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DEVELOPMENT OF LOOSE FACE POWDER CONTAINING WATER-ENTRAPPED SILICA PARTICLES

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Cosmetic Science
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Thesis Title	DEVELOPMENT OF LOOSE FACE POWDER CONTAINING WATER-ENTRAPPED SILICA PARTICLES
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อสมาภรณ์ บุญญสิทธิกุล : การพัฒนาแป้งฝุ่นทาหน้าที่มีอนุภาคซิลิกาที่กักเก็บน้ำ (DEVELOPMENT OF LOOSE FACE POWDER CONTAINING WATER-ENTRAPPED SILICA PARTICLES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ภก. ดร.วันชัย จงเจริญ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: อ. ภญ. ดร.ดุษฎี ชาญวาณิช, 96 หน้า.

วัตถุประสงค์ของการศึกษานี้เพื่อพัฒนาแป้งฝุ่นสำหรับทาหน้าที่ประกอบด้วยอนุภาคซิลิกาที่กักเก็บน้ำ โดยอนุภาคซิลิกาที่กักเก็บน้ำสามารถเตรียมได้โดยกระบวนการผสมที่ไม่ซับซ้อน โดยมีการดำเนินการด้วยแรงเฉือนสูงและเติมน้ำทั้งหมดลงไปผสมในคราวเดียว ผลิตภัณฑ์ที่เตรียมขึ้นนี้มีลักษณะโครงสร้างแบบการห่อหุ้มแกนกลางด้วยเปลือกซึ่งเกิดขึ้นจากการก่อรวมกันเอง แกนกลางด้านในเป็นหยดน้ำขณะที่เปลือกหุ้มเกิดจากการจับตัวแบบโครงตาข่ายหลวมๆของซิลิกาชนิดไม่ชอบน้ำ (Aerosil® R812S) อัตราส่วนโดยน้ำหนักระหว่างผงซิลิกาต่อน้ำที่ 3 ต่อ 97 เป็นอัตราส่วนที่เหมาะสมในการทำให้เกิดอนุภาคที่กักเก็บน้ำที่มีลักษณะเป็นผงแห้ง มีการไหลที่ยอมรับได้ รวมถึงมีประสิทธิภาพในการกักเก็บน้ำไว้ได้สูง (มากกว่าร้อยละ 95) ถึงแม้จะเก็บรักษาภายใต้สภาวะเร่งเป็นระยะเวลา 3 เดือน อนุภาคซิลิกาที่กักเก็บน้ำที่เตรียมขึ้นจะถูกนำไปผสมกับสูตรพื้นฐานของแป้งฝุ่นสำหรับทาหน้า แต่เนื่องจากความไม่คงตัวเชิงกายภาพที่ต่ำของอนุภาคซิลิกาที่กักเก็บน้ำทำให้ต้องคัดเลือกรูปแบบการผสมที่ไม่รุนแรงเกินไป แป้งฝุ่นสำหรับทาหน้าสูตรพื้นฐานจะถูกเตรียมขึ้นด้วยเครื่องปั่นผสมแรงเฉือนสูงก่อน จากนั้นจึงนำไปผสมรวมกับอนุภาคซิลิกาที่กักเก็บน้ำที่เตรียมไว้ก่อนแล้วด้วยเครื่องผสมแบบเขย่า ระยะเวลาในการผสมโดยการเขย่าถือเป็นจุดวิกฤตที่ต้องคำนึงถึงการเขย่าผสมโดยใช้เวลา 5 นาทีเป็นเวลาที่เหมาะสมเนื่องจากโครงสร้างของการห่อหุ้มแกนกลางด้วยเปลือกของอนุภาคที่เติมลงไปยังคงปรากฏอยู่ แป้งฝุ่นสำหรับทาหน้าที่มีส่วนประกอบของอนุภาคซิลิกาที่กักเก็บน้ำในปริมาณร้อยละ 40 โดยน้ำหนักมีคุณสมบัติของแป้งฝุ่นสำหรับทาหน้าที่ยอมรับได้ตามเกณฑ์ที่กำหนด ผลิตภัณฑ์นี้สามารถให้ความรู้สึกเย็นในทันทีพร้อมกับให้ความชุ่มชื้นตามต้องการ อย่างไรก็ตามคุณสมบัติในการดูดซับความมันของสูตรตำรับข้างต้นนั้นมีความสามารถที่ด้อยกว่าสูตรตำรับที่เป็นกลุ่มควบคุมเชิงบวกของมัน โดยสรุปแป้งฝุ่นผัดหน้าที่พัฒนาขึ้นจะประกอบด้วยองค์ประกอบแรกคืออนุภาคซิลิกาที่กักเก็บน้ำ (ของผสมระหว่าง R812S และน้ำ) และองค์ประกอบที่สองคือสูตรพื้นฐานของแป้งฝุ่นสำหรับทาหน้า ซึ่งทั้งสององค์ประกอบจะถูกผสมเข้าด้วยกันด้วยแรงเขย่าเบาๆ ภายในระยะเวลาที่เหมาะสม

ภาควิชา	วิทยาการเภสัชกรรมและเภสัชอุตสาหกรรม	ลายมือชื่อนิสิต ....
		ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
สาขาวิชา	วิทยาศาสตร์เครื่องสำอาง	ลายมือชื่อ อ.ที่ปรึกษาร่วม ....
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ATSAMAPORN BOONYASITTIKUL: DEVELOPMENT OF LOOSE FACE POWDER CONTAINING WATER-ENTRAPPED SILICA PARTICLES. ADVISOR: WANCHAI CHONGCHAROEN, Ph.D., CO-ADVISOR: DUSADEE CHARNVANICH, Ph.D., 96 pp.

The objective of this study was to develop loose face powder containing water-entrapped silica particles. Water-entrapped silica particle was fabricated via simple mixing process operated with high shearing and pouring water all at once. The obtained product was core shell like structure and self-assembly form. The inner core was water droplet while the shell was the loose networking of hydrophobic silica (Aerosil® R812S). The weight ratio between R812S and deionized water of 3:97 was determined as the suitable quantity on the formation of water-entrapped silica particle. It provided an acceptable free flowing and dry powder including high percentage of water entrapment efficiency (more than 95%) even after storage in the accelerated condition up to 3 months. Water-entrapped silica particle produced was then incorporated in basic formulation of loose face powder. Due to the physical instability of water-entrapped silica particle, gentle mixing pattern was chosen. Basic loose face powder was initially produced by high shear mixer and then blended with the water-entrapped silica particle in tumble mixer. The mixing time during tumble was critically concerned. Five minutes of such mixing would be an optimal mixing time since the core shell structure of particle still retained. The loose face powder containing 40% of water-entrapped silica particles showed the acceptable property in accordance with the specified criteria. It provided desirable burst cooling sense with moisturizing effect. Nevertheless, oil absorption property of the above formulation had lower capacity than its positive control formulation. In conclusion, the developed formulation comprised of the first component of water-entrapped silica particles (the mixture of R812S and DI water) and the second component of the basic loose face powder. They were blend together in gentle mixer with optimum mixing time.

Department:	Pharmaceutics and Industrial Pharmacy	Student's Signature ....
		Advisor's Signature ....
Field of Study:	Cosmetic Science	Co-Advisor's Signature ....
Academic Year:	2016	

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LIST OF ABBREVIATIONS

DI water	Deinoized water
R812S	Aerosil® R812S
TGA	Thermogravimetric analysis
FE-SEM	Field Emission Scanning Electron Microscope
rpm	round per minute
%	percentage
w/w	weight per weight
mg	milligram (s)
g	gram (s)
°C	Degree Celsius (centigrade)
ml	milliliter (s)
ml / min	milliliter per minute
°C / min	Degree Celsius per minute
EE	entrapment efficiency
W_s	weight loss
W_i	weight initial
ASTM	American Society for Testing and Materials
CI	compressibility index
d_{bulk}	initial bulk density
d_{tapped}	tapped density
USP	The United States Pharmacopoeia
kV	Kilo Voltage (s)
SEI	Secondary Electron Image
GB	Gentle Beam
RH	Relative Humidity
μm	Micrometer (s)
W	Formulation of water-entrapped silica particles

LW	Formulation of loose face powder containing water-entrapped silica particles
OTS	n-Octyltriethoxysilane

CHAPTER I

INTRODUCTION

Powder cosmetic is well known and widely used for a variety of purposes such as eyeshadow, blush on, loose facial powder. However, they are also used in personal care products such as baby dusting powders, foot and hair care product including powder base for a variety of medicated products. The advantages of product in powder form are their ability to absorb water, thereby assisting in drying damp or perspiring skin, able to absorb excess sebum from the skin or hair, portability and ease of application. Despite widely usage and more effective for the intended purposes, there are some limitations. By nature, powders tend to scatter, and may not remain in place after application. In addition, one of their main advantages, the ability to absorb moisture, contributes to one of their main disadvantages. Due to the course of absorbing moisture, it can cause the discomfort of the skin particularly when it is frequently used. To compensate the lower level of moisture the skin, adding water is the best answer. However, adding water in powder form is led to the losing of dry powder properties such as poor flow and unevenness on the skin (Lahanas et al., 2001).

Water-entrapped silica particle is one of the technique to encapsulate a large amount of water with powders. It can be applied to various types of cosmetic products to achieve a cosmetic with unique characteristics. Water-entrapped silica particles consisted of aqueous droplet surrounded by a protective shell formed silica particles. It was spontaneously formed via self-assembling of silica as a hydrophobic networking layer (Forny et al., 2007). Encapsulated liquids could be of up to 95% by weight and easily be released after which mechanical stress like rubbing or pressing was applied. Therefore, water-entrapped silica particles remained in place after freshly prepared and would be deformed after applied on the skin. One of the most interesting benefit of water-entrapped silica particles for cosmetic purpose was to deliver water onto the skin which eventually provided a burst cooling sense with moisturizing effect (Lahanas et al., 2001 and Saleh et al., 2011). In addition, the valuable water soluble actives could also be incorporated in water droplet of water-entrapped silica particles and finally delivered into skin after gently applied with rubbing. (Lahanas et al., 2001).

Water-entrapped silica particles can be applied to various types of cosmetic products, making them unique, and add more value for such products through the addition of active ingredients. The powder cosmetic can be changed into liquid by application of friction on the skin, gives more comfortable of applying and provides a watery and cool feeling. It also provides excellent makeup function by spreading smoothly on skin to from a uniform makeup coating (Igarashi, Sagara and Egawa 2008).

This study was focusing on the preparation of loose face powder containing water-entrapped silica particles to create special attributes. The powder provided a watery, cool feeling and moist the skin. These effects were not what ordinary face powders can offer. Moreover, using water-entrapped silica particles as a part of the loose face powder could reduce the powder weakness, dust diffusion, and potentiate the adhesion of powder on the skin longer.

Objectives

General objectives

To develop the loose face powder containing water-entrapped silica particles

Specific objectives

1. To study the effect of ratio between hydrophobic silica and water on preparation of water-entrapped silica particles
2. To observe the stability of water-entrapped silica particles produced
3. To study the appropriate preparation method of loose face powder containing water-entrapped silica particles
4. To study the effect of ratio between loose face powder and water-entrapped silica particles on properties of the product
5. To investigate the stability of loose face powder containing water-entrapped silica particles

CHAPTER II
LITERATURE REVIEW

Cosmetics in a typical powder form are widely used, especially coloring and make up cosmetics such as eyeshadow, blush on, loose face powder, or even personal care products like body powder. The benefit of this type of product are ease of handling and able to absorp the excess of oil retained on facial skin. Although it has been widely used, and more effective for the intended purposes, there are some limitation of the use of powder. Naturally, powders tend to scatter, and may not remain in place after application. In addition, one of their main advantages, the ability to absorb moisture, contributes to one of their main disadvantages. Due to the course of absorbing moisture, it can cause discomfort to the skin particularly when it was frequently used (Lahanas et al., 2001). The solution that could address a mentioned issue is the addition of add water in such products in order to compensate the loss of skin moisture. However, adding water to the powder based product would perturb their flow properties. If there is a way to create a powder based product which consists of water-entrapped particles, it would be a good candidate product. Water-entrapped silica particles preparation could be applied to produce powder based cosmetics. Water-entrapped silica particles is one of the technique to encapsulating a large amount of water with powders to achieve a cosmetic with many unique characteristics. Generally, these particles look just like regular dry powder, but when applied on skin which mechanical stress like rubbing or pressing, they would release the entrapped liquid. Cosmetics that consist of these water-entrapped silica particles would have the ability to provide a watery, cool feel to the skin, which regular cosmetic products cannot. They are also unique due to provide excellent long lasting effect. The value-added of this product could be done by incorporating water-soluble active ingredients in inner core of water-entrapped silica particles such as hyaluronic acid, vitamin C, collagen (Lahanas et al., 2001 and Yoichiro, Yuriko and Shinji 2002).

