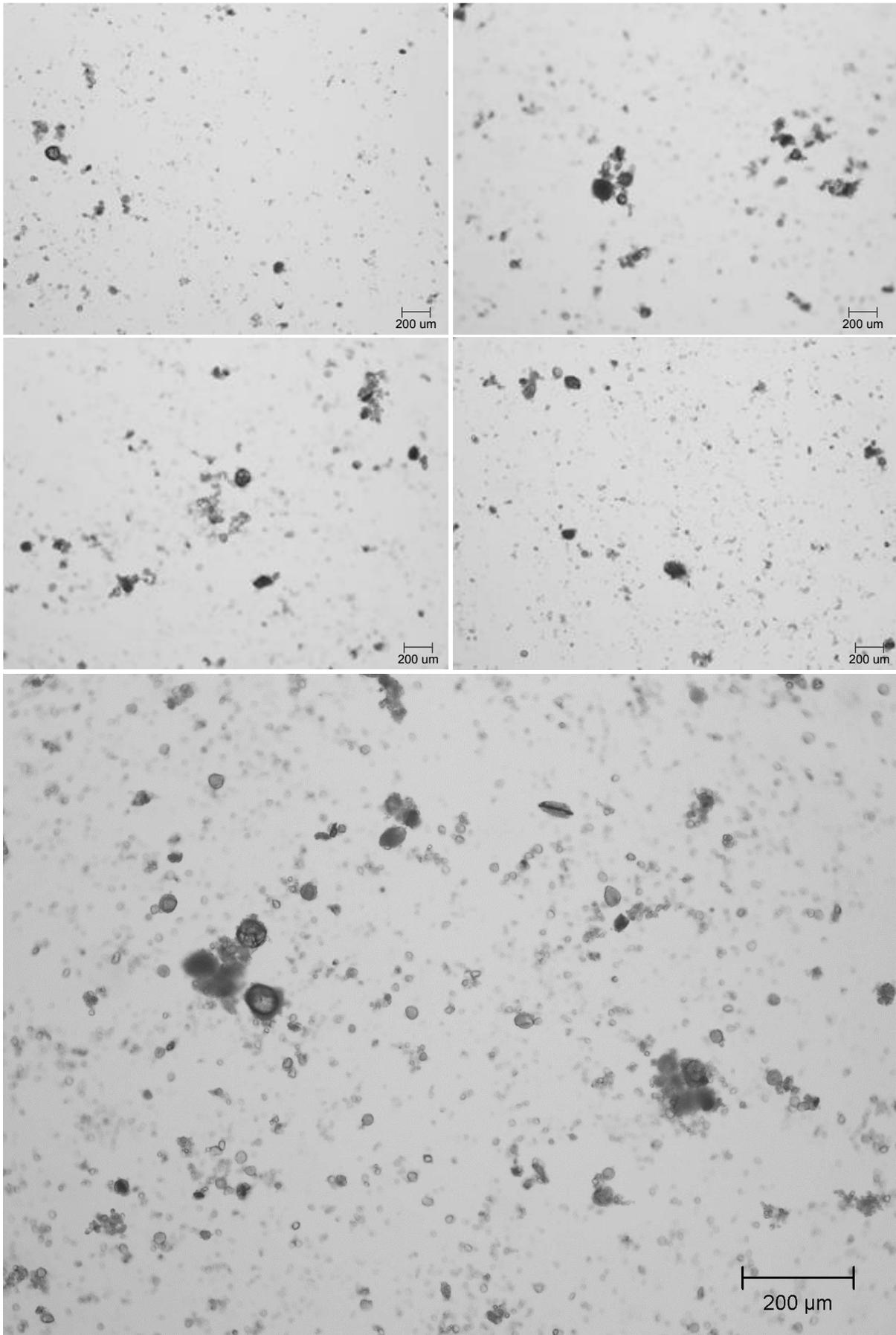
**L'Oreal Tecniart Texture Dust**



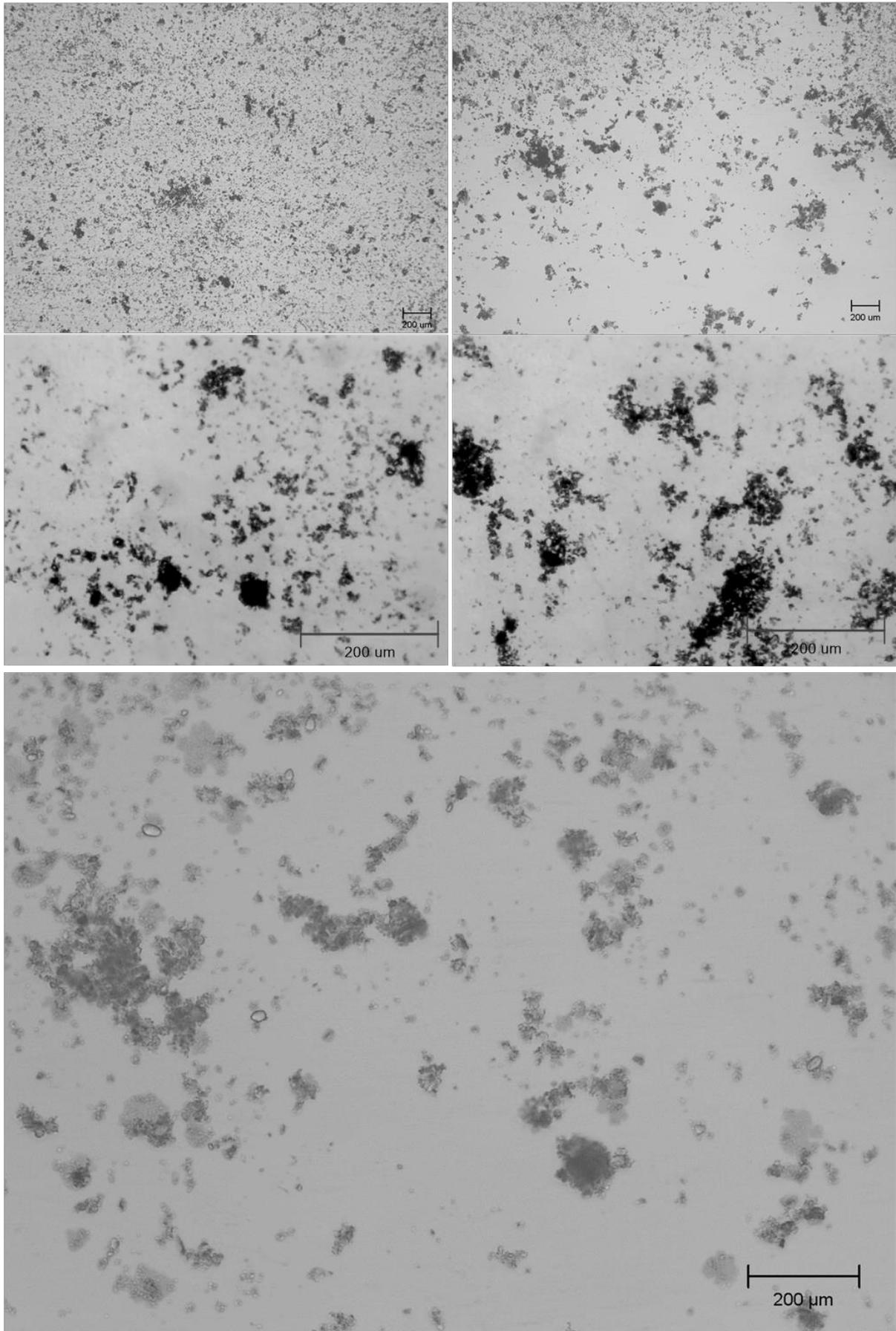
**L'Oreal Tecniart Super Dust**



**Nak done.n.dusted**



**Sexy hair concepts Big Sexy Hair Powder**





C

Appendix C

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## Appendix C: Moisture Content Raw Data

The moisture content of the commercial liquid marble samples was determined by drying approximately 0.1 g samples at 105°C and weighing them every 24 hours until no significant change in weight could be observed, usually within  $\pm 0.001$  g. The Following section provides the raw weighing data used to calculate moisture content.

### C.1 Foundation Products

**Table C-I: Raw data for changing weight over time of Foundation Products**

	<b>Trial 1</b>	<b>Trial 2</b>
<b>Weight of Petri Dish (g)</b>		
1. Dior IOD	30.4355	32.5080
2. Aqua powder	31.3495	30.3584
3. MAP_15	30.5180	31.2150
<b>Weight of Petri Dish + Sample: Before drying (g)</b>		
4. Dior IOD	30.5314	32.6236
5. Aqua powder	31.4870	30.5192
6. MAP_15	30.6123	31.3111
<b>Weight of Petri Dish + Sample: 24h drying (g)</b>		
1. Dior IOD	30.4386	32.5223
2. Aqua powder	31.4522	30.4763
3. MAP_15	30.5379	31.2336
<b>Weight of Petri Dish + Sample: 48h drying (g)</b>		
1. Dior IOD	30.4338	32.5213
2. Aqua powder	31.4479	30.4832
3. MAP_15	30.5370	31.2328
<b>Weight of Petri Dish + Sample: 72h drying (g)</b>		
1. Dior IOD	30.4364	32.5203
2. Aqua powder	31.4476	30.4762
3. MAP_15	30.5373	31.2320
<b>Weight of Petri Dish + Sample: 96h drying (g)</b>		
1. Dior IOD	30.4359	32.5196
2. Aqua powder	31.4479	30.4749
3. MAP_15	30.5355	31.2333
<b>Percentage Moisture Content (%)</b>		
1. Dior IOD	99.58	89.97
2. Aqua powder	28.44	27.55
3. MAP_15	81.44	80.96

Table C-II: Average Moisture Content of Foundation Products

Powder	Moisture Content (% weight)
1. Dior IOD	94.8
2. Aqua powder	28.0
3. MAP_15	81.2
4. Prescriptives Magic	60.1

## C.2 Hair Styling Products

Table C-III: Raw Data for changing weight over time of Hair Styling Products

	Trial 1	Trial 2
<b>Weight of Petri Dish (g)</b>		
1. OSIS Dust It Mattifying Powder	30.5191	31.2160
2. Instant rockstar star dust	31.3528	30.5769
3. Volume Powder	32.5085	45.8615
4. Tecniart texture dust	31.3513	32.3739
5. Tecniart super dust	29.3694	32.5477
6. Nak done.n.dusted	30.5747	30.8464
<b>Weight of Petri Dish + Sample: Before drying (g)</b>		
1. OSIS Dust It Mattifying Powder	30.6258	31.3250
2. Instant rockstar star dust	31.4466	30.6705
3. Volume Powder	32.6092	46.0126
4. Tecniart texture dust	31.4908	32.5264
5. Tecniart super dust	29.4520	32.6810
6. Nak done.n.dusted	30.6930	30.9787
<b>Weight of Petri Dish + Sample: 24h drying (g)</b>		
1. OSIS Dust It Mattifying Powder	30.5393	31.2439
2. Instant rockstar star dust	31.3705	30.6011
3. Volume Powder	32.5327	45.9025
4. Tecniart texture dust	31.3543	32.3799
5. Tecniart super dust	29.4058	32.5999
6. Nak done.n.dusted	30.6464	30.9240
<b>Weight of Petri Dish + Sample: 48h drying (g)</b>		
1. OSIS Dust It Mattifying Powder	30.5420	31.2456
2. Instant rockstar star dust	31.3700	30.5999
3. Volume Powder	32.5294	45.9031
4. Tecniart texture dust	31.3523	32.3804
5. Tecniart super dust	29.4033	32.6015
6. Nak done.n.dusted	30.6447	30.9287
<b>Weight of Petri Dish + Sample: 72h drying (g)</b>		
1. OSIS Dust It Mattifying Powder	30.5408	31.2434
2. Instant rockstar star dust	31.3763	30.5935
3. Volume Powder	32.5283	45.9007

4. Tecniart texture dust	31.3526	32.3783
5. Tecniart super dust	29.4039	32.5999
6. Nak done.n.dusted	30.6446	30.9124
<b>Weight of Petri Dish + Sample: 96h drying (g)</b>		
1. OSIS Dust It Mattifying Powder	30.5433	31.2404
2. Instant rockstar star dust	31.3748	30.5921
3. Volume Powder	32.5271	45.9000
4. Tecniart texture dust	31.3530	32.3780
5. Tecniart super dust	29.4034	32.5995
6. Nak done.n.dusted	30.6446	30.9067
<b>Percentage moisture content (%)</b>		
1. OSIS Dust It Mattifying Powder	77.32	77.61
2. Instant rockstar star dust	76.55	83.76
3. Volume Powder	81.53	74.52
4. Tecniart texture dust	98.78	97.31
5. Tecniart super dust	58.84	61.14
6. Nak done.n.dusted	40.91	54.42

Table C-IV: Average Moisture Content of Hair Styling Products

<b>Powder</b>	<b>Moisture Content (% weight)</b>
<b>1. OSIS Dust It Mattifying Powder</b>	77.5
<b>2. Instant rockstar star dust</b>	80.2
<b>3. Volume Powder</b>	78.0
<b>4. Tecniart texture dust</b>	98.1
<b>5. Tecniart super dust</b>	56.0
<b>6. Nak done.n.dusted</b>	47.7



D

Appendix D

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## Appendix D: Raw Particle Size Frequency Distribution Table

A series of 30 optical microscope images were taken and Image J was used to determine the particle sizes. The optical microscopy method minimises stress on the marbles and ensures the measured size of the liquid marbles is not compromised by shear forces which may cause marble rupture. The Feret's diameter was used to characterise the liquid marble size distribution. Particle size data was adjusted for liquid marbles by excluding particles smaller than 20  $\mu\text{m}$ , as most of the insoluble excipients are expected to have a particle size less than this.