Water-entrapped silica particles consisted of aqueous droplet surrounded by a protective shell formed silica particles. The schematic, cross-sectional view of water-entrapped silica particles revealed the core shell like structure (Figure 1) (Fassih et al., 2014). It was spontaneously formed via self-assembling of silica as a hydrophobic networking layer (Forny et al., 2007). The silica powder used for the technique is fumed silica or pyrogenic silica which generally are categorized into two types, hydrophilic and hydrophobic fumed silica. Fumed silica is usually used in many liquid systems for controlling the viscosity and provides an anti-settling behavior. All of these effects are based on the ability of dispersed fumed silica particles to form a network of aggregates via hydrogen bridge linkage and van der Waals attractive forces in liquid media. Hydrophobic silica more often exhibits lower thickening efficiency compared to that of hydrophilic types. However, hydrophobic grades have an other that may also be an option when maximum viscosity is not required. One of the most interesting point of hydrophobic fumed silica is its aggregation ability between particles via van der Walls force. Such aggregation can be easily broken, provides suspension without the higher resulting viscosity. For example, suspended pigments in lip gloss allows better skin feel during application. Due to its hydrophobicity, the product mixed with fumed silica is granted for water-repellent ability (Evonik industries). This characteristic of hydrophobic fume silica is led to develop in the form of water-entrapped silica particles to entrap water by a protective shell formed silica particles. It was spontaneously formed via self-assembling of silica as a hydrophobic networking layer. The Water-entrapped silica particles obtained is a free flowing and fluffy powder. Water can be easily released by mechanical stress, e.g. rubbing (Forny et al., 2007 and Fassih et al., 2014). Water-entrapped silica particles was composed of 0.05-10% w/w of hydrophobic fume silica and 50-90% w/w of liquid such as water, floral water, alcohol, water soluble polymer or water soluble actives (Yoichiro et al., 2002).

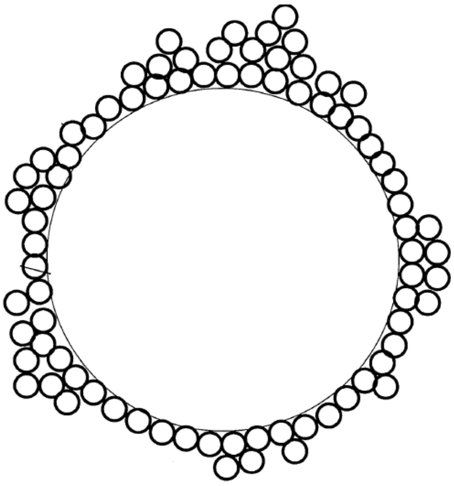


Figure 1 The schematic, cross-sectional view of water-entrapped silica particles comprising liquid core (Fassih et al., 2014).

The formation of water-entrapped silica particles depended on the preparation method and type of silica. Water-entrapped silica particles could be commonly prepared by both low shear and high shear processes. The high shear process could be performed with a regular blender, which was suitable for a preparation in laboratory scale. The result from laboratory scale study showed that high shear blender with pouring whole water at once was succeeded to fabricate water-entrapped silica particles. The mechanisms involved on water-entrapped silica particles formation which was prepared in vessels were shearing action. Shear force would firstly sprit the whole volume of water into large drops which would be finally surrounded by the networking of silica and air. This phenomenon was ensured by convective axial flow. Once the large droplets were formed further mixing led to more homogeneous and finer droplets provided that the particles were sufficiently hydrophobic. If not, a mousse or suspension was formed. Therefore, the most efficient impeller would be a polyvalent impeller producing both axial and radial flows (e.g. the helical propeller) (Figure 2) (Saleh et al., 2011).

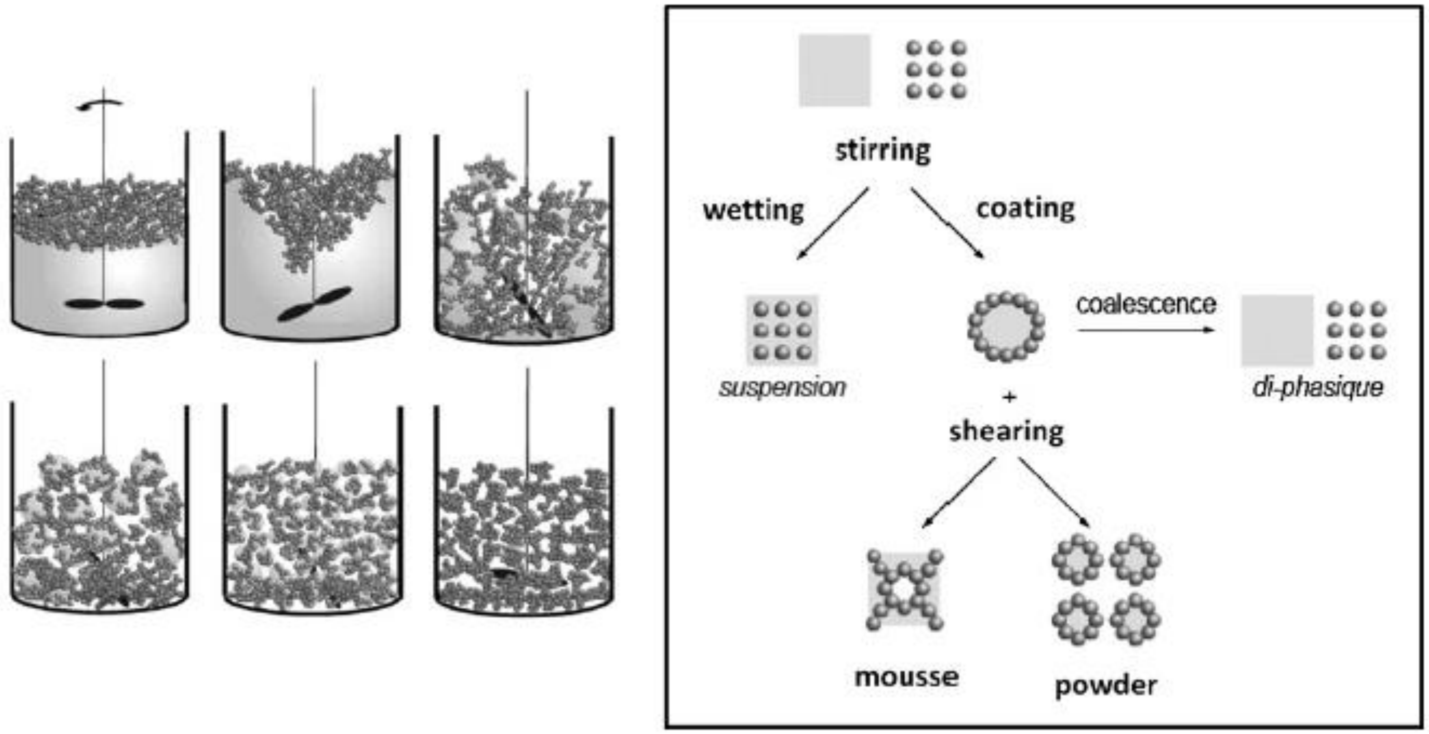


Figure 2 Mechanisms of water-entrapped silica particle formation (Saleh et al., 2011).

Meanwhile, low shear mixer (Triaxe®) with water atomization was possible to form water-entrapped silica particles in large scale (Figure 3) (Forny et al., 2007). Factors affecting on the formation of water-entrapped silica particles were atomization pressure, stirring conditions and spraying nozzle spacing. Appropriate atomization pressure requirement were more than 8 bar and rotating speed was 155 rpm (Forny et al., 2009).

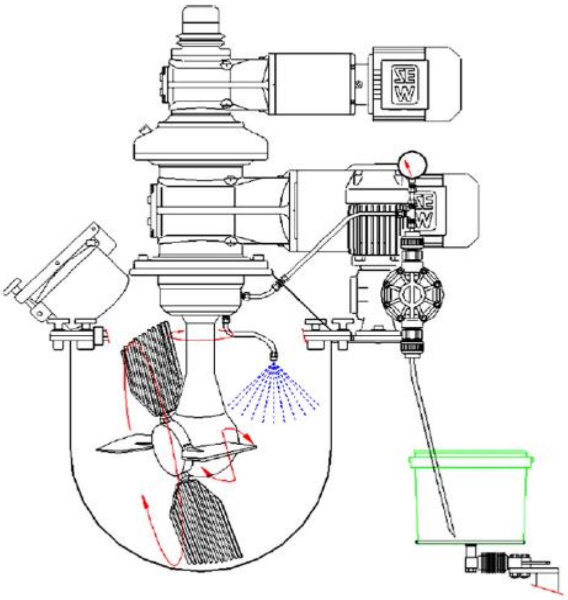


Figure 3 General assembly drawing of the Triaxe® (Forny et al., 2009).

High shear blender with the adding of water all at once was seemed to be the most appropriate method of water-entrapped silica particles preparation in laboratory scale because of the simple and easy to handle process (Forny et al., 2007). Moreover, the influence of type of silica on the possibility of the formation was addressed. The difference in behavior between fumed silica was attributed to particle hydrophobicity (Figure 4). High-hydrophobicity at nano-sized of silica (Aerosil® R812S) would produce water-entrapped silica particles and hold water inside of up to 98% (by weight). While, low-hydrophobic silica provided a mousse (Aerosil® R972), a suspension (Aerosil® R711) or diphasic phase separation (Aerosil® 300) (Forny et al., 2009).

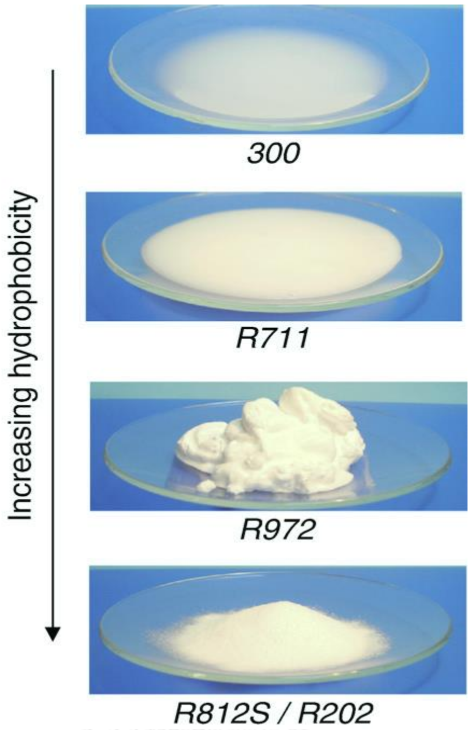


Figure 4 Influence of fumed silica hydrophobicity from Aerosil® range on final product quality obtained by blending 96 g of water and 4 g of silica particles by high shear blender (Forny et al., 2009).

It could be therefore seen that, water encapsulation by silica particle assembling required highly hydrophobicity of fumed silica in conjunction strong turbulent flow conditions produced by high shear mixer. Meanwhile, penetration of solid particles into water phase is enhanced by low hydrophobicity and high shearing forces delivered by high rotational speed. The different behavior amidst fumed silica is attributed to mainly particles hydrophobicity. High hydrophobicity nature of R812S was thus appropriate on the formation of water-entrapped silica particles (Forny et al., 2009).

Characterization of **water-entrapped silica particles**

1. In term of physical appearance, it was used to be a good powder with free flowing and no aggregation. It should also hold the water inside as intact form and easily later released the encapsulated water after pressure applied. The perfectness of water-entrapped silica particles was clearly observed from the absence of residual water droplet on the inner surface wall of mixer during and after processing (Forny et al., 2007).

2. Water entrapment efficiency was evaluated using gravimetric and calorimetric methods. Gravimetric analyses were composed of accurate humidity and temperature controlled microbalance. The sample of powder was placed in the cup and weight change was recorded continuously at relative humidity of 0% at 25 °C. The difference between the initial and the steady state weight loss after complete drying was evaluated in order to access the ratio of incorporated water. Calorimetric analyses were possibly carried out using a Differential Scanning Calorimeter. The sample powder was cooled from ambient temperature to −60 °C with specified cooling rate followed by heating cycle from −60 °C to 20 °C at the same heating cycle. The total heat flow during the cycle was directly proportional to the amount of water in the sample (Forny et al., 2007).

Moreover, Fielden et al., (1988) used thermogravimetric analysis (TGA) to analyses the interaction between water and microcrystalline cellulose to indicate that water was held within a system.

3. The particle size and size distribution (PSD) were generally analysed by laser diffraction. Measurements were performed without pneumatic transportation which may disturb the initial system. The powder was dispersed in front of the laser beam using a vibrating feeder placed at approximately 10 cm from the top of the measuring area. Spherical shape hypothesis allows the determination of the diameter from the measured volume. The instrument gives the particle size distribution from which the mean size diameters of equivalent spherical particles (d10, d50 and d90) were obtained. Span coefficients have been used to appreciate the dispersion of the PSD calculated according to Equation (1) (Forny et al., 2007).

$$span = \frac{d_{90}-d_{10}}{d_{10}} \tag{1}$$

Where d_{90} is the diameter of the particle that 90% of a sample's mass is smaller than this value and d_{10} is the diameter at which 10% of the sample's mass is comprised of particles with a diameter less than this value.

Because the water-entrapped silica particles were prepared with sensitive networking of silica, thus the shell structure was destroyed by vibrating feeder from particle size analyzer. The measurements of particle size and size distribution by using optical microscope (400x magnification) calibrated with a stage micrometer (ASTM E1382-97) seemed to be more appropriate than other particle size measurement methods for water-entrapped silica particles. Gently sprinkled the water-entrapped silica particles sample over the glass slide and subjected under optical microscope. The diameter of 500 water-entrapped silica particles was determined and calculated to provide a mean with standard deviation of diameter and the size distribution of particle.

4. Flow properties of water-entrapped silica particles were evaluated from the relationship between bulk density and tapped density of the sample by using a tapped density tester. The compressibility index (%CI) could be then calculated as Equation (2) (Forny et al., 2007).

$$\%CI = \frac{(d_{tapped} - d_{bulk})}{d_{tapped}} \times 100 \tag{2}$$

Where d_{bulk} is the initial bulk density and d_{tapped} is the final tapped density.

5. Surface morphology of water-entrapped silica particles was visually observed after removal of the water phase by means of an Environmental Scanning Electronic Microscope (ESEM) (Figure 5). This equipment may be operated with a poor vacuum allowing the imaging of wet systems. Preliminary experiments were performed by simply reducing the pressure inside the specimen chamber but observations showed that the sample had collapsed. Complementary experiments were accomplished after water sublimation. For this purpose, the powder sample was firstly pre-cooled at −6 °C in a freezer and then deposited onto a Peltier thermoelectric device placed in the microscope and maintained at −5 °C. The pressure was then reduced down to 1.4 Torr provoking the sublimation of the water phase. Before imaging, the obtained sample undergoes gold metallization in order to improve picture resolution (Forny et al., 2007).

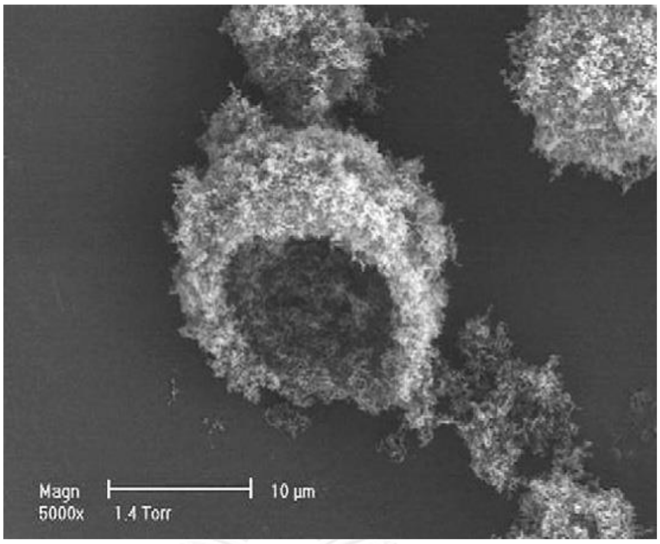


Figure 5 ESEM observation of water-entrapped silica particles prepared using R812S which containing 96% (w/w) of water (Forny et al., 2007).

The field emission scanning electron microscope (FE-SEM) was a type of electron microscope that images the sample surface by scanning with a high-energy beam of electrons in a raster scan pattern. Electron emitters from field emission gun was used. These types of electron emitters could be produced up to 1000x the emission of a tungsten filament. However, they required much higher vacuum conditions. After the electrons beam exited the electron gun, they then confined and focused into a thin focused, monochromatic beam using metal apertures and magnetic lenses. Finally, detectors of each type of electrons are placed in the microscopes that collect signals to produce an image of the specimen. Compared with convention scanning electron microscopy (SEM), field emission SEM (FESEM) produces clearer, less electrostatically distorted images. Reduced penetration of low-kinetic-energy electron probes closer to the immediate material surface. Provided high-quality, low-voltage images with negligible electrical charging of samples (Lemine and Alyamani 2012).

As could be seen from the previous section, water-entrapped silica particles could be applied to various types of cosmetic products. In order to achieve a cosmetic with unique character. In addition, the valuable active substance could also be incorporated in particles as a value-added product. Additional ingredients at 25 %

(by weight) could be incorporated and yield a product with desired characteristics. Example of substance incorporated were colors, nylon-12, boron nitride, PMMA or methyl methacrylate crosspolymer. This particle could be added to the cosmetic formulation for the purpose of coloring effect, makeup effect, ultra-violet radiation shielding effect. In addition, feel adjustment effect could be composed such as inorganic particles, photoluminescent particles or organic particles. As these particles, particles exhibiting hydrophobicity, hydrophobic particles further treated using a hydrophobicizing agent to increase the degree of hydrophobicity. As the hydrophobicizing agent, organic silicon compounds such as trymethylsilylization agent and methylhydrodiene polysyloxane, fluorine compounds such as perfluoropolyether alkyl phosphate and perfluoropolyether silane, metallic soaps, oil agents, and the like can be given. These agents may be used individually or in combination of two or more. For example, the mixing of hydrophobic silica powder with colors to create a unique eyeshadow with water-entrapped silica particle. This eyeshadow may have ordinary exterior, but then went on smoothly and stay very well when pressed gently around the eye. It is due to the release of entrapped color liquid, making it a unique eyeshadow. In addition, cooling and refreshing the skin without being greasy or sticky was presented (Figure 6,7) (Yoichiro et al., 2002 and Igarashi et al., 2008).

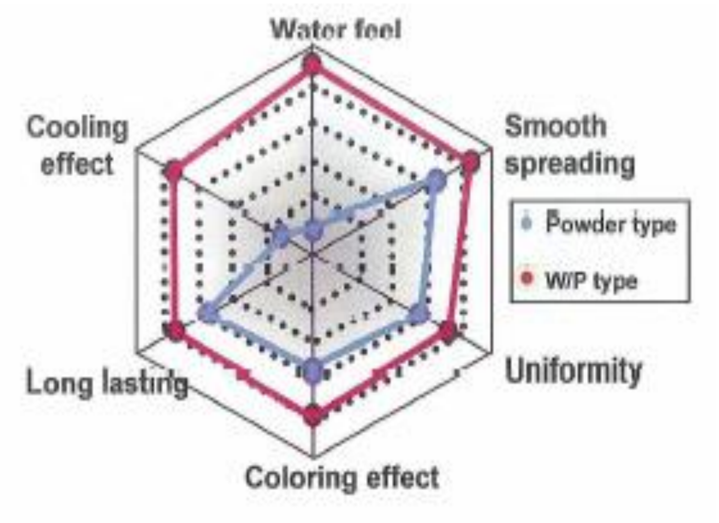


Figure 6 The characteristic of the W/P type cosmetic (Igarashi et al., 2008).

Figure 7 The coloring effect of each eye shadow type (Igarashi et al., 2008).

Water-entrapped silica particles could be also applied in different types of cosmetic such as a loose face powder that finally transformed in to liquid form itself with better coverage effect. It may know as a powder to liquid foundation providing long lasting effect (Lahanas et al., 2001). For powder based skin care product, whitening active ingredients were also incorporated with water-entrapped silica particles, the particles helped moisturizing the facial skin while maintained the stability of active ingredients such as sodium ascorbyl phosphate (Yoichiro and

Junichiro 1998). Antiperspirant powder with water-entrapped silica particles could store aluminium zirconium tetrachlorohydrexgly within particles, the product provided a cool and comfortable touch on the body including underarm or feet (Lahanas et al., 2001). For sunscreen products containing sunscreen-entrapped silica particles, the dry powder would release water-soluble sunscreen when applied on the skin, making skin cooled and refreshed without being greasy like other products (Lahanas et al., 2001).

Typically, face powder is consisted of silica at 3 to 40% by weight depending on the purpose of product (Sivamani et al., 2015). HD powder from Makeup forever is consisted entirely of silica without talcum in formulation (Makeupforever 2016). However, safety regulation of silica usage TRGS 900 indicates the concentration regulatory exposure limit at 4 mg/m^3 (Cabot Corporation 2015). Applying water-entrapped silica particle into the facial powder would reduce the amount of silica usage in production, hence should bring a positive effect for the human respiratory health system.

The preparation method of water-entrapped silica particle in face powder could be done through the method of Lahanas et al., (2001), which was simple, easy, and only required a single shear blender. It would be started by mixing all the dry ingredients together and then added liquid at the last step. This method seemed to be simple and easy. However, it was not a perfect solution because the liquid could be absorbed by other dry components including silica. If there was another efficient way to prepare loose face powder containing with perfect structure of water-entrapped, the product is more elegance, luxurious and valuable.

CHAPTER III

MATERIALS AND METHODS

Materials

- Aerosil® R812S	(Lot. No. 154091835, Evonik Degussa, Germany)
- OTS-2 Talc JA46R	(Lot. No. K-96226, Daito Kasei, Japan)
- OTS-2 Mica Y-2300	(Lot. No. K-25240, Daito Kasei, Japan)
- OTS-2 Titanium dioxide CR-50	(Lot. No. K-43410, Daito Kasei, Japan)
- OTS-2 Yellow LLXLO	(Daito Kasei, Japan)
- OTS-2 Red R-516L	(Daito Kasei, Japan)
- OTS-2 Black BL-100	(Daito Kasei, Japan)
- Squalene	(Sophim, France)
- Deinoized water	

Equipment

- Analytical balance 5 digits	(XP205, Mettler Toledo, Switzerland)
- Analytical balance 3 digits	(ME303, Mettler Toledo, Switzerland)
- Analytical balance 2 digits	(PB3002, Mettler Toledo, Switzerland)
- Low shear mixer	(IKA®-WERKE, EUROSTAR digital, Germany)
- High shear mixer	(ROH-FP135, Ronic, France)
- Tumble mixer	
- Mini spray gun	(F-2, WUFU, China)
- Thermogravimetric analysis	(SDTA851^{e}, Mettler Toledo, Switzerland)
- Moisture balance	(HR83, Mettler Toledo, Switzerland)
- Light microscope	(Model C-SHG, Nikon, Japan)
- Tapped density tester	
- Field Emission Scanning Electron Microscope (FE-SEM)	(JSM-7610F, JEOL, Japan)
- Hot air oven	(Model UL 80, Memmert, Schwabach, Germany)
- Hot air oven	(Model KBF 720, Memmert, Schwabach, Germany)

Methods

1. Preparation of water-entrapped silica particles

1.1 Selection of the appropriate method of preparation of water-entrapped silica particles

The prototype of water-entrapped silica particles consisted of 5% R812S and 95% by weight of DI water (Forny et al., 2007). In term of the preparation method, shear force and the method of water addition were two key parameters. In this study, three different methods were compared and are shown as follows:

1.1.1 Low shear with water added all at once

Water-entrapped silica particles was produced by using a lab mixer stirrer (EUROSTAR digital, IKA®-WERKE, Germany). The beaker was loaded with 1 g of R812S and 19 g of DI water. Mixing was achieved at constant speed 1,000 min^{-1} for 40 s.

1.1.2 High shear with water added all at once

Water-entrapped silica particles was produced using a rotating knife-blade blender (ROH-FP135, Ronic, France). The mixing bowl was loaded with 1 g of R812S and 19 g of DI water. Mixing was achieved at constant speed 4,000 min^{-1} for 40 s.

1.1.3 High shear with water atomization (F-2, WUFU, China)

The mixing bowl was loaded with 1g of R812S and 19 g of DI water via atomizer during mixing at constant speed 4,000 min^{-1} for 50 s.

It was visually observed by naked eye. The criteria of acceptable water-entrapped silica particles produced was declared as no leaking of water incorporated, free flowing including no aggregation. It should also hold the water droplet and easily later released the encapsulated water after pressure applied. Furthermore, the perfectness of water-entrapped silica particles was clearly observed from the absence of residual water droplet on the inner surface wall of mixer during and after processing. Water-entrapped silica particles produced was kept into a foil bag in order to avoid the possibility of water evaporation during storage. Acceptable water-entrapped silica particles was further characterized according to the topic 2.1-2.5.

1.2 The effect of different weight ratios between R812S and DI water on water-entrapped silica particles formation

From the result in 1.1, the appropriate method of preparation was obtained. Then, the effect of R812S and DI water ratio was studied by varying the weight ratio between R812S and DI water and fixing total weight of ingredients prepared in each time. The composition of each formulation is presented in Table 1.

Table 1 Formulation of water-entrapped silica particles with different weight ratios between R812S and DI water.