**Table D-I: Frequency Distribution Table for Foundation Products**

Range ( $\mu\text{m}$ )	Frequency Distribution			
	Dior IOD	Aqua Powder	MAP_15	Prescriptives Magic
<b>0</b>	0.000	0.000	0.000	0.000
<b>20</b>	0.143	0.000	0.000	0.000
<b>60</b>	2.014	2.000	2.222	2.212
<b>100</b>	0.251	0.325	0.199	0.222
<b>140</b>	0.079	0.100	0.043	0.044
<b>180</b>	0.043	0.042	0.021	0.014
<b>220</b>	0.019	0.016	0.007	0.005
<b>260</b>	0.008	0.009	0.002	0.002
<b>300</b>	0.006	0.004	0.002	0.001
<b>340</b>	0.002	0.003	0.001	0.000
<b>380</b>	0.003	0.001	0.002	0.000
<b>420</b>	0.002	0.001	0.001	0.000

**Table D-II: Frequency Distribution Table for Hair Styling Products**

<b>Range (<math>\mu\text{m}</math>)</b>	<b>Frequency Distribution</b>					
	<b>OSIS+</b>	<b>Star dust</b>	<b>Volume powder</b>	<b>Texture dust</b>	<b>Super dust</b>	<b>NAK</b>
<b>0</b>	0.000	0.000	0.000	0.000	0.000	0.000
<b>20</b>	0.129	0.000	0.116	0.126	0.127	0.096
<b>60</b>	1.961	1.942	1.773	2.029	1.923	1.897
<b>100</b>	0.310	0.345	0.353	0.281	0.311	0.323
<b>140</b>	0.087	0.121	0.144	0.074	0.115	0.129
<b>180</b>	0.043	0.050	0.079	0.029	0.044	0.046
<b>220</b>	0.018	0.021	0.034	0.011	0.021	0.027
<b>260</b>	0.008	0.009	0.025	0.006	0.013	0.015
<b>300</b>	0.003	0.006	0.016	0.003	0.004	0.003
<b>340</b>	0.003	0.004	0.010	0.002	0.003	0.006
<b>380</b>	0.001	0.001	0.003	0.002	0.003	0.004
<b>420</b>	0.001	0.001	0.003	0.001	0.000	0.002

Table D-III: Calculated  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  values.

Product type	Product name and Company	$d_{10}$	$d_{50}$	$d_{90}$
Foundation Products	IOD Aqua Powder Aquatique by Christian Dior	23.5	42.5	65.5
	MAP-15 regenerator™ by Dermalogica®	24.5	42.5	65.0
	Magic Liquid Powder by Prescriptives*	23.5	42.5	65.5
	Aqua Powder by Physicians Formula	25.0	45.0	91.0
Hair Styling Products	OSIS Dust it Mattifying Powder by Schwarzkopf	24.0	44.0	89.0
	Stardust by Instant Rockstar	25.0	46.0	95.0
	Volume Powder by Schwarzkopf	24.5	47.0	118.0
	Tecniart Texture Dust by L'Oreal	23.5	43.5	82.0
	Tecniart Super dust by L'Oreal	24.0	44.5	94.0
	Nak done.n.dusted	24.5	45.5	97.0



**E**

Appendix E

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## Appendix E: Drying images of liquid marbles

A series of images of liquid marbles with and without a film former is taken using a SMZ stereo microscope with a 2MP Motic moticam camera at 10 minute intervals. A selected few images from each drying process are given below to give an indication of how the liquid marble dries through key stages in its overall survival time. Liquid marbles of 15  $\mu\text{L}$ , 30  $\mu\text{L}$  and 50  $\mu\text{L}$  of 0%, 2% and 5% (w/w) VP/VA copolymer solution was investigated. Height and width profile of the repeats are given.

### Imaging of marbles

#### Aerosil and water:

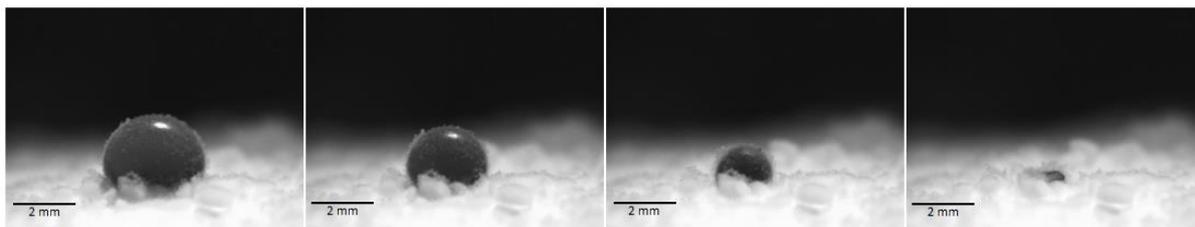


Figure E-I: Small Aerosil and water marble.

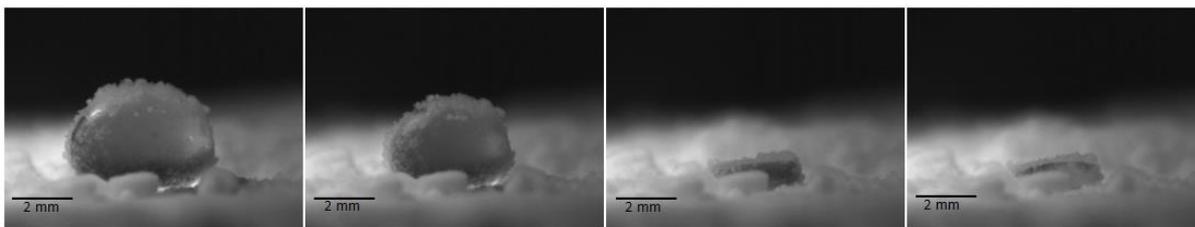


Figure E-II: Medium aerosil and water marble.

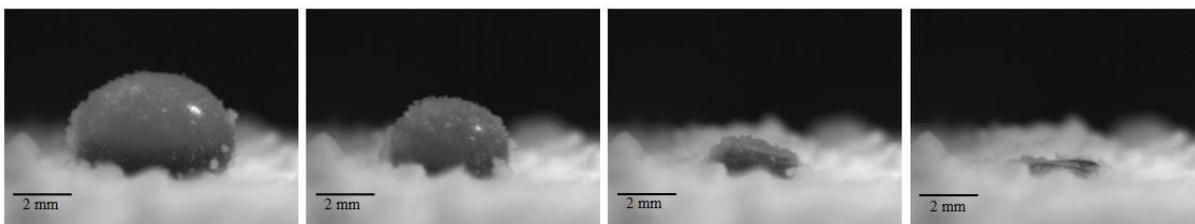
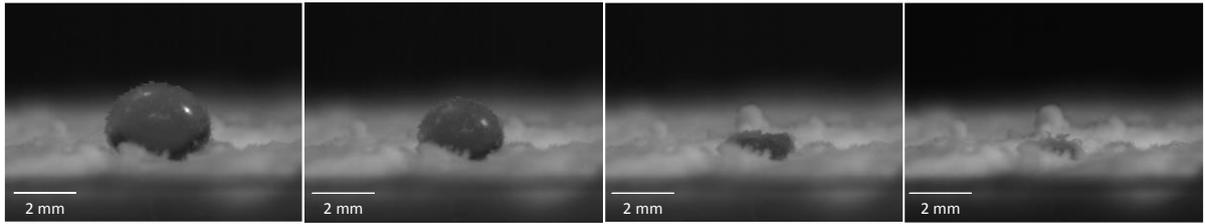
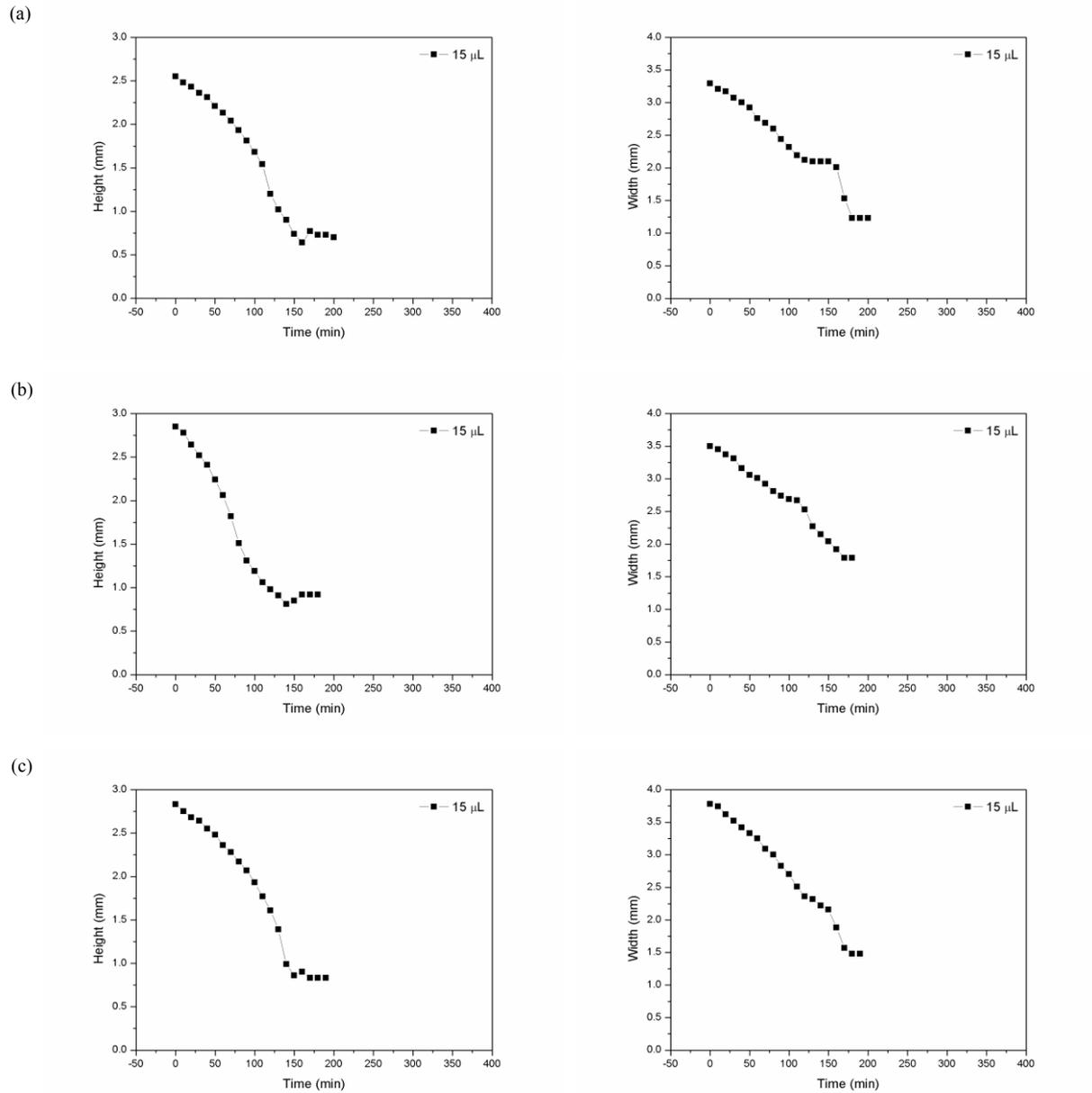


Figure E-III: Large aerosil and water marble.

**2% VP/VA copolymer**



**Figure E-IV: Small 2% copolymer marbles.**



**Figure E-V: Height and Width profiles of 15 µL 2% VP/VA copolymer liquid marbles a) trial 1 b) trial 2 and c) trial 3**

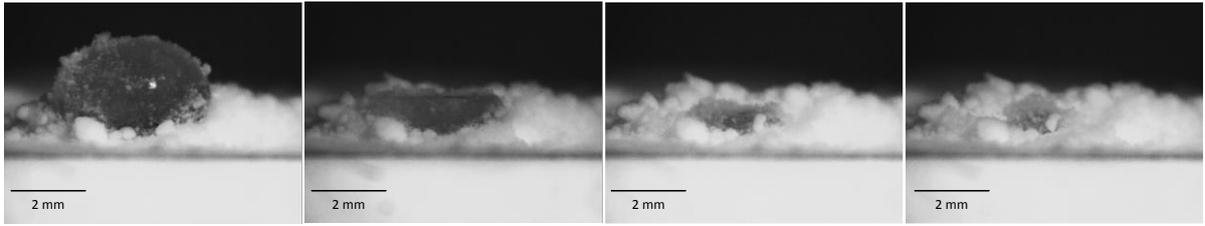


Figure E-VI: Medium 2% copolymer marbles.