Ingredients	% w/w				
	W1	W2	W3	W4	W5
R812S	1	2	3	4	5
DI water	99	98	97	96	95

It was prepared according to the suitable process from the result on topic 1.1. The criteria of acceptable water-entrapped silica particles produced was the same as described in topic 1.1. Moreover, it would be further characterized according to the topic 2.1-2.5.

2. Characterization of water-entrapped silica particles

2.1 Physical appearance (Forny et al., 2007)

Visual observation of the acceptable water-entrapped silica particles was performed by naked eye. The water-entrapped silica particles would be spread over a white paper to investigate the perfectness of water-entrapped silica particles. Water-entrapped silica particles produced should provide no leaking of water incorporated and no aggregation of particle.

2.2 Water entrapment efficiency (Fielden et al., 1988)

Efficiency of water entrapment of water-entrapped silica particles was determined by using thermogravimetric analysis (TGA). Approximately 10 mg of sample was accurately weighed into alumina crucible and was then heated from 25 to 200°C at the heating rate of 10°C/min with purge gas of nitrogen at 50 ml/min. The weight loss at steady state was recorded. The water entrapment efficiency (%EE) was calculated according to Equation (3).

$$\%EE = \frac{W_s}{W_i} \times 100 \tag{3}$$

Where W_s is the weight loss at steady state and W_i is the initial water weight of water-entrapped silica particles sample.

2.3 Particle size and size distribution (ASTM E1382-97, 2010)

Particle size and size distribution of water-entrapped silica particles were analyzed by using optical microscope (400x magnification) calibrated with a stage micrometer. Gently sprinkle the water-entrapped silica particles sample over the glass slide was performed and subjected under optical microscope. The diameter of 500 water-entrapped silica particles was determined and calculated to provide a mean with standard deviation of diameter and the size distribution of particle.

2.4 Flowability (Forny et al., 2007)

Flow properties of water-entrapped silica particle was evaluated from the relationship between bulk density and tapped density of the sample by using a tapped density tester. A 50 ml cylinder was filled with 20 g of the sample. It was then progressively tapped until the final volume was constant (around 480 taps). The compressibility index (%CI) could be then calculated as Equation (2).

The calculated %CI was compared to the criteria of USP 34/NF 29 (Table 2) in order to define the flow character of a sample.

Table 2 Flow property criteria (USP 34/NF 29)

Compressibility index	**Flow property**
≤10	Excellent
11-15	Good
16-20	Fair
21-25	Passable
26-31	Poor
32-37	Very poor
>38	Very, very poor

2.5 Surface morphology of water-entrapped silica particles (Forny et al., 2007)

Surface appearance of water-entrapped silica particles was visually observed by Field Emission Scanning Electron Microscope (FE-SEM) (JSM-7610F, JEOL, Japan). A sample powder was randomly deposited on carbon tape placed on stub. Before imaging, the prepared sample was underwent gold metallization in order to improve picture resolution. The photomicrograph was taken at accelerating voltages of 2.00 kV with Secondary Electron Image probe (SEI) and the Gentle Beam (GB) mode.

3. Stability of water-entrapped silica particles

Eventhough water-entrapped silica particles produced was initially screened as no leaking of water incorporated and no aggregation, long term stability of water-entrapped silica particles produced was also investigated. Primary screening criteria of the appropriate formulation were %EE of more than or equal to 95% including %CI of less than or equal to 25%. It was then kept in a sealed foil and stored under three different conditions as follows: ambient condition (25±2°C / 60±5 %RH), 40±2°C / 75±5 %RH and 30±2°C / 75±5 %RH for 1, 3 and 6 months.

In order to observe the stability, the physical appearance, water entrapment efficiency, particle size and size distribution and flowability were considered followed topics 2.1, 2.2, 2.3 and 2.4., respectively.

The specification for stability study had been declared as:

- In term of physical appearance, it should be no leaking of water incorporated and no aggregation.

- For water entrapment, the %EE should also be more than or equal to 95%.

- The flowability was evaluated as %CI that should be less than or equal to 25%.

- Acceptable specification of particle size and size distribution was a diameter range of approximately 20 to 200 μm including monodistribution character.

4. Development of loose face powder containing water-entrapped silica particles

4.1 Selection of the appropriate method of preparation of loose face powder containing water-entrapped silica particles

The basic formulation of loose face powder was selected. It was prepared by the powder blending of ingredient lists in Table 3 (อรัญญา มโนสร้อย 2533). Incorporation of water-entrapped silica particles which was passed the stability study was performed. The prototype formulation in this study comprised of water-entrapped silica particles and basic loose face powder. The weight ratio between water-entrapped silica particles and basic loose face powder was 40:60. The ingredient lists of the prototype formulation are presented in Table 4.

Table 3 Formulation of basic loose face powder.

Ingredients	Function	% w/w
Talcum	Bulking agent	70
Mica	Filler	20
Titanium dioxide	Covering agent	10
Color	Coloring agent	qs.

Table 4 Prototype formulation of loose face powder containing water-entrapped silica particles.

Ingredients	% w/w
Talcum	38.11
Mica	10.89
Titanium dioxide	10
Color	1
Water-entrapped silica particles	40

In this study, two different preparation methods were proposed and investigated which were shown as below:

4.1.1 Single step process

Adapted from Lahanas et al., (2001), basic loose face powder was prepared by mixing talcum, mica, titanium dioxide and color in high shear mixer at constant speed of mixing at 4,000 rpm for 40 seconds. Periodically color uniformity checking was performed by scooping out and spreading the sample over white and clean paper. If the pigment was not evenly distributed or lumpy of pigment existed, further mixing for 10 seconds was operated. Rechecking the color uniformity has been done until the homogeneous color powder was achieved. R812S was then added into the mixing bowl with 20 seconds of mixing. Finally, DI water was poured all at once with a mixing time of 30 seconds.

4.1.2 Multiple step process

Water-entrapped silica particles was initially prepared with high shear force using the same method as described earlier. Meanwhile, basic loose face powder was obtained by simple mixing of talcum, mica, titanium dioxide and color in high shear mixer as conducted in 4.1.1. Both compositions were blended together in low shear mixer (tumble mixer) at specified mixing time of 1, 3, 5, 7, 9 and 11 minutes. At different mixing time, the sample was investigated in term of color uniformity and %EE. The mixing time which provided the sample with better color uniformity and the %EE of more than 80% was determined. The criteria of 80% EE was indicated the result of organoleptic testing. High %EE (≥80% EE) would provide an touchable feeling of cooling burst.

To evaluate the suitable preparation of method of loose face powder containing water-entrapped silica particles, the sample powder after mixing was tested by the characterization according to 4.3.1, 4.3.2 and 4.3.3.

The test specification of loose face powder containing water-entrapped silica particles should be good color uniformity with no aggregation. The encapsulated water should be easily released after applied on the skin. The feeling after applied would be dusty with no wet appearance. In addition, water-entrapped silica particles structure needed to be existed after mixing.

4.2 The effect of different amounts of water-entrapped silica particles incorporated into basic loose face powder formulation

From the result in 4.1, the appropriate method of preparation was obtained. Therefore, the effect of the weight ratio between water-entrapped silica particles and basic loose face powder on the properties of loose face powder containing water-entrapped silica particles was proposed at 40:60, 30:70, 20:80 and 10:90 weight ratio. In term of the basic loose face powder component, titanium dioxide and color pigment was remained constant at 10 and 0.1% w/w while the quantity of talc and mica was varied but the weight ratio was maintained. The final formulation is shown in Table 5.

Table 5 Formulation of loose face powder containing water-entrapped silica particles.

Ingredients	% w/w			
	LW 1	LW 2	LW 3	LW 4
Talcum	38.11	45.89	53.67	61.45
Mica	10.89	13.11	15.33	17.55
Titanium dioxide	10	10	10	10
Color	1	1	1	1
water-entrapped silica particles	40	30	20	10

Characterization of loose face powder containing water-entrapped silica particles (LW 1 to LW 4) was performed as described in 4.3.1 and 4.3.2.

4.3 Characterization of loose face powder containing water-entrapped silica particles

4.3.1 Physical appearance

Visual observation of the loose face powder containing water-entrapped silica particles was performed by naked eye. The sample would be further spread over a white and clean paper to clearly investigate the perfectness of formulation. The physical appearance of finished product must be good color uniform powder with no aggregation of particle.

4.3.2 Physical appearance after applied on the skin

Approximately 0.5 g of loose face powder containing water-entrapped silica particles was accurately weighed and applied on the area behind the palms by blush brush. The feeling after applied would be dusty with no wet appearance but good adhering. The water was easily released after applied which eventually provided a burst cooling sense with moisturizing effect. The degree of cooling burst sense was recorded by scoring. The number of + represents the effect of cooling burst sense after applied (+: Feel a bit cooling burst, ++: Feel cooling burst, +++: Cooling burst obviously and -: Not feel cooling burst).

The formulation which conformed both 4.3.1 and 4.3.2 criteria was further characterized below.

4.3.3 Surface morphology of loose face powder containing water-entrapped silica particles, followed topic 2.5.

4.3.4 Water entrapment efficiency

Efficiency of water entrapment in the loose face powder containing water-entrapped silica particles produced was proceeded by using moisture balance. Approximately 0.5 g of sample was accurately weighed and transferred to the sample pan. It was then heated from 25 to 105°C and held at that temperature for a period of time until constant weight reached. The weight loss at steady state was monitored. The percent entrapment efficiency (%EE) of water was calculated according to Equation (3).

4.3.5 Particle size and size distribution of loose face powder containing water-entrapped silica particles followed topic 2.3.

4.3.6 Flowability of loose face powder containing water-entrapped silica particles was evaluated as the method described in topic 2.4

4.3.7 Oil absorption property (ASTM D281-95, 2002)

In order to evaluate the oil absorption property, approximate 1.0 g of sample was accurately weighed and placed on a slab. Squalene, sebum representative molecule, was dropwise added into the powder sample. Thorough incorporation of squalene was done by rubbing up with a spatula. The end point of the test was found when squalene had been incorporated completely which could be seen from the very stiff, putty-like paste with no oil leakage. Percentage of oil absorption was calculated by comparing the number of grams of squalene required to exactly wet a 100 grams of sample.

Positive control of this evaluation was required to determine oil absorption property. It was the mixture of all ingredients that existed in test formulation without water. They were prepared by simple mixing until well blended. The oil absorption of the positive control was conducted with the same method as described above. Difference of oil absorption capacity between the test formulation and a positive control would be evaluated for the effect of water-entrapped silica particles structure.

4.4 Stability of loose face powder containing water-entrapped silica particles

Before going to investigate long term stability of loose face powder containing water-entrapped silica particles, the appropriate formulation should be evaluated. Such formulation would be the loose face powder that contained existing water-entrapped silica particles. The physical appearance of finished product must be good color uniform powder. It also provided the burst cooling effect from the water encapsulated after applied on the area behind the palms by blush brush. Dusty like with no wet feeling would be occurred after applied as well. The character of powder was found to be free flowing, no leaking of water incorporated. In term of oil absorption capacity, the acceptable product should show such value higher than or at least equal to that of its positive control.

When comparing with water-entrapped silica particles stability testing, loose face powder containing water-entrapped silica particles was kept into a plastic jar under 40±2 °C / 75±5 %RH for a period of three months. The study was done at initial, 1 and 3 months in order to assess the physical appearance of both before and after applied on the area behind the palm, water entrapment efficiency, particle size and size distribution, flowability and oil absorption property as followed in topic 4.3.1, 4.3.2, 4.3.4, 4.3.5, 4.3.6 and 4.3.7, respectively. The stability of a control group, pure water-entrapped silica particles kept in a plastic jar, was also investigated and employed as a reference.

5. Statistical analysis

All experiments were triplicate done and reported as mean ± standard deviation. Statistical data were analyzed by Independent-Samples T-test, One Way ANOVA with Tukey's post-hoc test at the level of *p*-value < 0.05.

CHAPTER IV

RESULTS AND DISCUSSION

1. Preparation of water-entrapped silica particles

Water-entrapped silica particles could be commonly prepared by simple mixing process. However, a few parameters were governed on the formation of water-entrapped silica particles. The magnitude of shear force and the incorporation method of water were critically concerned on the preparation of water-entrapped silica particles.

Three different processes which combined difference of shear force and method of water incorporation were designed and used to prepare water-entrapped silica particles in this studies. The physical appearance of mass gained from different methods are shown in Figure 8. The result obtained from low shear with water added all at once showed an unacceptable product (Figure 8A). Phase separation was happened. R812S separated and floated over water both during and after mixing. In addition, water phase still sunk down at the bottom of the mixing bowl even the mixing time was increased. However, the process may be improved if the speed of mixing was achieved at above 1,000 rpm. Unfortunately, the result showed that R812S was scattered and the water phase still remained at the bottom of the mixing bowl. Our result was not in good agreement with the previous study (Saleh et al., 2011). It may be due to the dissimilarity of impeller geometry and efficiency. High shear mixer equipped with knife shape blade typically provided higher shear force than low shear mixer with 4 blades helix impeller.

When water-entrapped silica particles was produced by using high shear mixer with adding water all at once, the water-entrapped silica particles powder with a free flowing and no separation of R812S and water was observed. No trace of water was found during the transferring of the product from mixing bowl to storage container (Figure 8B). The encapsulated water could be easily released by rubbing on the skin. The process of high shearing with adding water all at once was assumed to be the suitable preparation method of water-entrapped silica particles since higher shearing action would sprit the whole volume of water into large drop which would be finally surrounded by the networking of R812S and air. This phenomenon was related to the balancing between the convective axial and radial mass flow. The higher the axial mass flow the more possible the formation of water-entrapped silica particles (Saleh et al., 2011). High shear blender in conjunction with liquid atomizer was expected to be able to better control the particle size and shape of the water-entrapped silica particles produced. The result revealed that the free flowing powder was not formed including water separation was found. In addition, the longer mixing time of up to 50 seconds provided white mousse texture floating on the top of water added (Figure 8C). It might be according to the formation of very fine water droplet from the synergistic effect of atomization and high shearing. Thus, it could potentiate the fusion of R812S particles itself including air entrapment which eventually resulted in a white floatable mousse. Additionally, the water was synchronously impeded, separated and laid down at the bottom.

Therefore, the most suitable method of preparation of water-entrapped silica particles was the utilization of high shear force with adding water all at once.

Figure 8 Physical appearance of water-entrapped silica particles containing 5% of R812S prepared with different methods: (A) Low shear mixer and adding water all at once, (B) High shear mixer and adding water all at once, and (C) High shear mixer with water atomization.

The surface morphology of water-entrapped silica particles indicated the core shell like structure which could be seen from FE-SEM photomicrograph (Figure 9). The FE-SEM on the right side showed a broken water-entrapped silica particles that revealed the empty core of the silica particulate which was occupied by water. It was the remarkable evidence to confirm the existence of silica networking layer surrounding the water droplet.

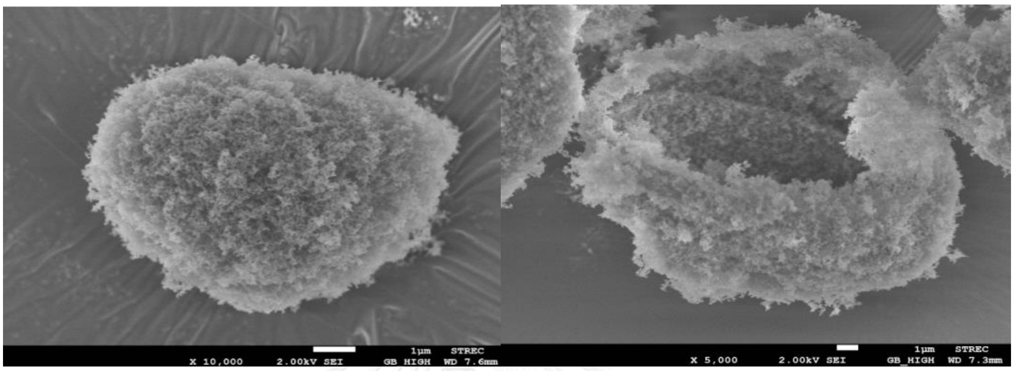


Figure 9 FE-SEM photomicrograph of water-entrapped silica particles containing 5% of R812S prepared with high shear force with adding water all at once.

The result from laboratory scale study showed that high shear blender with pouring whole water at once was successfully to be used for preparing water-entrapped silica particles. It provided a free flowing powder with no aggregation powder and also holding water inside that would be released upon application. Meanwhile, low shear mixer with water atomization was also possible to form water-entrapped silica particles for large scale preparation (Forny et al., 2007 and Saleh et al., 2011).

Nevertheless, another governing factor of the formation of water-entrapped silica particles was the ratio between hydrophobic silica and water. Forny et al., (2007) reported that water-entrapped silica particles produced from R812S at the concentration of 4 up to 10% by weight in conjunction with DI water were potentially prepared. The product from 4% R812S showed the high %EE of water which reflected to the complete encapsulation. It was found to be poor flow powder with %CI of 26. In addition, the particle size was in the range of approximately 20 to 400 µm. Somehow, the product characteristic produced from higher % of R812S hadn’t been reported. In other word, R812S should be reconsidered in term of toxicity via inhalation (Cabot Corporation 2015). Therefore, the lowest amount of R812S that could be used to prepare water-entrapped silica particles was the major concern in this study. The range of 1 to 5 % of R812S was hence observed.

Five different ratios between R812S and DI water were investigated on the possibility of the formation of water-entrapped silica particles. The acceptable criteria of water-entrapped silica particles produced were also indicated. Optimal ratio between R812S and DI water should be the ratio that provided completely formed water-entrapped silica particles with no leaking of water incorporated. Furthermore, it should provide the appearance of good powder with free flowing and no aggregation. It should also hold the water inside and easily released the encapsulated water after pressure applied. In term of the perfectness of water-entrapped silica particles, it was observed from the absence of residual water droplet attached the inner surface wall of mixer during and after processing.

From this study, the appearance of mass produced from different ratios between R812S and DI water are shown in Figure 10.

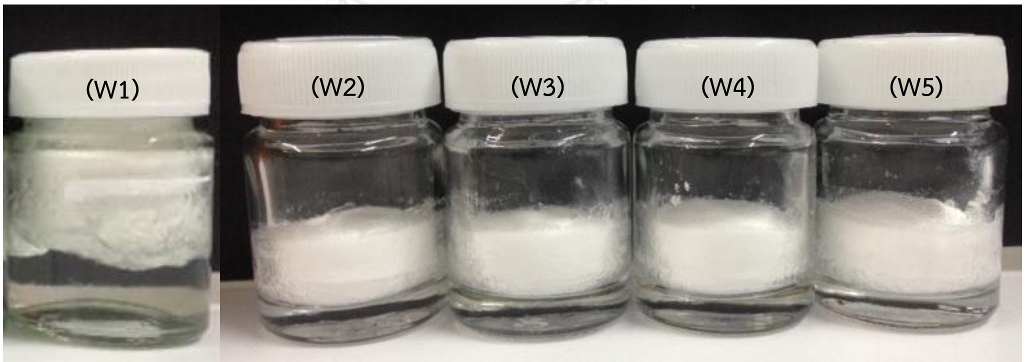


Figure 10 Physical appearance of water-entrapped silica particles produced with different weight ratio between R812S and DI water: (W1) 1:99, (W2) 2:98, (W3) 3:97, (W4) 4:96 and (W5) 5:95.

The result revealed that the mass gained from 1% of R812S did not succeed on the formation of water-entrapped silica particles due to unacceptable characteristics (Figure 10 (W1)). Free flowing powder was not formed including water separation was found. However, the processing condition in term of mixing time was limited at 40 seconds. Thus, it was hypothesized that longer mixing time might provide water-entrapped silica particles formation. To prove such hypothesis, further mixing time of 41 up to 70 seconds was observed. The result presented that white mousse texture which floated on the top of water added was seen. It might be due to the formation of a plenty of tiny water droplet from high shear inducing. Thus, it could potentiate the fusion of R812S itself including air entrapment which eventually resulted in a white floatable mousse. The amount of R812S in the system was not enough to hold the excess of water. The water droplet was later get together which separated and laid down at the bottom (Saleh et al., 2011). On the other hand, the physical appearance of water-entrapped silica particles containing 2 to 5% of R812S completely formed water-entrapped silica particles which could be observed from the powder with no leaking of water incorporated, free flowing powder and no aggregation (Figure 10 (W2-W5)). From this results, the optimal ratio between R812S and DI water was found to be 2:98 to 5:95 weight ratios.

In order to further evaluation of the optimal ratio between R812S and water, 4 different weight ratios were considered. The most important character of water-entrapped silica particles in our study should be the high efficiency of water encapsulation. The %EE was the representative value of water encapsulation when compared to the initial water added. The higher the %EE the more efficient the water encapsulation. The result of %EE of all weight ratio showed the high %EE (more than 95%) (Figure 11) (Appendix B). They were not significantly different. It was clearly demonstrated that almost of water added was fully encapsulated. The ratios between R812S and DI water of 2:98, 3:97, 4:96 and 5:95 seemed to be the acceptable ratios for water-entrapped silica particles preparation.

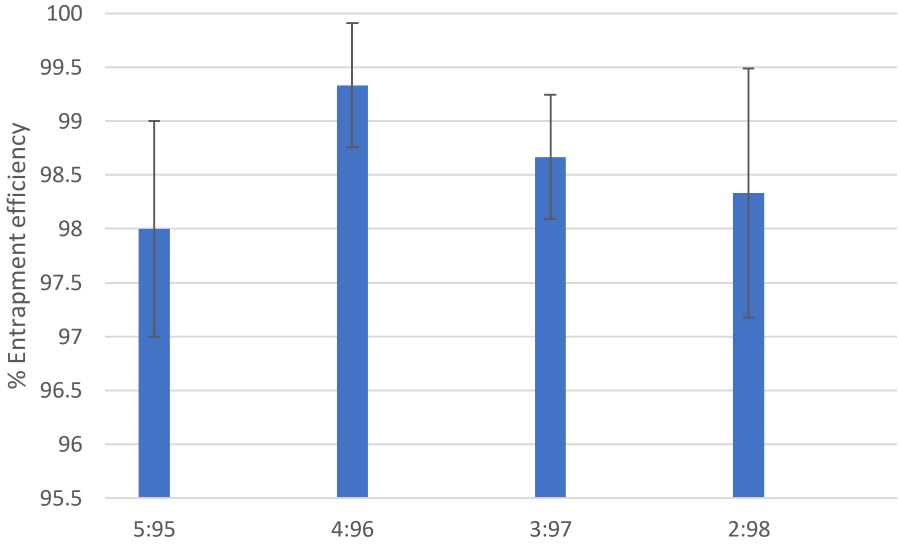


Figure 11 The water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water (mean ± SD, n=3).

However, the mass gained from all weight ratios presented the different powder characteristics. In this study, good flowable powder produced was more favorable. The value of %CI was introduced in order to evaluate the powder flow character. The higher the %CI the poorer the flow property. The %CI of water-entrapped silica particles produced with 5%, 4%, 3% and 2% of R812S was found to be 21.47±1.96%, 21.89±1.72%, 20.44±0.29% and 14.58±1.44%, respectively (Figure 12) (Appendix C).

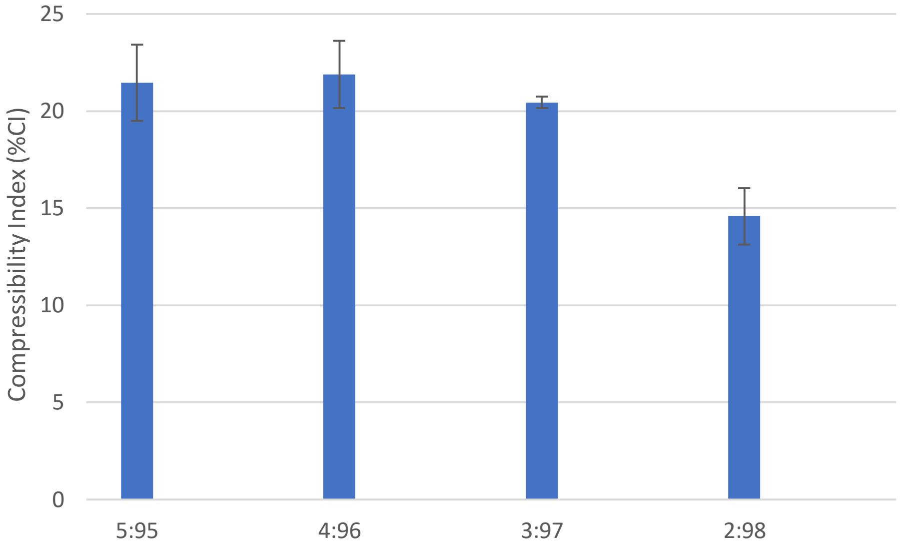


Figure 12 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water (mean ± SD, n=3).