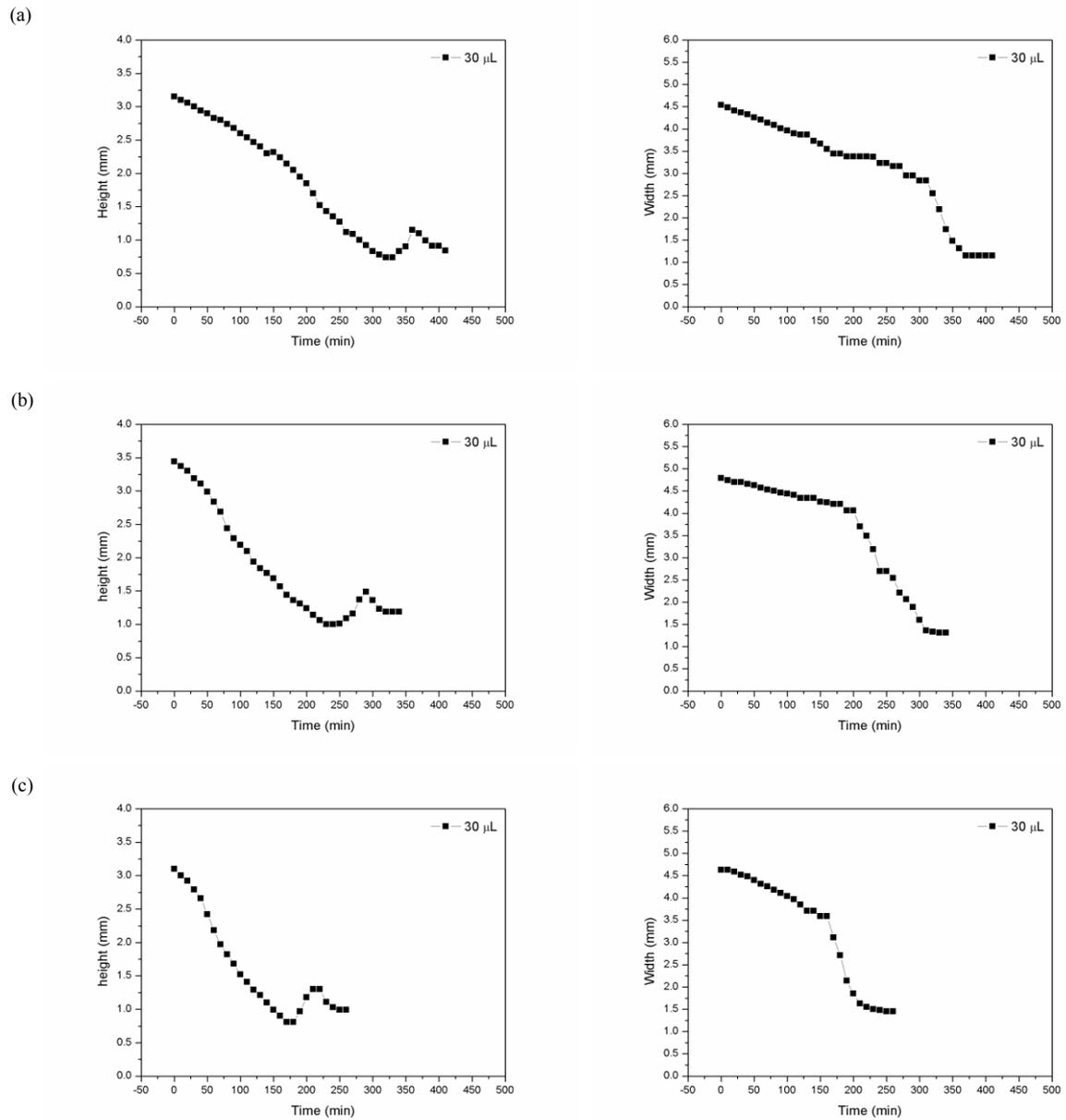


Figure E-VII: Height and Width profiles of 30  $\mu\text{l}$  2% VP/VA copolymer liquid marbles a) trial 1 b) trial 2 and c) trial 3

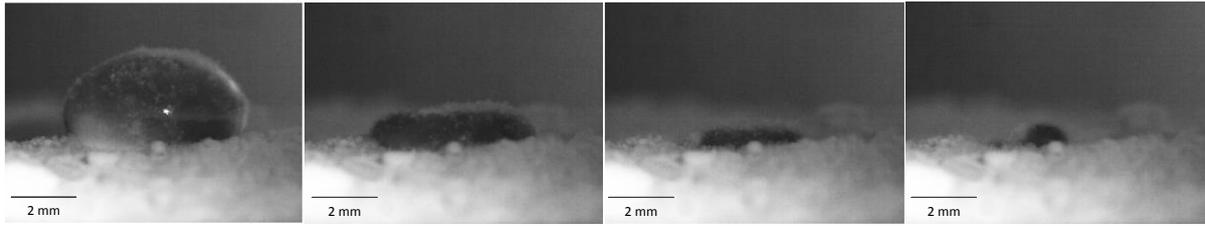


Figure E-VIII: Large 2% copolymer marble

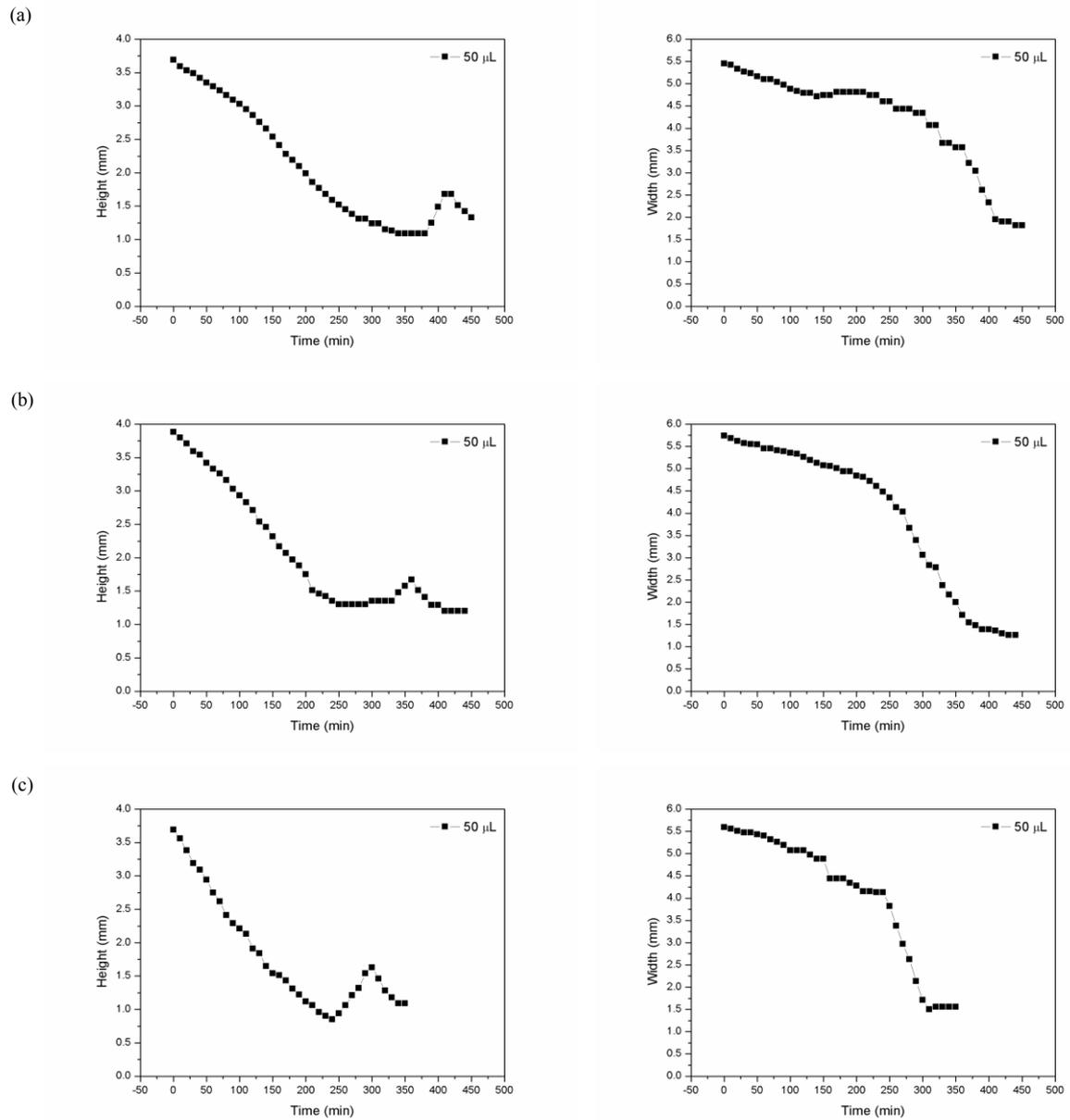


Figure E-IX: Height and Width profiles of 50  $\mu\text{L}$  2% VP/VA copolymer liquid marbles a) trial 1 b) trial 2 and c) trial 3

5% VP/VA copolymer

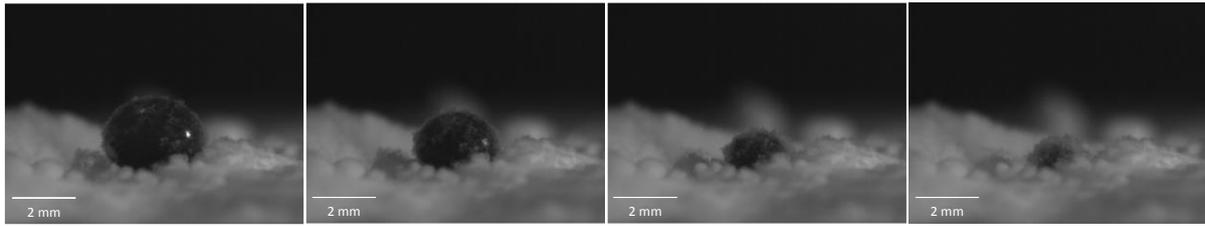


Figure E-X: Small 5% copolymer marble

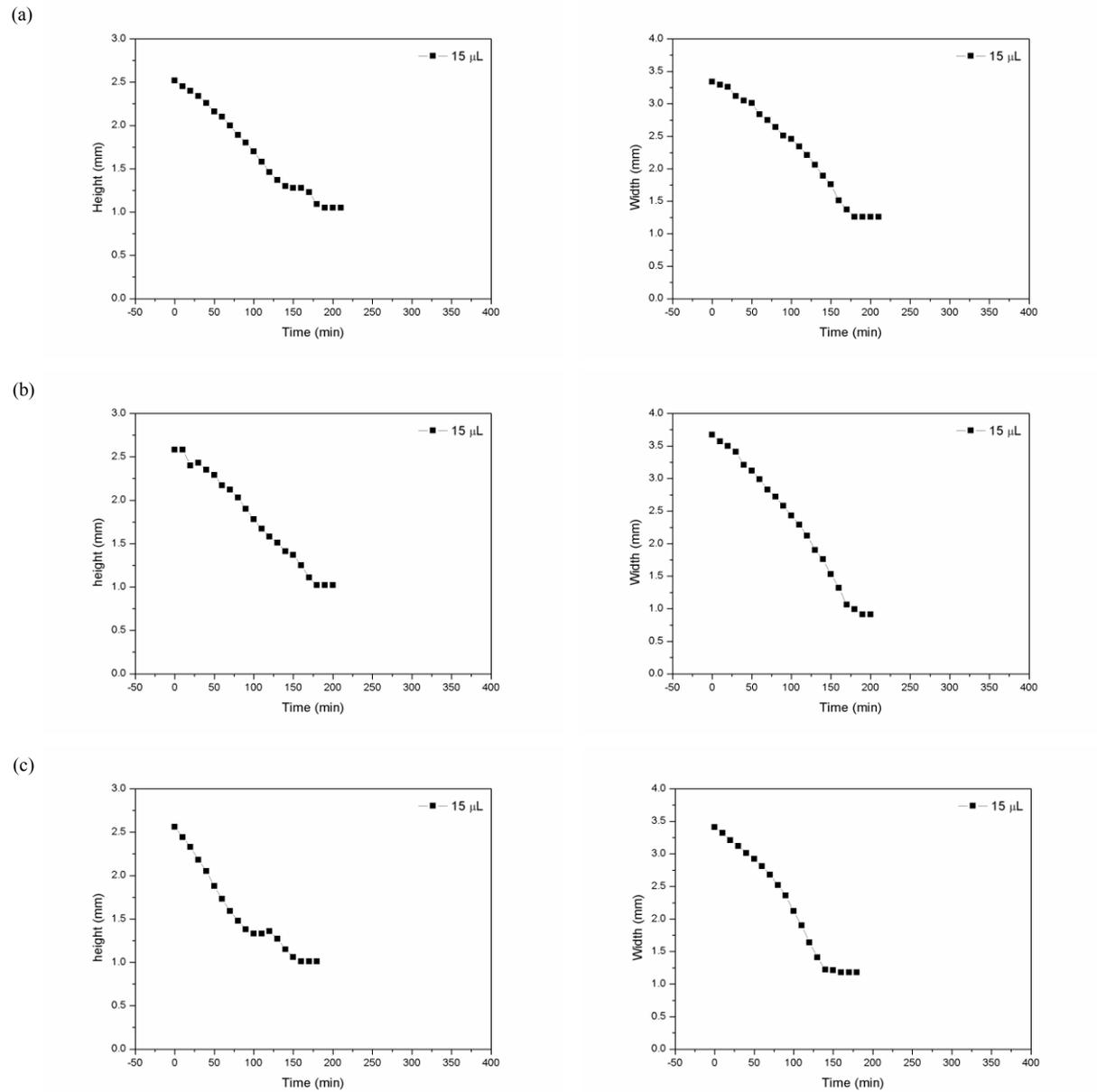


Figure E-XI: Height and Width profiles of 15  $\mu\text{L}$  5% VP/VA copolymer liquid marbles a) trial 1 b) trial 2 and c) trial 3