The %CI of water-entrapped silica particles produced with 2% of R812S was around 15 meant good flow powder according to USP 34/NF 29 criteria. Meanwhile, water-entrapped silica particles produced with 3%, 4% and 5% of R812S were in the range of passable to fair flow powder. This result showed that %CI was affected from the amount of R812S used. At the lower amount of R812S, it was adequate to form a layer around water droplet and hold it inside with no more free R812S in the system. It was seen from the FE-SEM photomicrograph of water-entrapped silica particles produced (Figure 13B). Free R812S was not almost observed from the sample. Therefore, the electrostatic force between free R812S was less and eventually resulted in less friction with high flowability. Meanwhile, the higher the amount of R812S in system the more excess the free R812S (Figure 13A). It hence provided the more friction between free R812S itself and more impact on the flowability. Generally, not only the %CI that should be used to determine the flow property but the particle size and size distribution was also considered. The particle size and size distribution of all weight ratios were found to be in good agreement with microscopic observation. The particulate diameter was in the range of approximately 20 to 200 µm with similar monodisperse size distribution. Water-entrapped silica particles produced from 5%, 4%, 3% and 2% of R812S showed the mean and SD of 68.04 ± 3.23 µm, 79.92 ± 4.77 µm, 78.74 ± 9.16 µm and 90.88 ± 8.36 µm, respectively (Figure 14). It was clearly demonstrated that 5% R812S had the lowest particle size which commonly provided poor flowability nature. While the remaining of 3 different ratios showed the insignificant particle size and eventually gained a better flow.

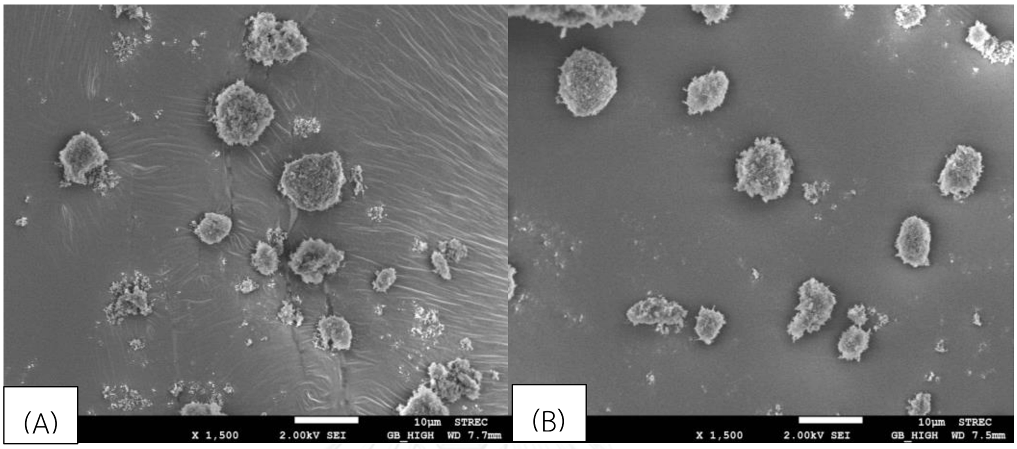


Figure 13 FE-SEM photomicrograph of water-entrapped silica particles produced with different ratios between R812S and DI water: (A) 5:95 and (B) 2:98.

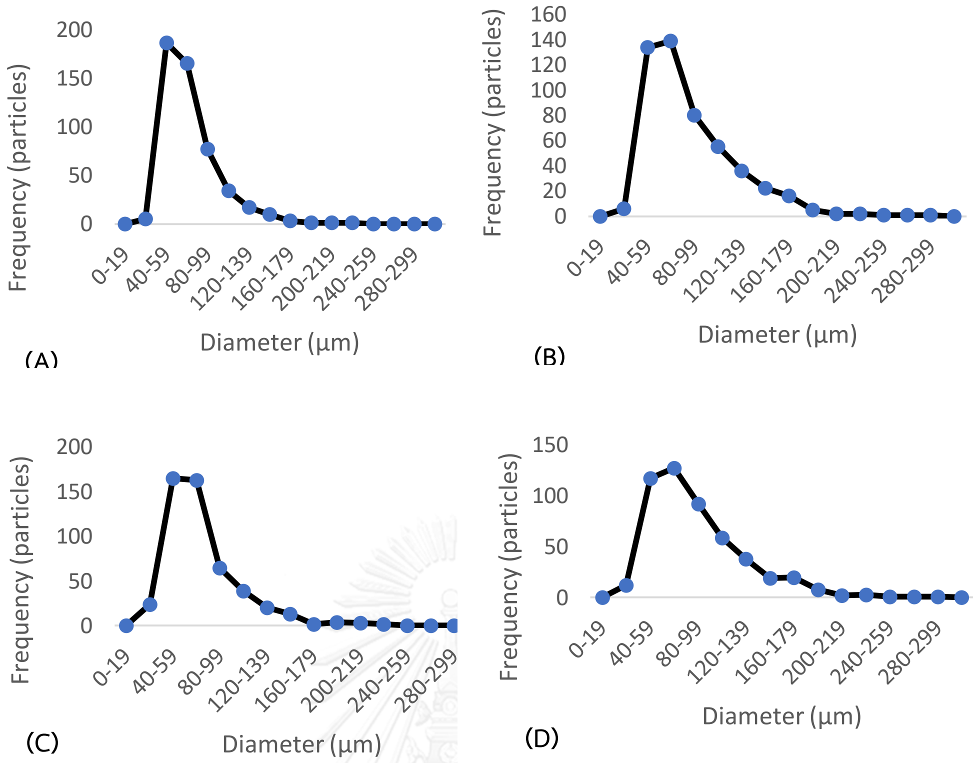


Figure 14 Particle size and size distribution of water-entrapped silica particles produced with different ratios between R812S and DI water: (A) 5:95, (B) 4:96, (C) 3:97 and (D) 2:98.

The surface morphology of water-entrapped silica particles revealed the core shell like structure which could be seen from FE-SEM photomicrograph (Figure 15). The photomicrograph on the left hand side showed the whole encapsulated particle. The outer surface of water-entrapped silica particles was composed of the assembly of R812S particle. On the right hand side of Figure 15, it showed a broken water-entrapped silica particles that represented the empty core of the R812S particulate which occupied water droplet internally. It was the remarkable evidence to confirm the existence of silica networking layer surrounding the water droplet or the formation of water-entrapped silica particles. Further evidence that indicated the encapsulation of water inside water-entrapped silica particles was observed using light microscope (Figure 16). Water-entrapped silica particles was initially subjected under light microscope. The physical appearance of water-entrapped silica particles was recorded as seen in Figure 16A. The turbid agglomerated particle was observed. When the observing time passed, such agglomerated particle was clearer or less turbid with shrinkage in size of agglomerate (Figure 16B and 16C). It was due to the evaporation of volatile substance or water in this situation after the temperature of light beam was accumulated. Thus, the final product of this experiment should be the agglomerate of R812s containing water inside.

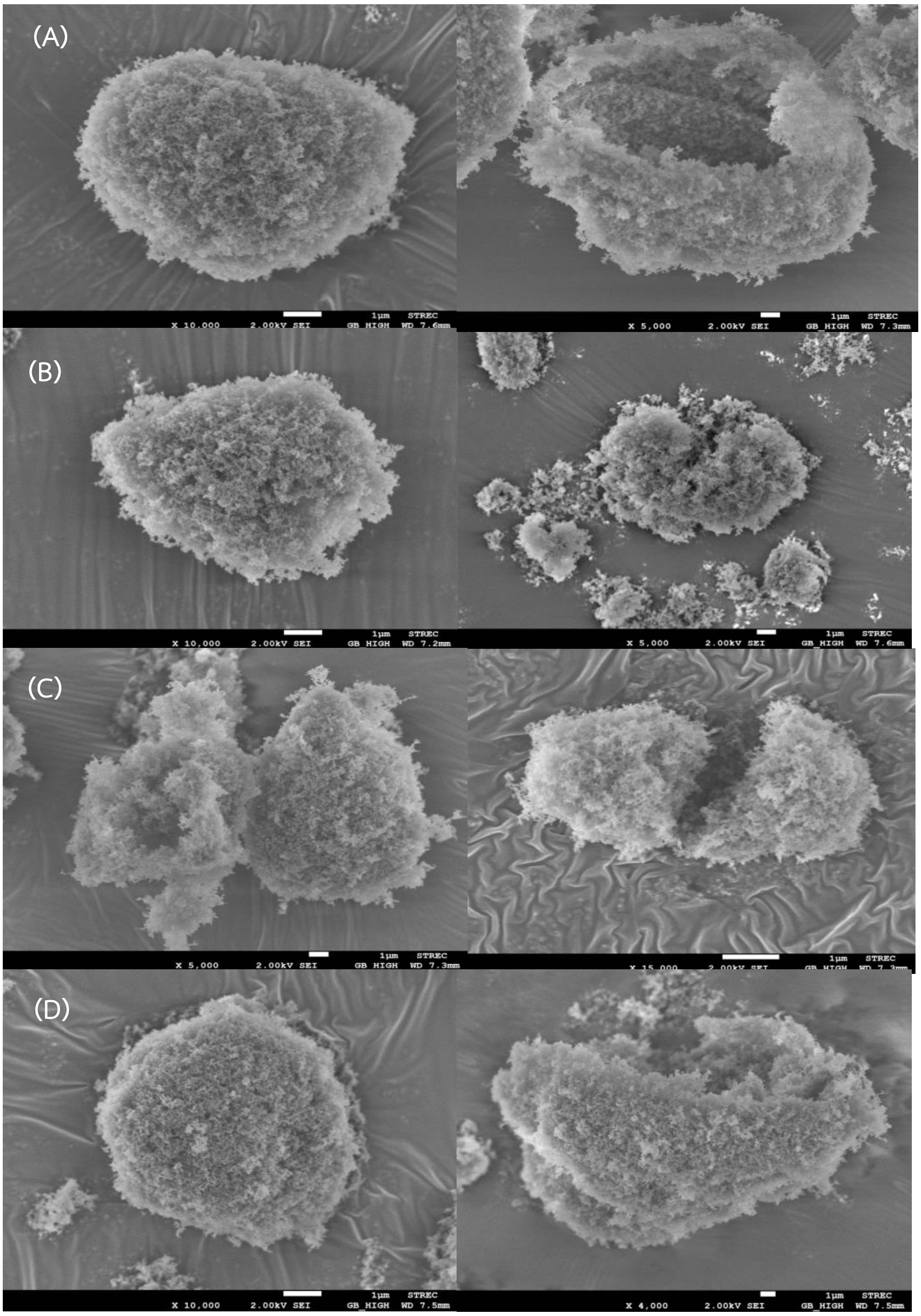


Figure 15 FE-SEM photomicrograph of water-entrapped silica particles produced with different ratios between R812S and DI water: (A) 5:95, (B) 4:96, (C) 3:97 and (D) 2:98.

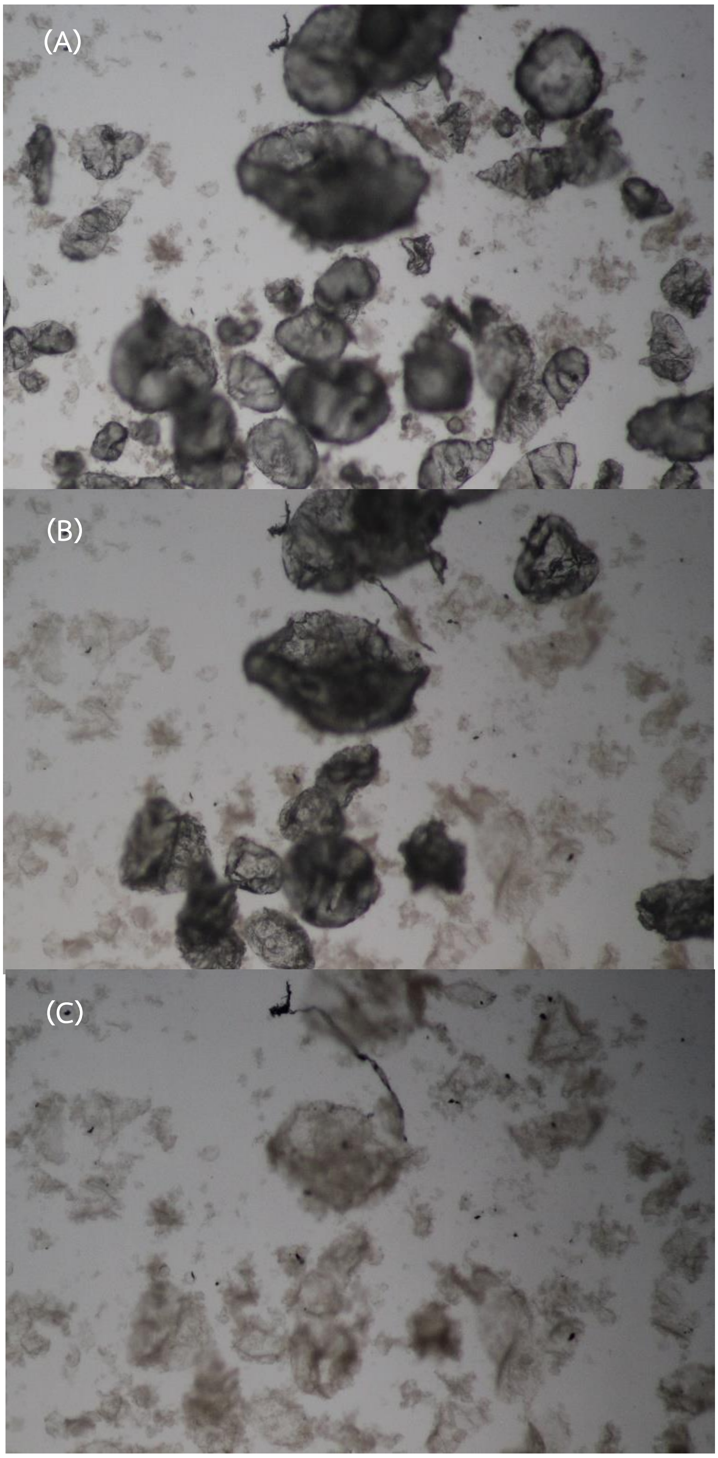


Figure 16 The photomicrograph of water-entrapped silica particles produced with 2% of R812S under light microscope: (A) initials rate, (B) 20 seconds of light exposure and (C) 40 seconds of light exposure.

Conclusively, water entrapped silica particle with 5% R812S have poor flow due to the excess of free R812S with smaller particle size. Whilst, 2 to 4% of R812S showed all acceptable characters of high %EE, free flowing and good physical appearance. They were then investigated in term of stability.

2. Stability of water-entrapped silica particles

Acceptable 3 different weight ratios between R812S and water of 4:96, 3:97 and 2:98 were investigated for the physical stability as described in the previous section. The physical appearance of water-entrapped silica particles after storage under three different conditions are shown in Table 6.

The stability data showed an unacceptable physical stability at the end of the stability studies (6 months). The water encapsulated of all formulation were squeezing out and obviously separated. Therefore, water-entrapped silica particles produced from this study was not appropriate to keep for more than 3 months. Focusing on the 3 months stability, 2% R812S prone to unstable due to the existing of water separation. The degree of physical instability was less when R812S was used more. The lower amount of R812S used might be sufficient to form water-entrapped silica particles after freshly prepared but not adequate to retain such core shell structure when temperature and humidity was changed over storage time. Consequently, the water could not hold internally and might migrate to the outside of the water-entrapped silica particles. It was thus provided the lower %EE (Figure 17C) (Appendix E). From the stability data, 2% R812S was not suitable for introducing in the preparation of loose face powder.

On the other hand, 3 and 4% R812S should be the good candidates for the next studies. It was due to the good physical stability within 3 months (Table 6). Slightly scattered of less water droplet was observed in the powder sample. The %EE of both weight ratio was found to be not less than 95%. The change of %EE over storage time under three different conditions negligibly decreased (Figure 17A and B) (Appendix E). Meanwhile, the powder characteristic in term of flowability was considered. The determination of particle size change of water-entrapped silica particles from both R812S concentrations were clearly observed (Figure 18). They found to be smaller (lowest at 60 µm) when comparing with initial size after freshly prepared (80 µm). It was the reason of the loss water inside that eventually providing the more free R812S in the system. The higher free R812S particle directly impacted on the higher friction force and lower flowability. However, it should be taken in to consideration with other value that reflect to the whole characteristic of powder flow such as %CI. The %CI of both concentrations of R812S were categorized as fair flow (Figure 19) (Appendix F). In addition, they were not critically changed even after storage up to 3 months. Hence, both concentrations of R812S could be used as a model water-entrapped silica particles for the preparation of loose face powder containing water-entrapped silica particles. Regarding the toxicity of fumed silica, several articles recommended the lowest level of silica used (as possible) in order to obtain the inhalation safety concerned (Cabot Corporation 2015). In this study, we selected only 3% R812S as the model due to the lower amount of silica used.

Table 6 Physical appearance of water-entrapped silica particles storage under three different conditions in 6 months (n=3).

Ratio of R812S: water	1 month									3 months									6 months								
	Ambient			30°C/ 75% RH			40°C/ 75% RH			ambient			30°C/ 75% RH			40°C/ 75% RH			ambient			30°C/ 75% RH			40°C/ 75% RH		
	N1	N2	N3	N1	N2	N3	N1	N2	N3	N1	N2	N3	N1	N2	N3	N1	N2	N3	N1	N2	N3	N1	N2	N3	N1	N2	N3
4:96	-	-	-	-	-	-	-	-	-	+	-	+	+	-	+	-	+	-	-	-	+++	+++	-	++	-	+++	-
3:97	-	+	-	-	+	-	-	-	-	-	+	-	-	+	-	-	-	-	+	-	+	+++	++	-	-	+	+
2:98	+	-	+	-	+	-	-	++	-	++	-	++	+++	++	++	++	++	++	-	++	++	+++	+++	+++	++	-	-

The number of + represents the number of free water droplet found in the sample

+: Small water droplet with less amount scattered

++: Small water droplet with more scattered throughout the sample

+++: Water separation from the powder

-: Unchanged sample

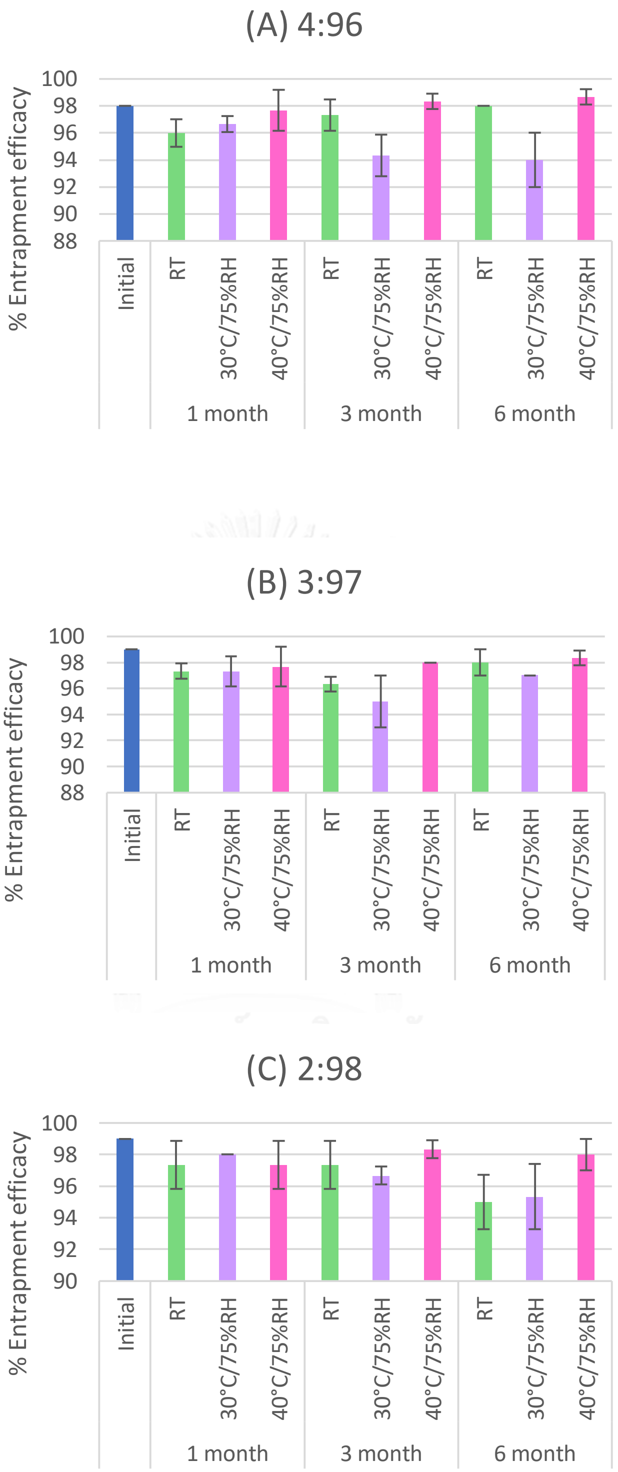


Figure 17 Water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water after storage under three different conditions (mean ± SD, n=3).

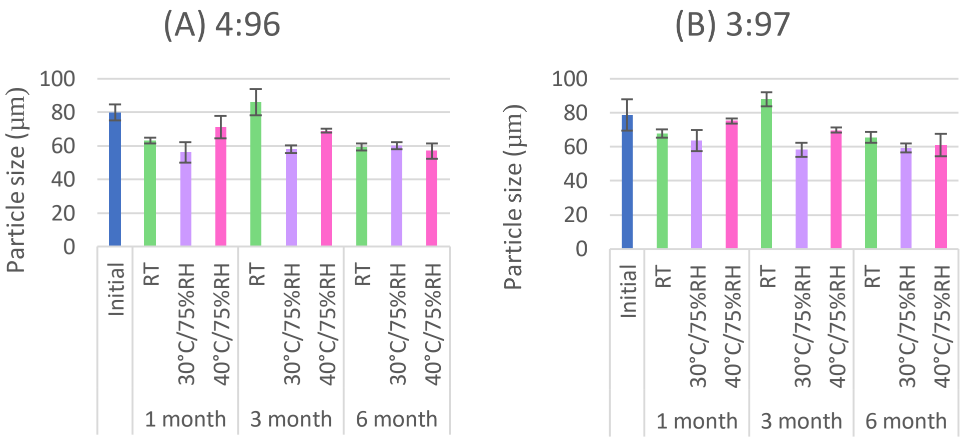


Figure 18 The particulate diameter of water-entrapped silica particles produced with different ratio between R812S and DI water after storage under three different conditions (mean ± SD, n=3).

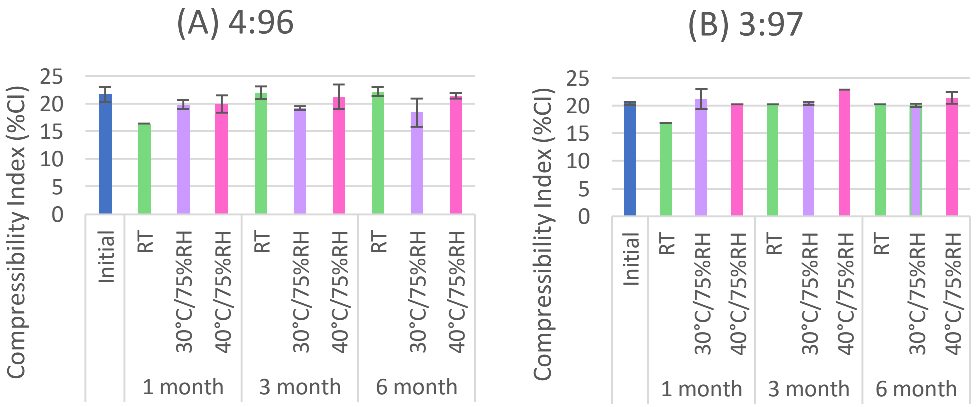


Figure 19 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water after storage under three different conditions (mean ± SD, n=3).

3. Development of loose face powder containing water-entrapped silica particles

Water-entrapped silica particles was the core shell like structure which held the water internally by the assembly of hydrophobic silica particles around the water droplet. It could not permanently encapsulate the inner core of liquid due to the force sensitive shell. Water-entrapped silica particles's shell was formed by the interaction of weak interparticulate forces such as van der Waals force (Forny et al., 2007). Therefore, it would be destroyed easily when outer force reaction introduced. It was clearly observed when water-entrapped silica particles was applied on the area behind palm by blush brush, burst cooling sense from water was recognized when compared to R812S particle without water. Water-entrapped silica particles could be developed as many of cosmetic products such as loose face powder. If water-entrapped silica particles needed to be mixed with other powders, the mixing process should be designed. Thus, the method of preparation of loose face powder containing water-entrapped silica particles would be investigated.

Two different methods of preparation was proposed. Single step of blending of all ingredients from basic loose face powder formulation and water-entrapped silica particles were combined together (Lahanas et al., 2001). Meanwhile, another preparation method was the multiple step process of the making of basic loose face powder prior to add water-entrapped silica particles. First method was investigated due to simple and ease to handle process including several economic advantages e.g. non time consuming and uncomplicated. The second one was tailor made in accordance with the sensitivity to break of water-entrapped silica particles's shell. Loose face powder typically comprised of inorganic materials such as titanium dioxide, talc and/or mica with pigments. High shearing process was necessary to apply for preparation in order to provide the uniform distribution of pigment throughout the powder blend. Hence, single step process might not be the suitable method of preparation in this case due to the required of high shear that might be impact on the retaining structure of water-entrapped silica particles. Multiple step process was then generated by the better protection of water-entrapped silica particles structure from the high shear-related process. The process of high shear was only used with basic loose face powder preparation until well blend of pigment was gained. Later, very low shear mixing process such as tumbling was then employed to blend the above powder with water-entrapped silica particles. Mixing time of such process should be optimized because the longer the mixing time the higher the destroying of water-entrapped silica particles structure from particle collision.