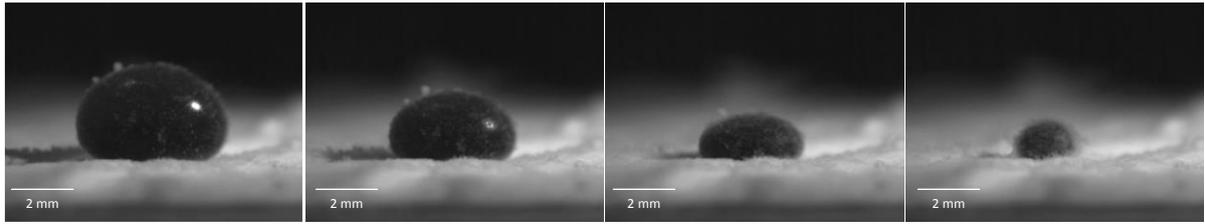


Figure E-XII: Medium 5% copolymer marble

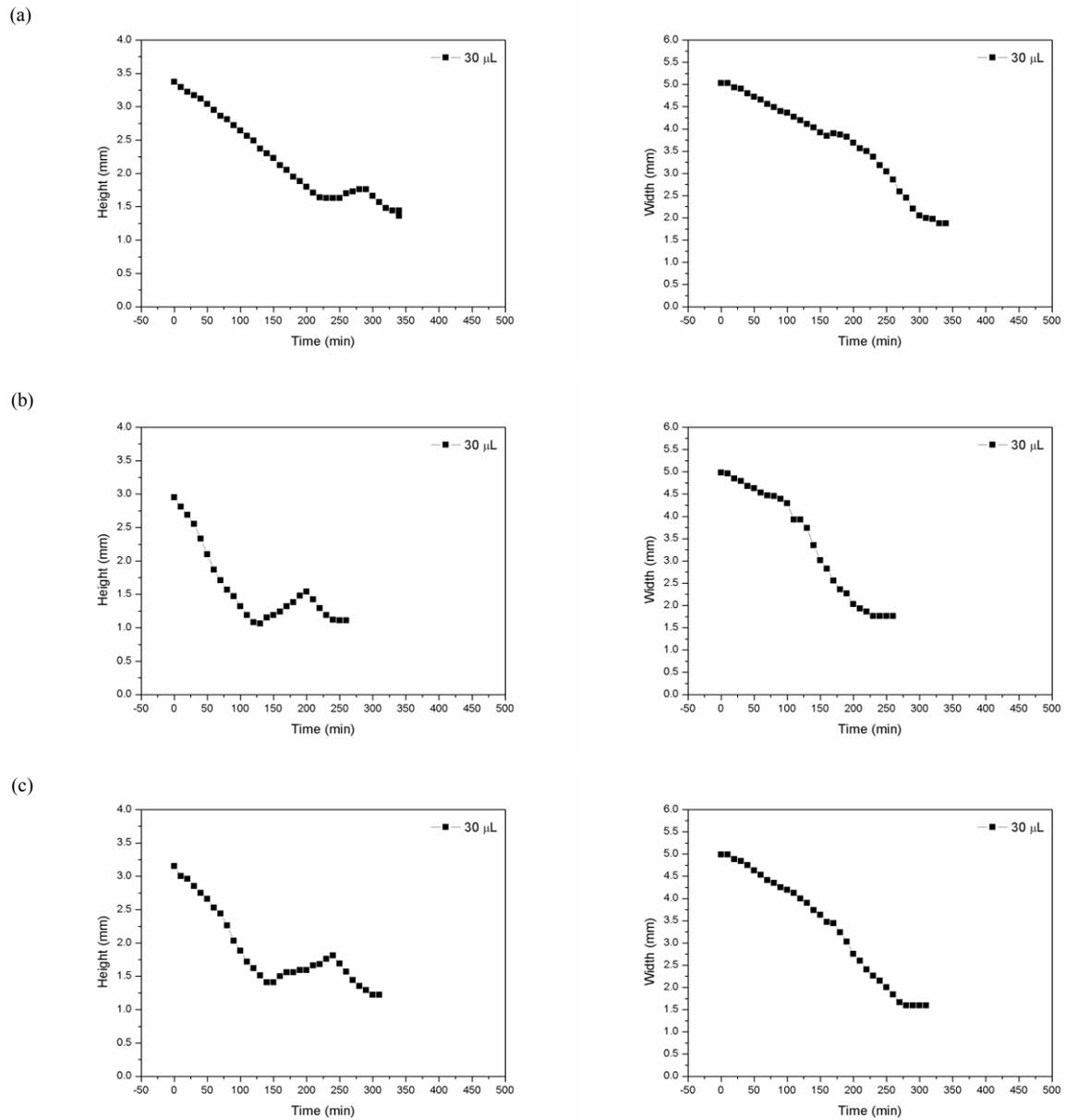
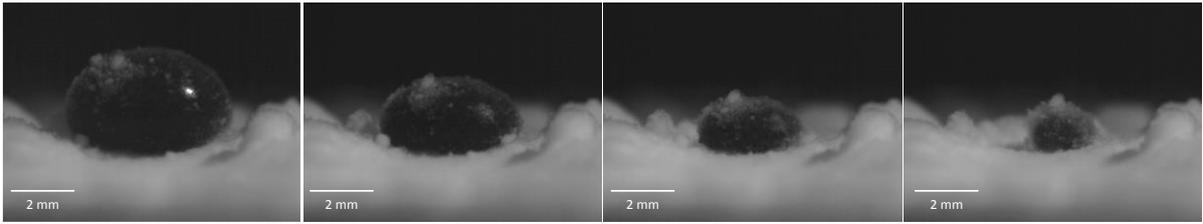
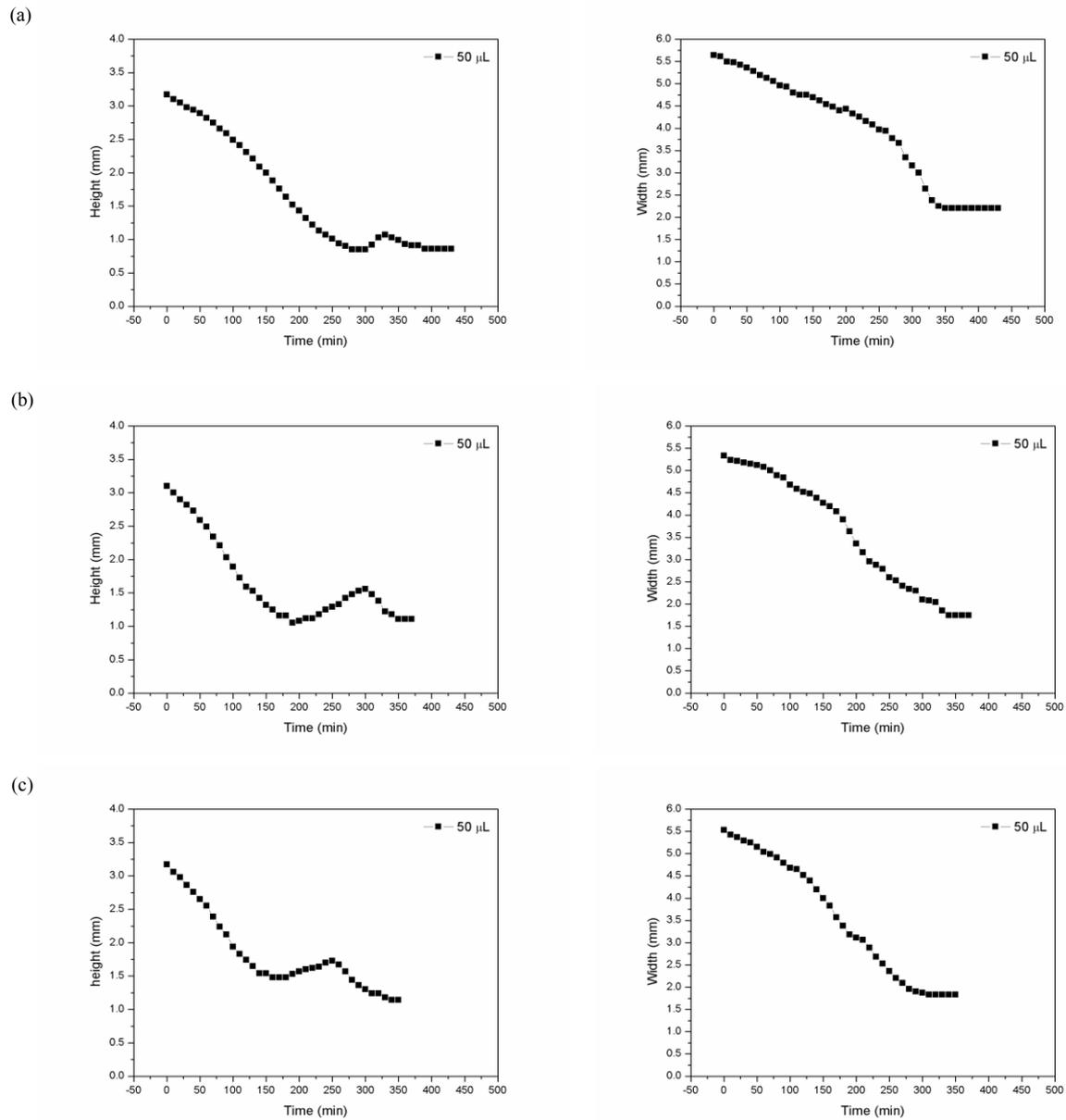


Figure E-XIII: Height and Width profiles of 30  $\mu\text{L}$  5% VP/VA copolymer liquid marbles a) trial 1 b) trial 2 and c) trial 3



**Figure E-XIV: Large 5% copolymer marble**



**Figure E-XV: Height and Width profiles of 50  $\mu$ l 5% VP/VA copolymer liquid marbles a) trial 1 b) trial 2 and c) trial 3**



**F**

Appendix F

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## Appendix F: Ohnesorge number, viscosity calculation and corresponding height graphs for repeated trials

The Ohnesorge number is used to describe the shape and rebound phenomenon of a drop impact on solid surface [1, 2]. It relates the viscous forces to the inertial and surface tension forces of the droplet and is described by equation 5.1.

$$Oh = \frac{\mu}{(\rho\gamma_{LV}R)^{0.5}} \quad (eq F. 1)$$

Where  $\rho$  = density of liquid

$\gamma_{LV}$  = surface tension at liquid vapour interface

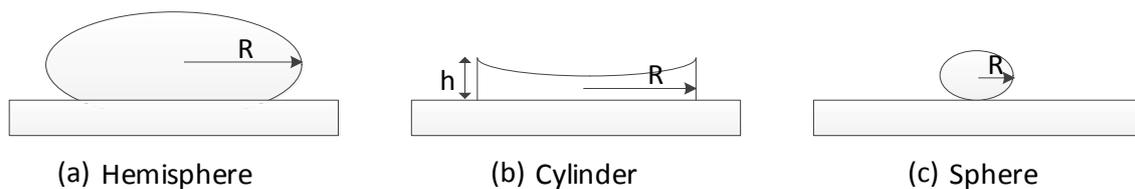
R = drop radius

$\mu$  = viscosity

To calculate the Ohnesorge number, the concentration of the marbles was required in order to extrapolate viscosity of the marbles throughout drying. Concentration of the copolymer solution could not be directly measured throughout the experiment; hence, it was derived using the concentration-volume law:

$$C_1V_1 = C_2V_2 \quad (eq F. 2)$$

Marble volume could not be measured directly due to the constantly changing shape during drying. Therefore basic estimations of liquid volume were obtained by modelling the marbles as three different shapes throughout the drying process. The three basic shapes of the marbles at various stages of drying and their corresponding shape for modelling is shown in Figure 5.1 below:



**Figure F-I: Diagram of general drying shapes and their corresponding shape for modelling (a) hemisphere (b) cylinder (c) sphere**

As such, the volumes of the marbles were estimated using the following calculations.

For the hemisphere stage, the volume is estimated by equation F.3. The hemisphere is mostly used to model the volume of medium and large marbles at the beginning of the drying process when the contact length with the powder surface is long.

$$V_{Hemisphere} = \frac{1}{2} \left( \frac{4}{3} \pi R^3 \right) \quad (eq F. 3)$$

Where R = radius of the marble measured from side to side of the liquid marble.

During some experiments, the contact line remains pinned and the marble collapses from the top resulting in a puddle like structure. This structure is estimated by equation F.4 below.

$$V_{cylinder} = \pi R^2 h \quad (eq F. 4)$$

Where R = radius of the cylinder/ marble.

h = height

For small marbles which always maintained a spherical structure and in cases where the marble rebounded back to a spherical structure for solutions with film formers; the marble volume was estimated using equation F.5.

$$V_{sphere} = \left( \frac{4}{3} \right) \pi R^3 \quad (eq F. 5)$$

Where R = radius of the marble

In this case, the radius is taken as the half width for consistency, as the height to width ratio should be close to one.

## F.1 Viscosity extrapolation and example Ohnesorge number calculation

### F.1.1: Viscosity extrapolation

Viscosity to concentration data was obtained from the Kollidon VA64 (VP/VA copolymer) handbook by BASF [3].

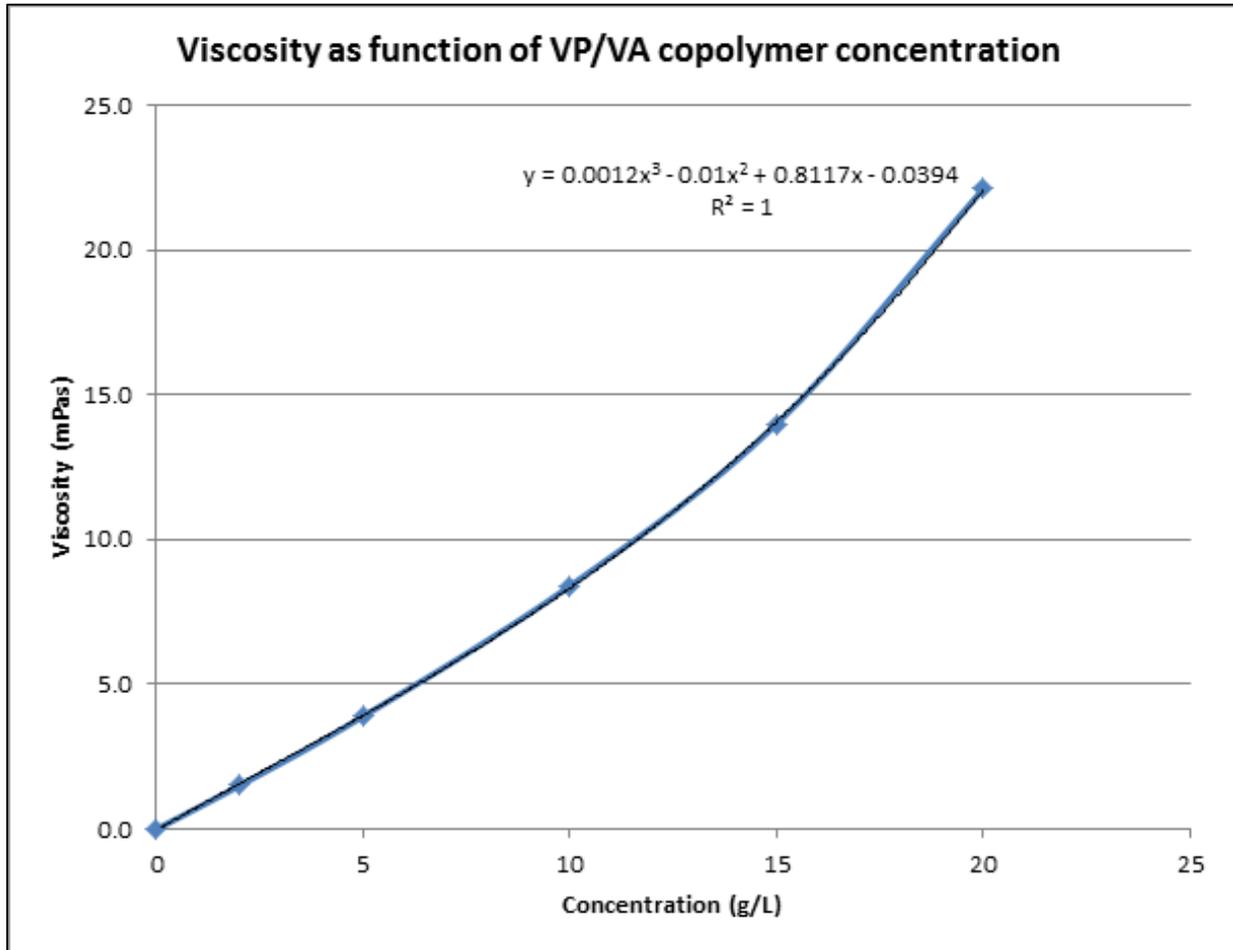


Figure F-II: Viscosity as a function of VP/VA copolymer concentration. Replicated from BASF handbook [3]

As the handbook only gives concentration up to 20 g/L, the polynomial trend line was verified by extrapolating the data through experimental data with the trend data given graphically in Figure F-III.

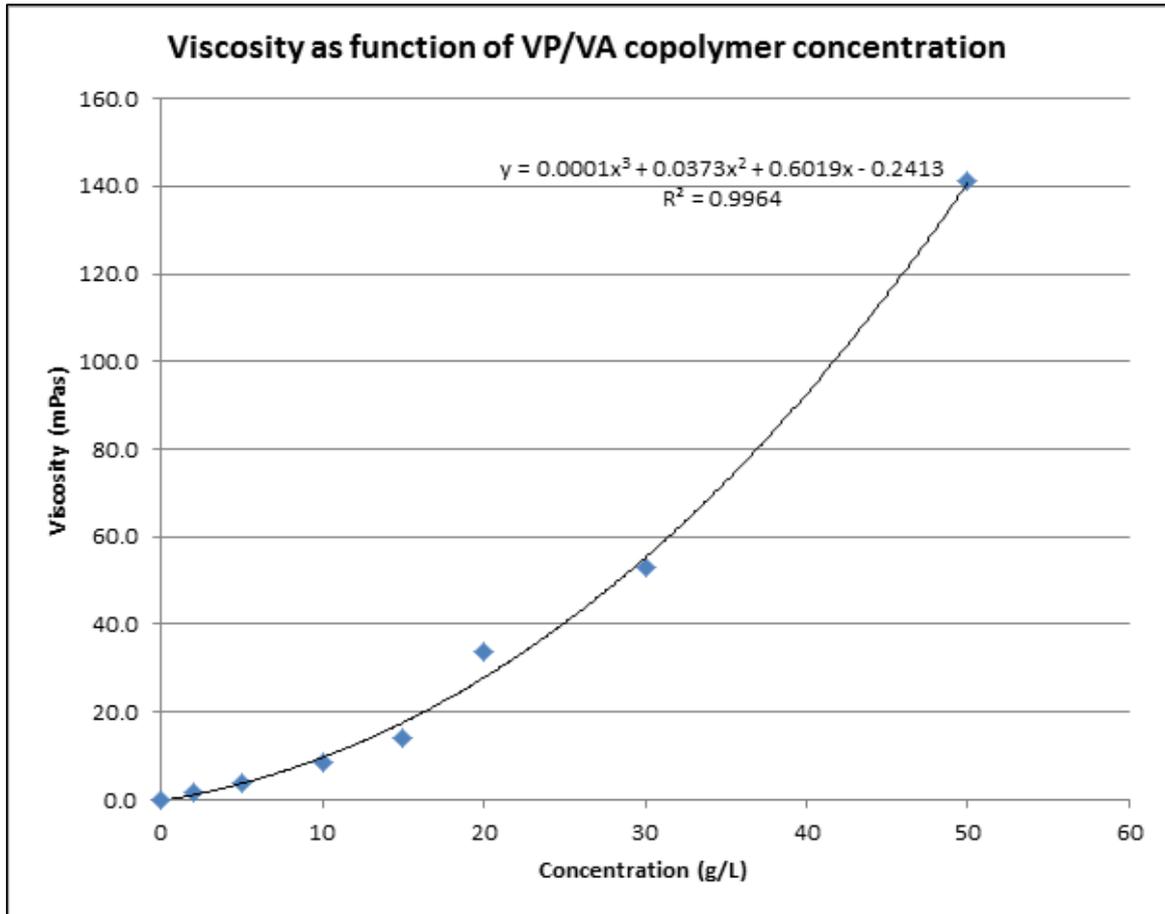


Figure F-III: Viscosity as a function of VP/VA copolymer concentration from experimental data

### F.1.2: Example Ohnesorge number calculation

The Ohnesorge number is made up of four different variables: viscosity ( $\mu$ ), density ( $\rho$ ), surface tension ( $\gamma_{LV}$ ) and radius ( $R$ ) (eq. F.1). Density and surface tension was determined previously for the different concentrations of copolymer solution. Surface tension was assumed to be constant for calculation purposes as increasing film former concentration did not show significant decrease in surface tension.

Using a 15  $\mu\text{L}$  2% VP/VA copolymer liquid marble as example, the Ohnesorge number was calculated accordingly.

Table F-I: Table of parameters for 2% VP/VA copolymer liquid marbles

Parameter	Value
Viscosity ( $\mu$ )	Viscosity (Pa.s)
Density ( $\rho$ )	998 $\text{kg/m}^3$
Surface tension ( $\gamma$ )	0.562 N/m
Radius ( $R$ )	Radius (m)

The height and width data of the liquid marble of interest is obtained through image analysis using Image J. Radius is defined as either half of the height or the width. An adjusted concentration is calculated based on a concentration volume correlation (eq F.2), with volume

estimates based on marble shape (eq F.3 –F.5). Using the adjusted concentration, the adjusted viscosity is obtained using the concentration – viscosity graph section F.1.1 Figure F.1 or extrapolated using the polynomial trend line. Ohnesorge (Oh) number is then calculated using the data.

For the 15 µL marble, the following data table is generated (Table F-II).

**Table F-II: Abstract of calculation table for 15 µL 2% VP/VA copolymer liquid marble**

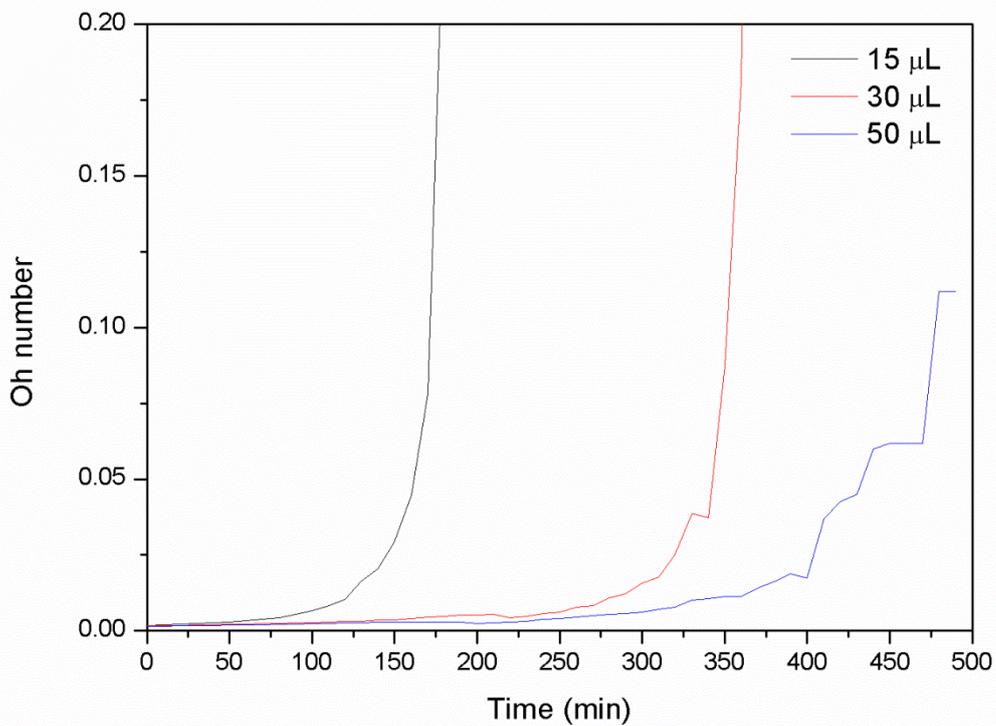
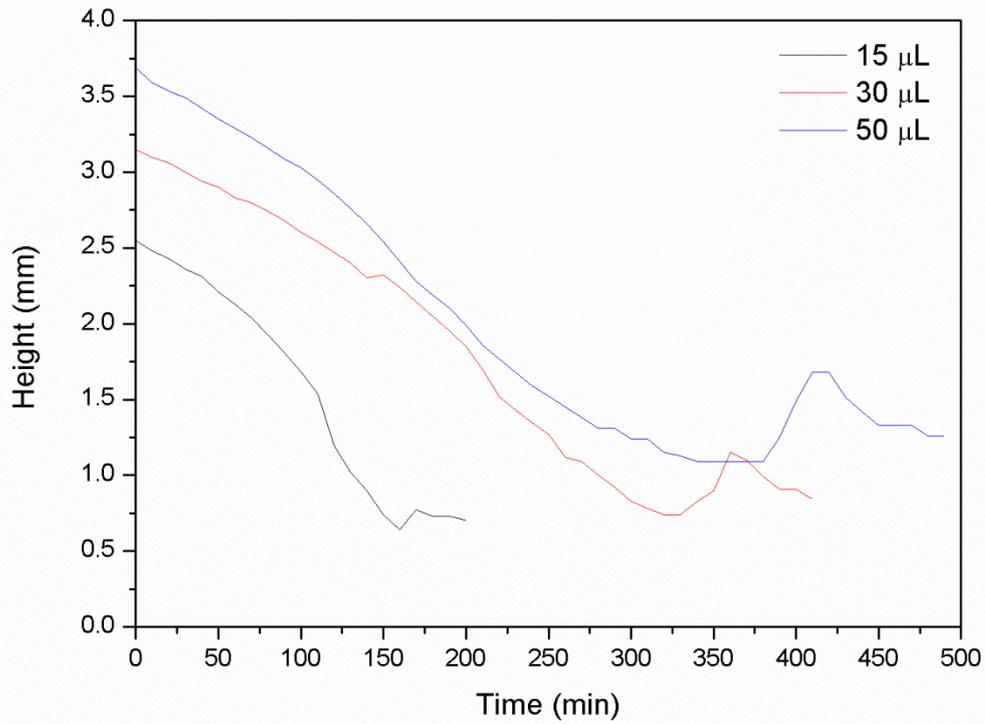
Time	Height (mm)	Width (mm)	Adjusted concentration (% w/v)	Adjusted viscosity (mPas)	Oh number (using height)	Oh number (using width)
0	2.55	3.29	2.00	1.6	0.00	0.00
10	2.48	3.21	2.15	1.7	0.00	0.00
20	2.43	3.17	2.24	1.7	0.00	0.00
30	2.36	3.07	2.46	1.9	0.00	0.00
40	2.31	3.00	2.64	2.1	0.00	0.00
50	2.21	2.92	2.86	2.2	0.00	0.00
60	2.13	2.76	3.39	2.6	0.00	0.00
70	2.04	2.69	3.66	2.9	0.00	0.00
80	1.93	2.60	4.05	3.2	0.00	0.00
90	1.81	2.44	4.90	3.8	0.01	0.00
100	1.68	2.32	5.70	4.5	0.01	0.01
110	1.54	2.19	6.78	5.4	0.01	0.01
120	1.20	2.12	7.47	6.0	0.01	0.01
130	1.02	2.10	10.56	8.8	0.02	0.01
140	0.90	2.10	11.96	10.3	0.02	0.01
150	0.74	2.10	14.55	13.3	0.03	0.02
160	0.64	2.01	18.36	18.9	0.04	0.03
170	0.77	1.53	26.34	36.3	0.08	0.06
180	0.73	1.23	42.99	111.7	0.25	0.19
190	0.73	1.23	42.99	111.7	0.25	0.19
200	0.70	1.23	44.84	124.4	0.28	0.21

## F.2 Height graph and corresponding calculated Ohnesorge number graph repeats

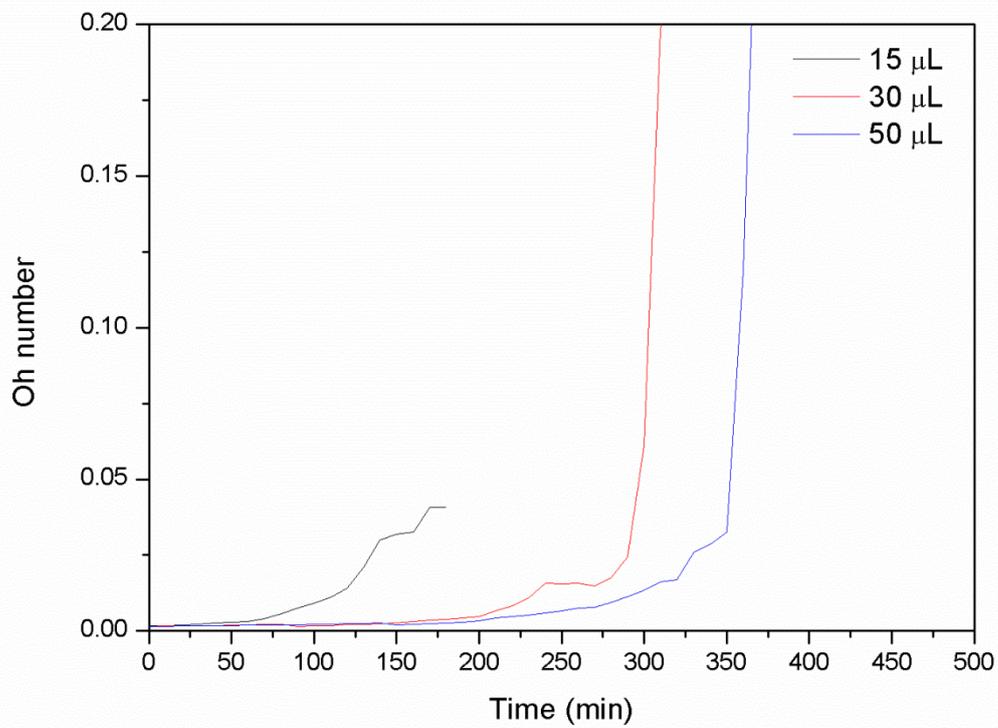
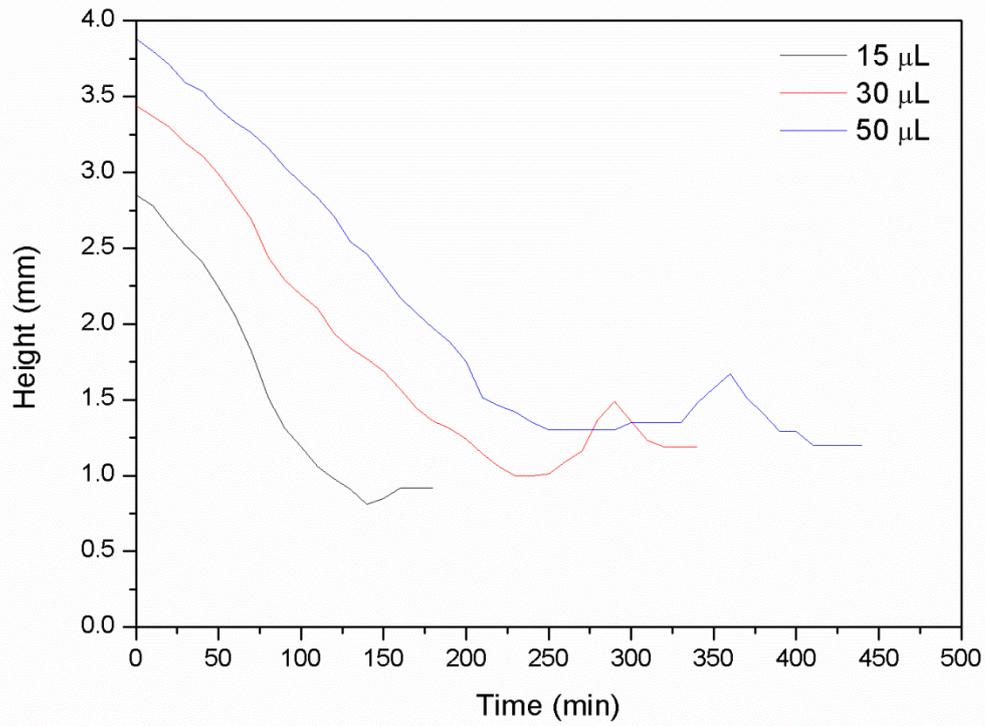
In the graphs below, the height data is used as comparison to the calculated Ohnesorge number as it shows a more distinct change at the ‘rebound’ point with the sudden increase in height. It is observed that in all cases where the ‘rebound’ phenomenon occurred, a point of inflection occurred in the Ohnesorge number graph, which is usually close to Oh = 0.05.

**F.2.1: 2% VP/VA copolymer liquid marbles**

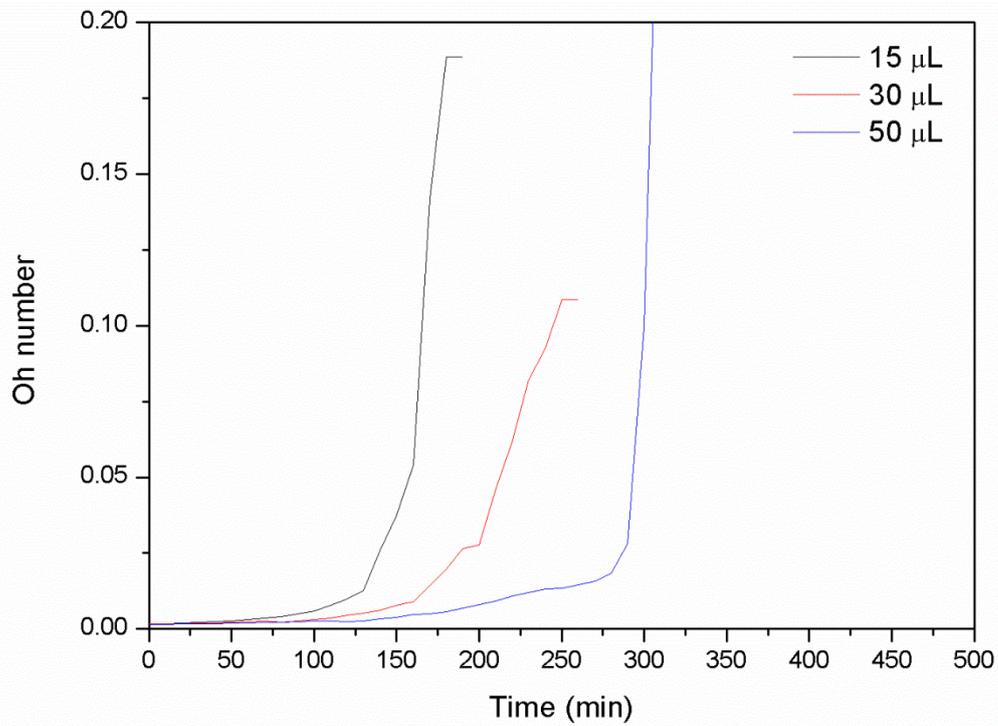
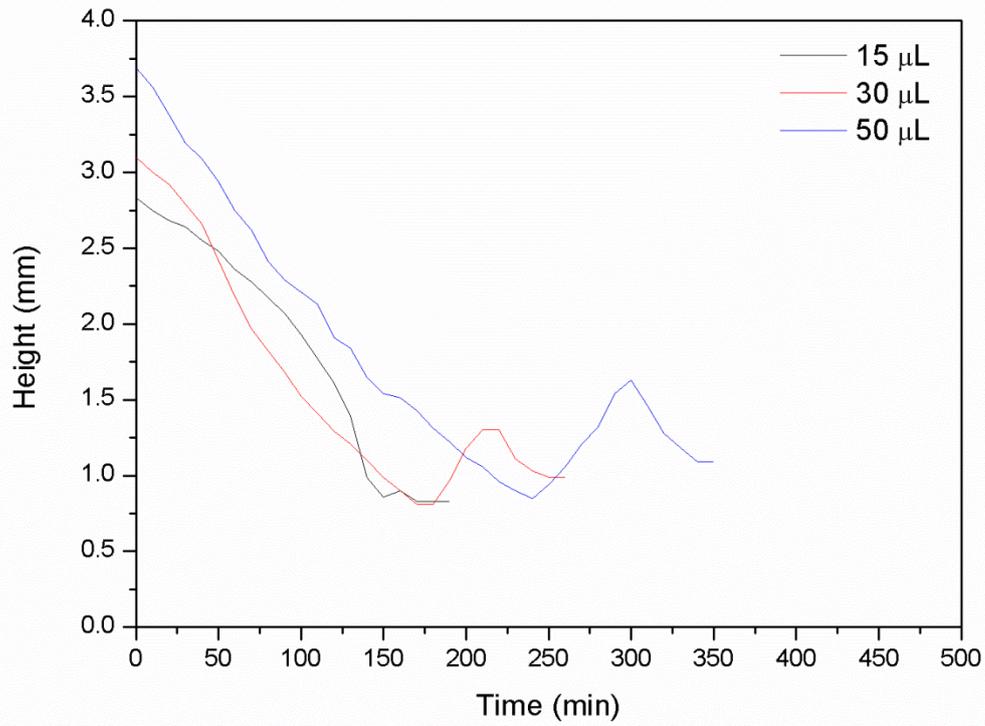
*Trial 1*



**Trial 2**

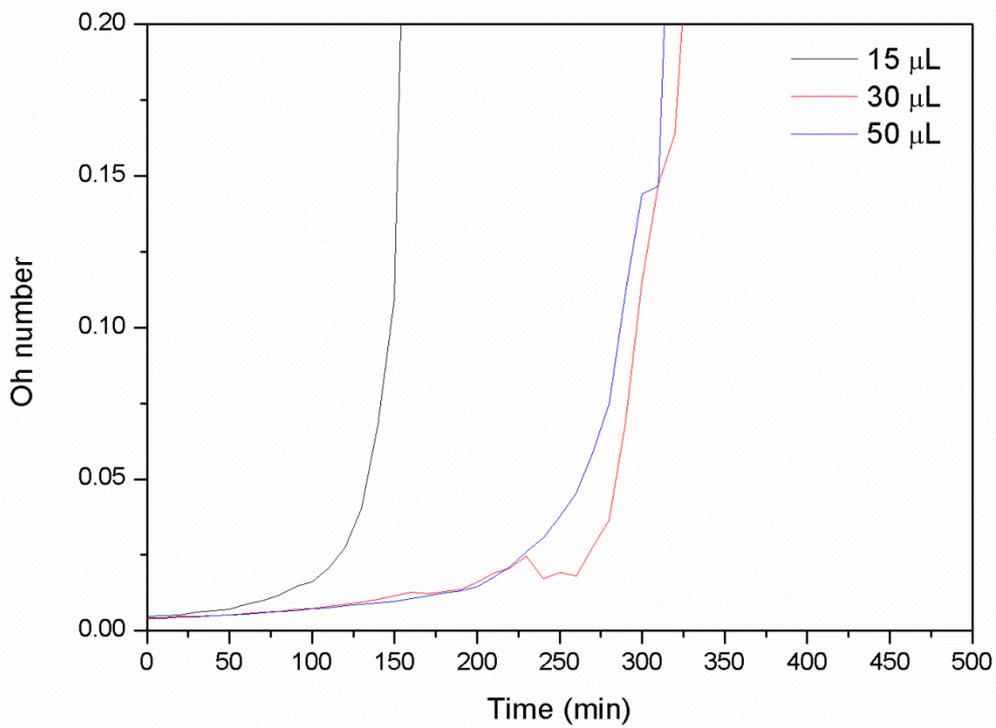
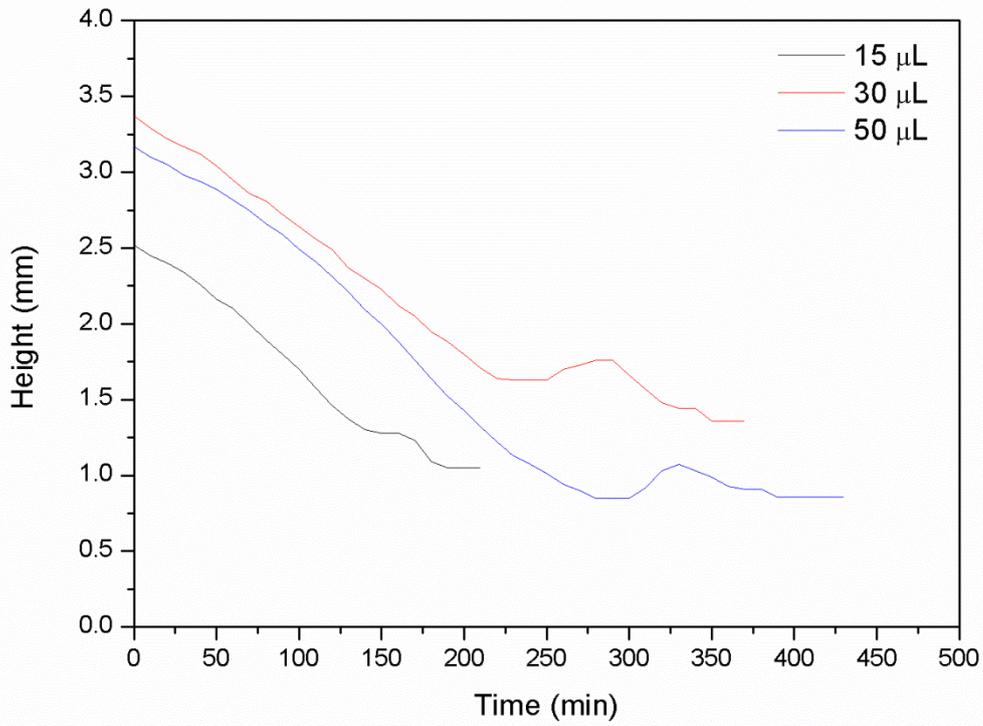


**Trial 3**

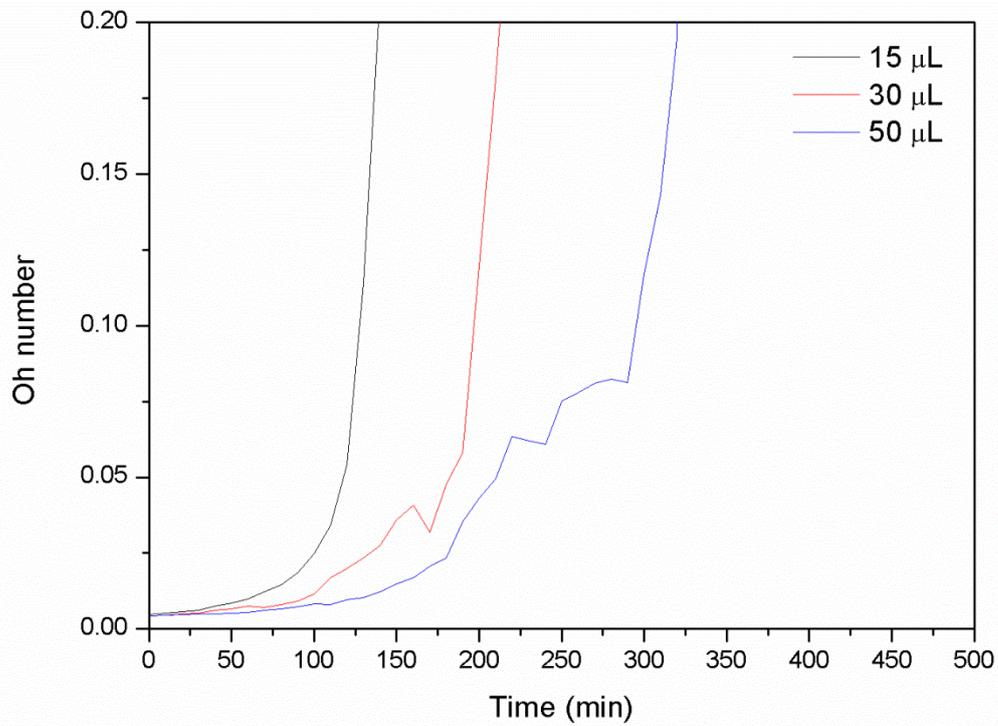
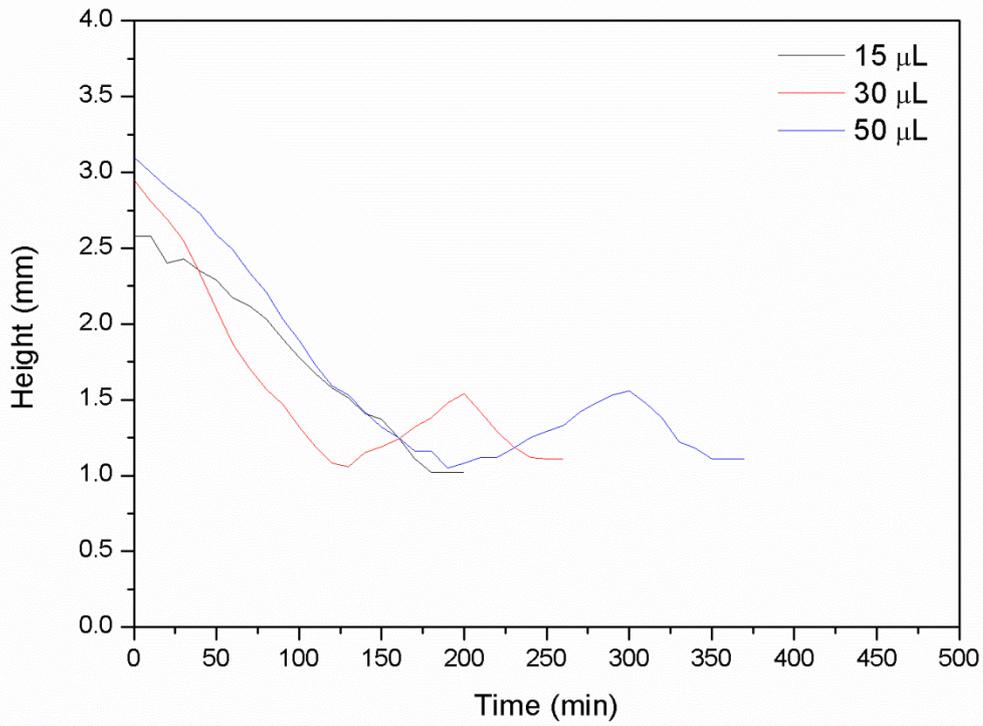


**F.2.2: 5% VP/VA copolymer liquid marbles**

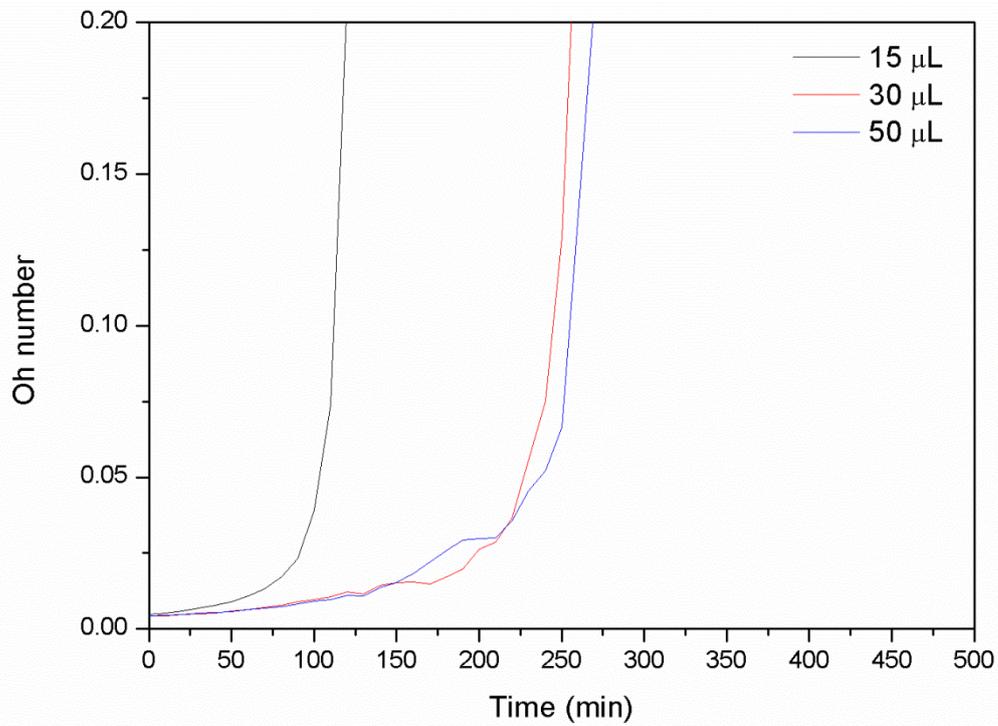
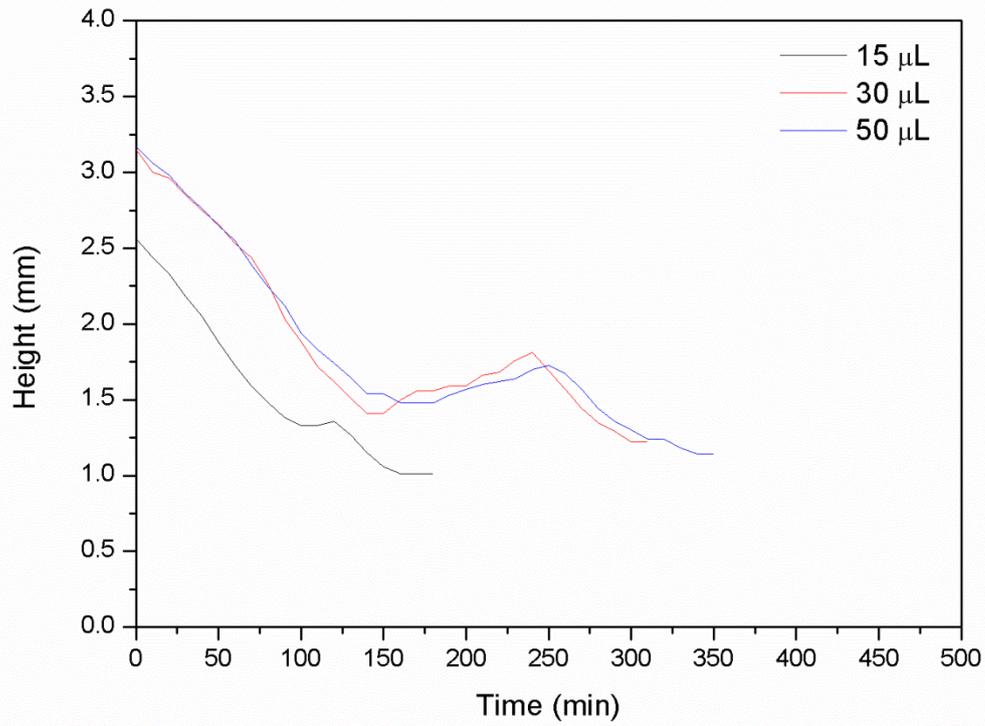
**Trial 1**



**Trial 2**



**Trial 3**



## References

1. Cossali, G., Coghe, A., and Marengo, M., (1997), The impact of a single drop on a wetted solid surface. *Experiments in fluids*, 22(6): p. 463-472.
2. Scheller, B.L. and Bousfield, D.W., (1995), Newtonian drop impact with a solid surface. *AIChE Journal*, 41(6): p. 1357-1367.
3. Bühler, V., (2008), Kollidon VA 64 grades (copovidone), in *Kollidon - Polyvinylpyrrolidone excipients for the pharmaceutical industry*. 2008, BASF: Ludwigshafen.

G

Appendix G

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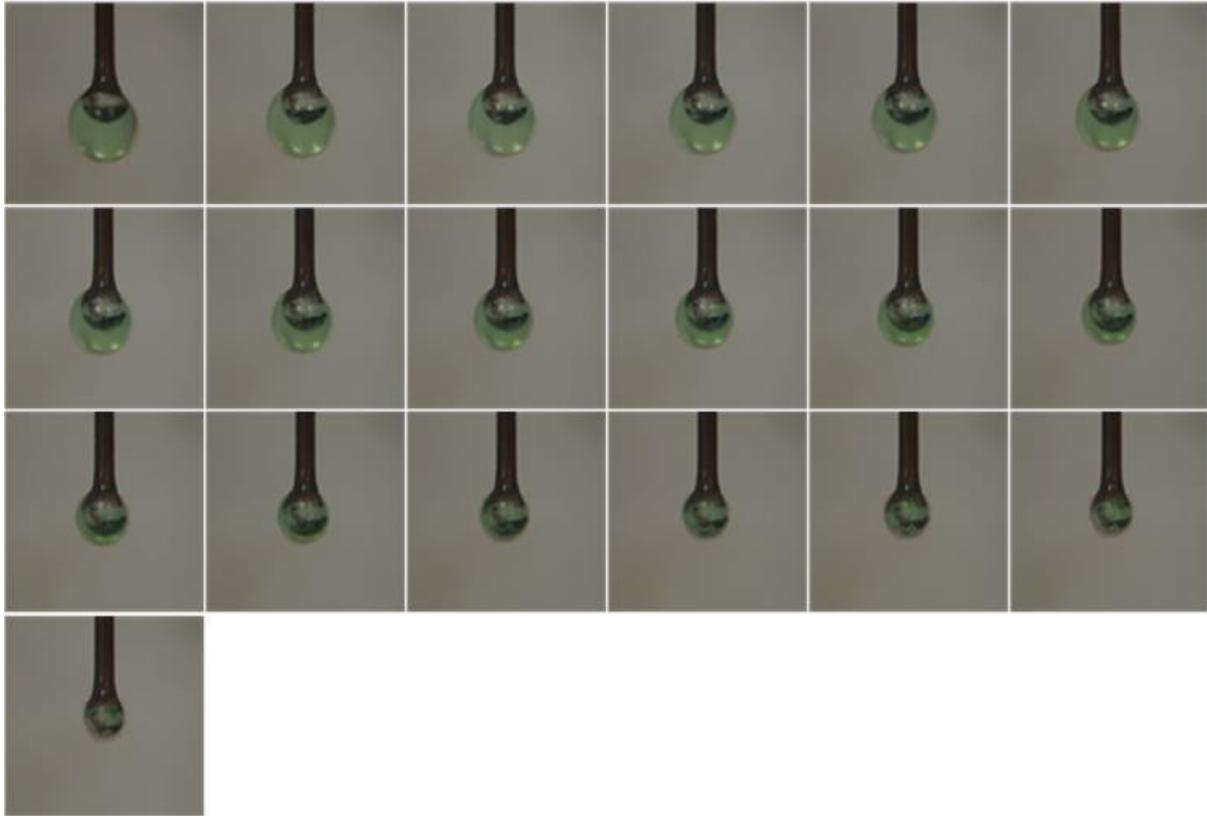


### Appendix G: Single Droplet Drying raw images

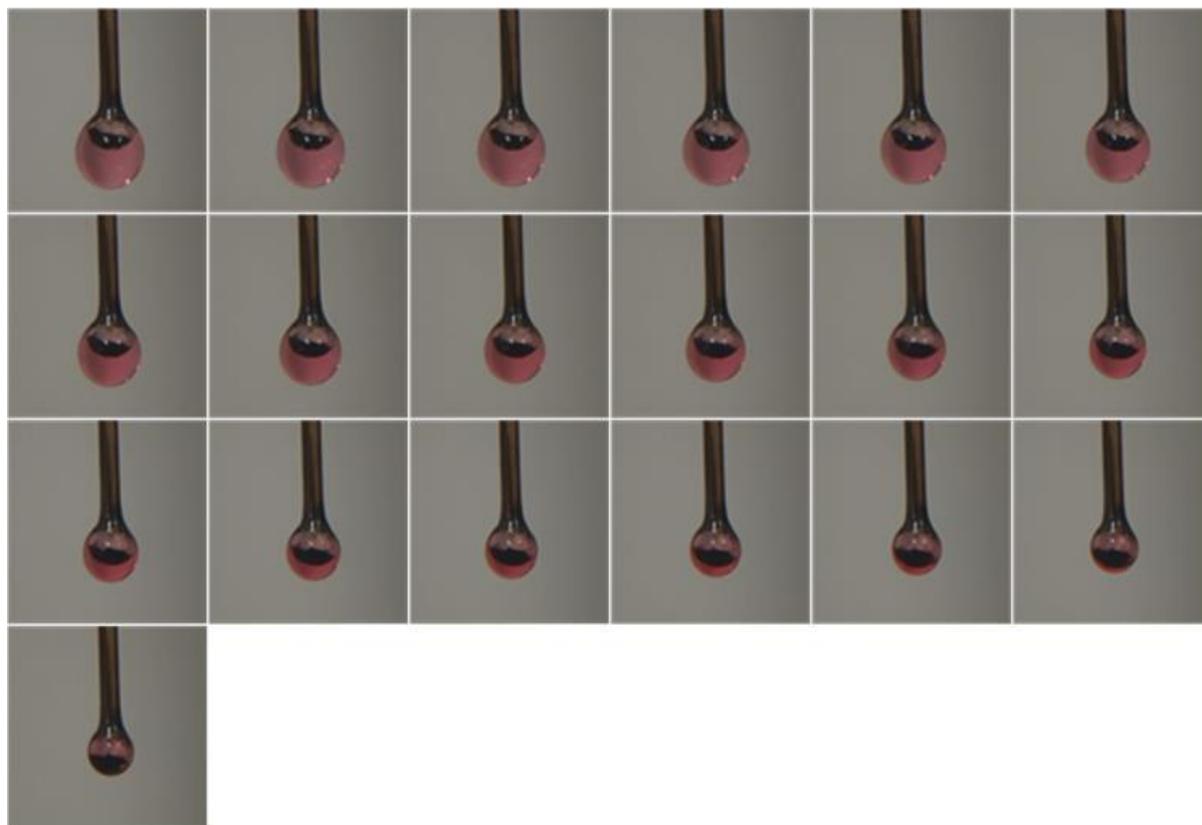
The drying process of 2  $\mu\text{L}$  liquid marbles created from solutions of 0% (pure deionised water droplet), 2% and 5% (w/v) VP/VA copolymer coated with Aerosil powder was recorded using a camcorder fitted with a magnification lens. The video was then analysed using Sony PMB program and still images taken at 2 minute intervals. The following section gives the raw images taken. Stem thickness is 0.5 mm for the following images.



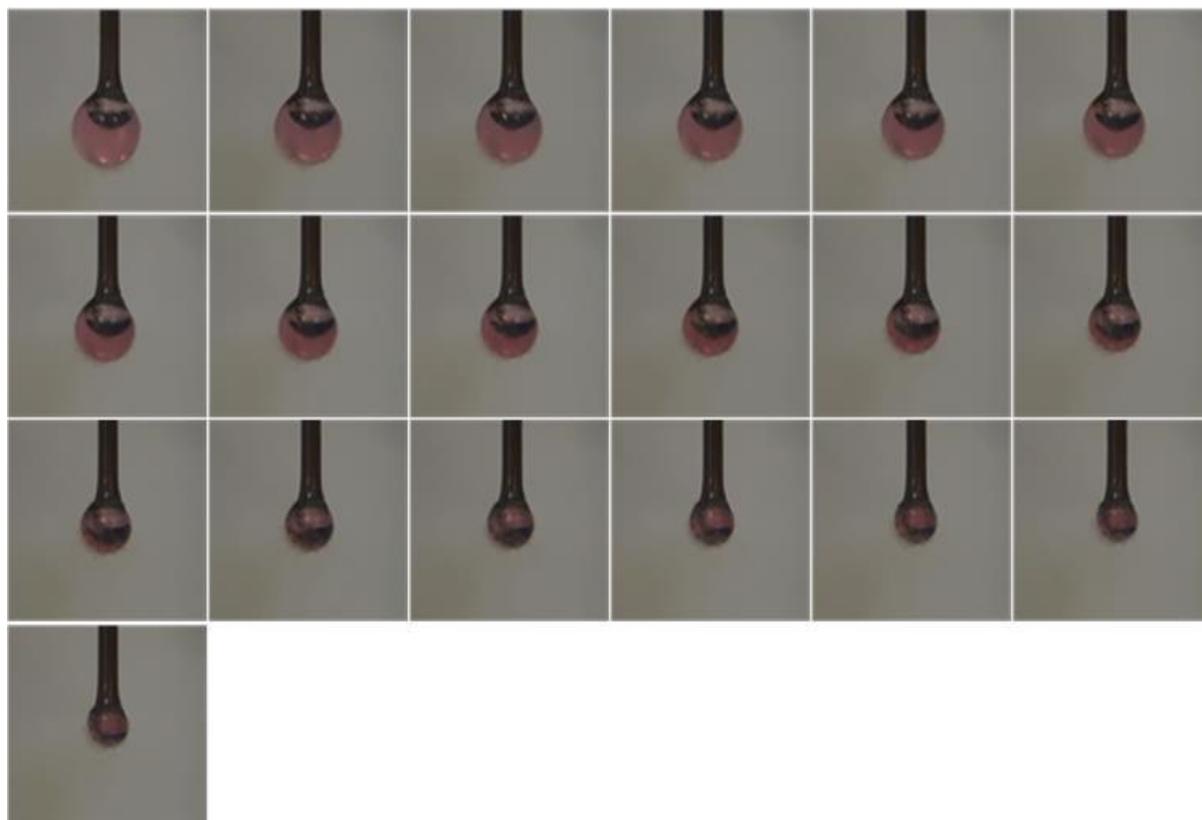
**Figure G-I: Images of 0% (w/v) VP/VA copolymer solution droplet with no Aerosil coating (i.e. Plain droplet) over time. (Spindle stem thickness of 0.5 mm)**



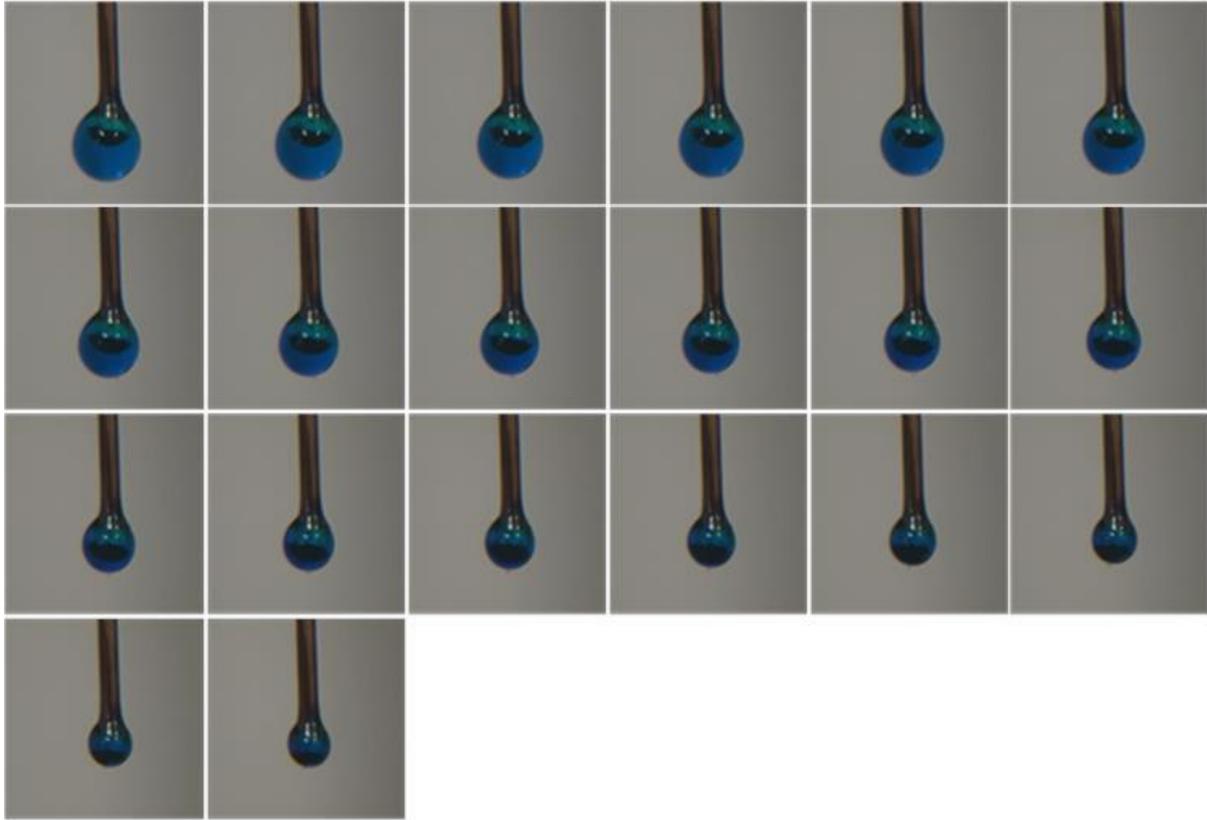
**Figure G-II: Images of 0% (w/v) VP/VA copolymer solution droplet with Aerosil coating (I.e. Pure water liquid marble) over time. (Spindle stem thickness of 0.5 mm)**



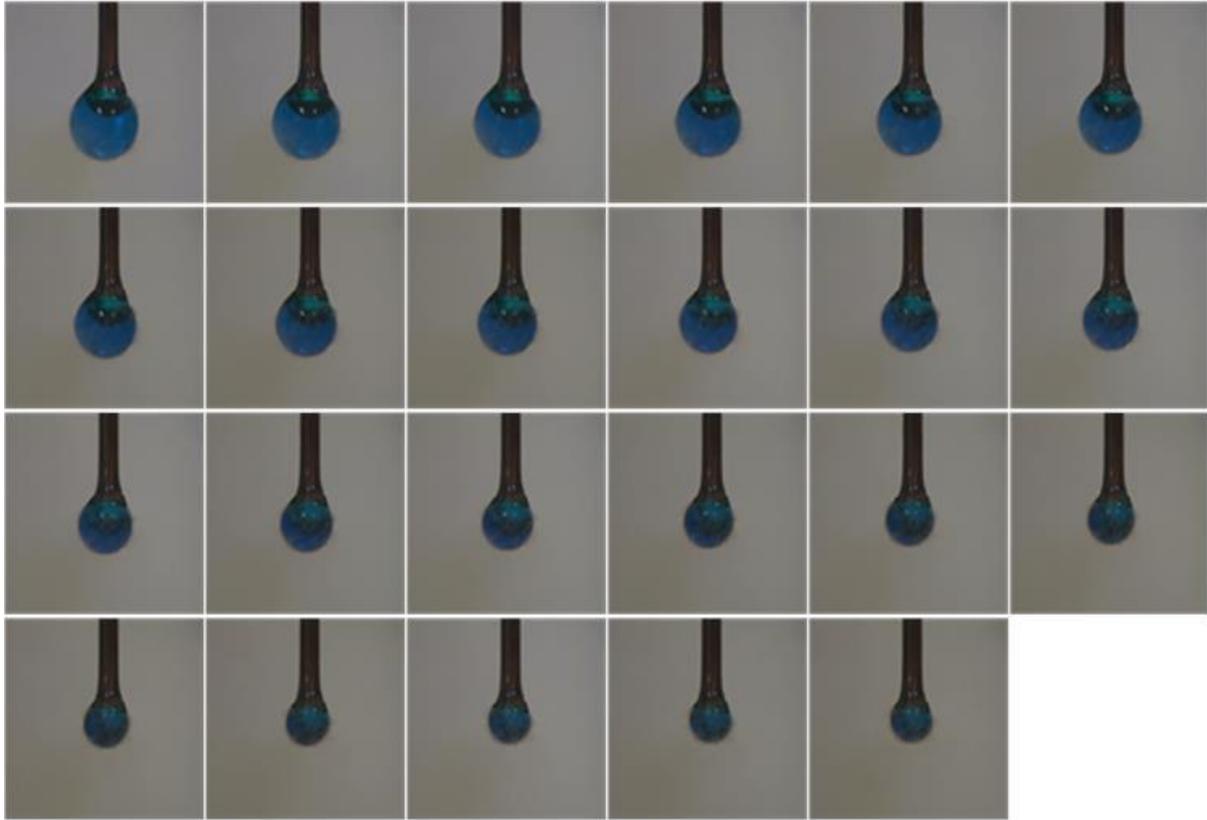
**Figure G-III: Images of 2% (w/v) VP/VA copolymer solution droplet with no Aerosil coating (I.e. Plain 2% VP/VA copolymer droplet) over time. (Spindle stem thickness of 0.5 mm)**



**Figure G-IV: Images of 2% (w/v) VP/VA copolymer solution droplet with Aerosil coating (I.e. 2% VP/VA copolymer liquid marble) over time. (Spindle stem thickness of 0.5 mm)**



**Figure G-V: Images of 5% (w/v) VP/VA copolymer solution droplet with no Aerosil coating (I.e. Plain 5% VP/VA copolymer droplet) over time. (Spindle stem thickness of 0.5 mm)**



**Figure G-VI: Images of 5% (w/v) VP/VA copolymer solution droplet Aerosil coating (I.e. 5% VP/VA copolymer liquid marble) over time. (Spindle stem thickness of 0.5 mm)**