Selection of the best method of preparation of loose face powder containing water-entrapped silica particles was studies. The result suggested that the final product from the single step process was found to be the free flowing powder and acceptable color uniformity. It spilled over when applied on the skin with dusty texture and no adhesion. In addition, the cooling burst feeling was not observed but only moist feeling was recognized. It was due to no formability of water-entrapped silica particles in final product. The FE-SEM result showed the agglomerate of particle but not look like water-entrapped silica particles structure (Figure 20A). Thus, the optical microscope was further studied. The aggregate particle was also observed and still turbid with remaining in size of agglomerate after exposed to the light beam for a period of time (Figure 21A). That would be the good evidence of no water-entrapped silica particles formation. The explanation “why single step process was not suitable for this studies” was described hereinafter. Mixing of all ingredients of inorganic material with R812S would generate the free flowing powder. It was due to the gliding effect of R812S which adsorbed on other particles. When R812S was incorporated as dry powder into other powder mixed, R812S particle evenly distributed over a surface of other particles due to the small particle with high surface area. Friction between particles that were coated with R812S was eventually reduced and subsequently more easily sliding. The free R812S in above system was less from the surface adhesion effect. When water was added, no more R812S was adequate to form the water-entrapped silica particles’s shell structure. The non-encapsulated water was simultaneously absorbed with other inorganic materials such as talc and mica. So, the unbalance of the ratio between R812S and water was the reason that why water-entrapped silica particles could not be formed. In other word, it might propose that silica particle of R812S might have an interaction with octyltriethoxysilane surface treated titanium dioxide, mica and/or talcum via silanol group. Therefore, surface treated inorganic compounds would possibly intercalate in the R812S shell which eventually resulted in non-forming of encapsulated particles (Figure 22).

On the other hand, the loose face powder prepared with the multiple step process provided the color uniform powder. When applied this final product on the area behind the palms by blush brush, the feeling after applied was good adhesion with no wet appearance. The water was also easily released which eventually provided a burst cooling sense with moisturizing effect. In this case, the formation of water-entrapped silica particles was found. The FE-SEM result showed the agglomerated of particle that closely related to the water-entrapped silica particles structure (Figure 20B). Focusing on the surface texture of agglomerate, it was nearly identical to the networking of R812S. The optical microscope investigation further confirmed the existing of water-entrapped silica particles. Interested aggregate particle was less turbid with a reduced in size of agglomerate after exposed to the light beam for a period of time (Figure 21B). The clearer and shrinkage of aggregate particle was due to the evaporation water encapsulated. That was the water-entrapped silica particles character. On the contrary with single step process, this process did not need a plenty of free R812S during making process because the ready to use of water-entrapped silica particles was formerly produced before blending.

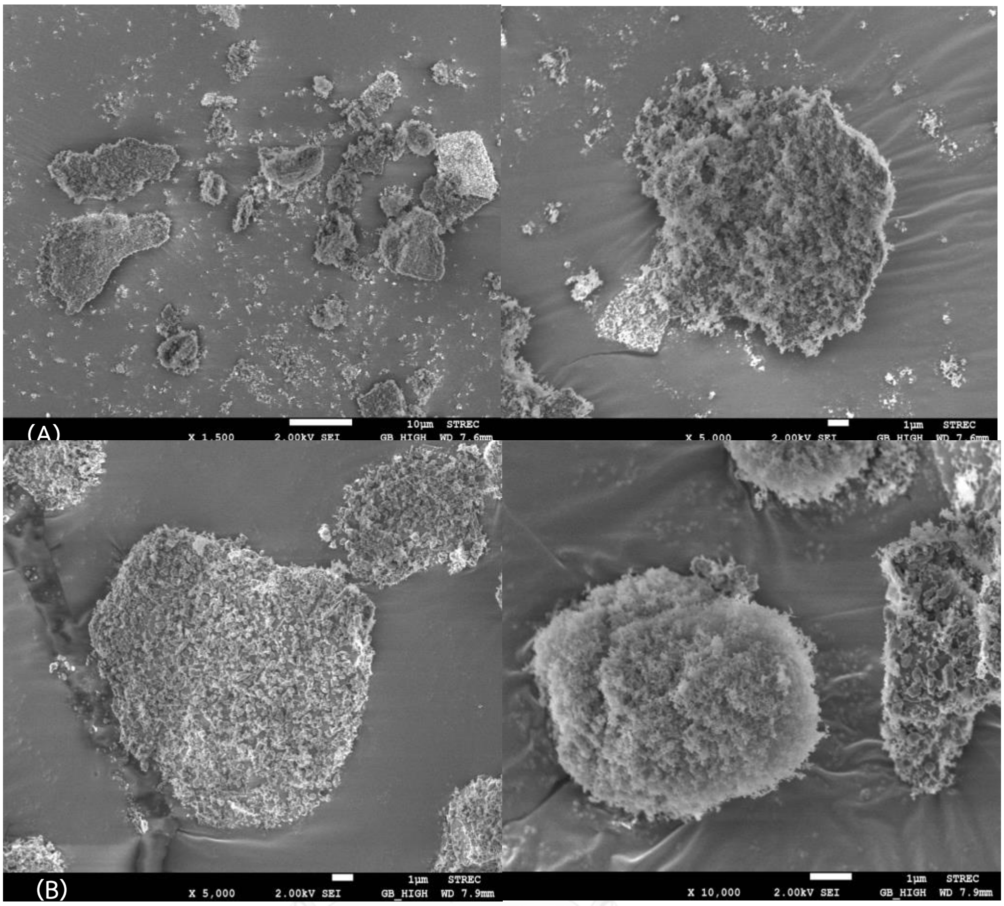


Figure 20 FE-SEM photomicrograph of loose face powder prepared with different methods: (A) Single step process and (B) Multiple step process.

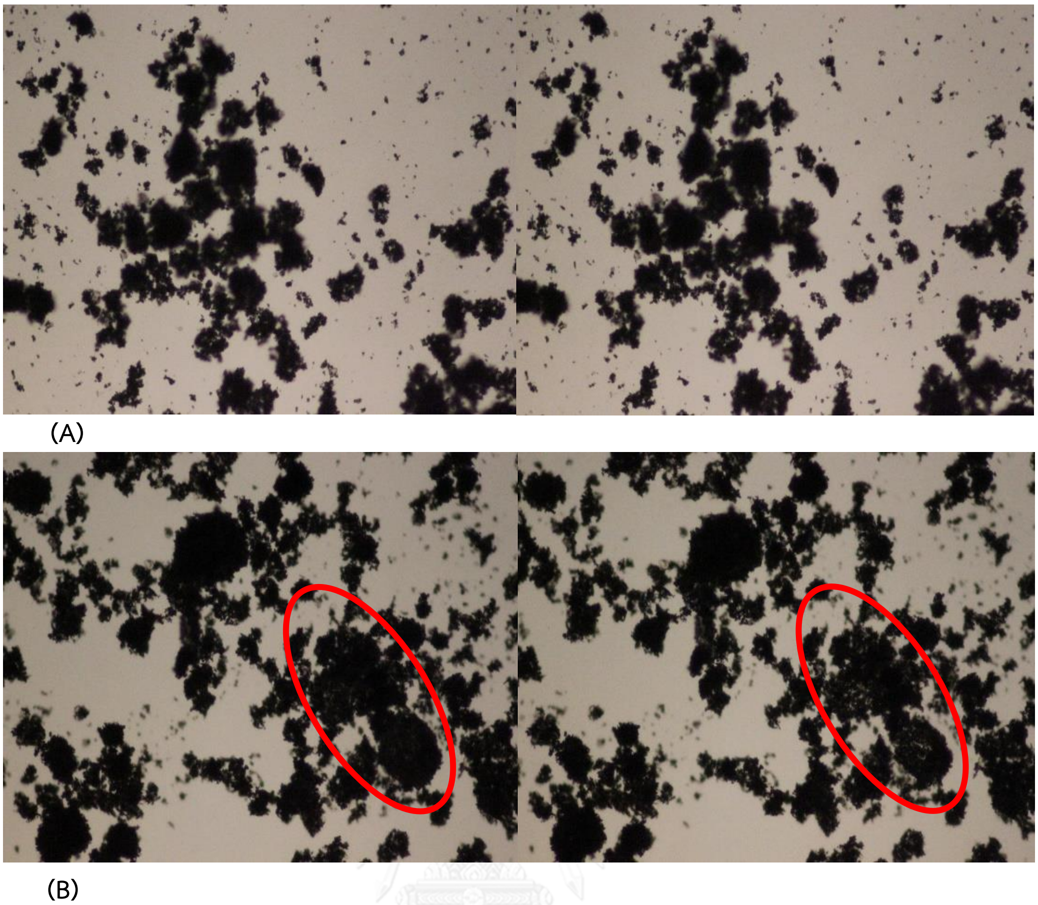


Figure 21 The photomicrograph of loose face powder prepared with different methods under light microscope when the observing time passed: (A) Single step process and (B) Multiple step process.

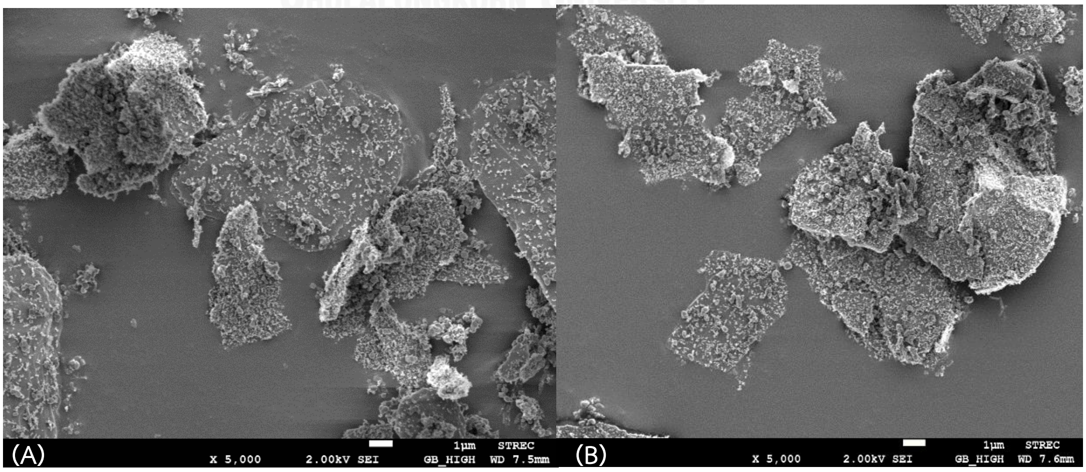


Figure 22 FE-SEM photomicrograph of loose face powder prepared with single step process: (A) Before water added and (B) After water added.

However, low shear blending might have the potential of destroying some of water-entrapped silica particles incorporated. It could be seen from the final product prepared by multiple step process of mixing with longer mixing time of 11 minutes. The powder showed color uniformity with no burst cooling sense after applied. Thus, it would be hypothesized that longer mixing time would perturb the physical stability of water-entrapped silica particles in loose face powder containing water-entrapped silica particles. Varying the mixing time revealed the difference in terms of physical appearance and %EE. The final products obtained from short range of mixing time (1 and 3 minutes) were non uniform color powder with more large agglomerate (Figure 23). The %EE of 1 minute mixing was not determined because of remarkable presenting of agglomerate separated from basic loose face powder. While the %EE of 3 minutes mixing was found to be close to 100% (Figure 24) (Appendix G). It might be due to the fact that water-entrapped silica particles added was not thoroughly distributed in the final product. Thus, water-entrapped silica particles could keep its intact structure from less collision with other particles. For the longer period of mixing (5 to 11 minutes), uniform color powder were gained and %EE were not significantly different. The lower %EE from the longer mixing time would be the result of more frequent particle collision. After collision occurred, the internal water of water-entrapped silica particles was possibly transferred via either mass transfer that to be absorbed from other component or evaporation. The evaporation would be proposed from the accumulating of temperature during mixing process. If the evaporation was major route of water loss from water-entrapped silica particles, the %EE should be lower. However, the result showed that no significant difference was investigated among 5 to 11 minutes of mixing. Thus, the water moving outward and to be absorbed should play a major role on the physical stability of water-entrapped silica particles after incorporated. To find out the optimal mixing time of the multiple step process in this study, the cooling burst sense was further evaluated. Primarily, 5 to 11 minutes would be the good choice of mixing time because they provided the final product conformed to our criteria. However, suitable final product should also have the cooling burst sense. The result of cooling burst sense testing revealed that 5 minutes of mixing time showed such effect whilst the longer time of 7, 9 and 11 minutes didn't give that sense (Table 7). Conclusively, the shortest time of the multiple step process that was efficient to provide the conforming final product was 5 minutes of mixing.

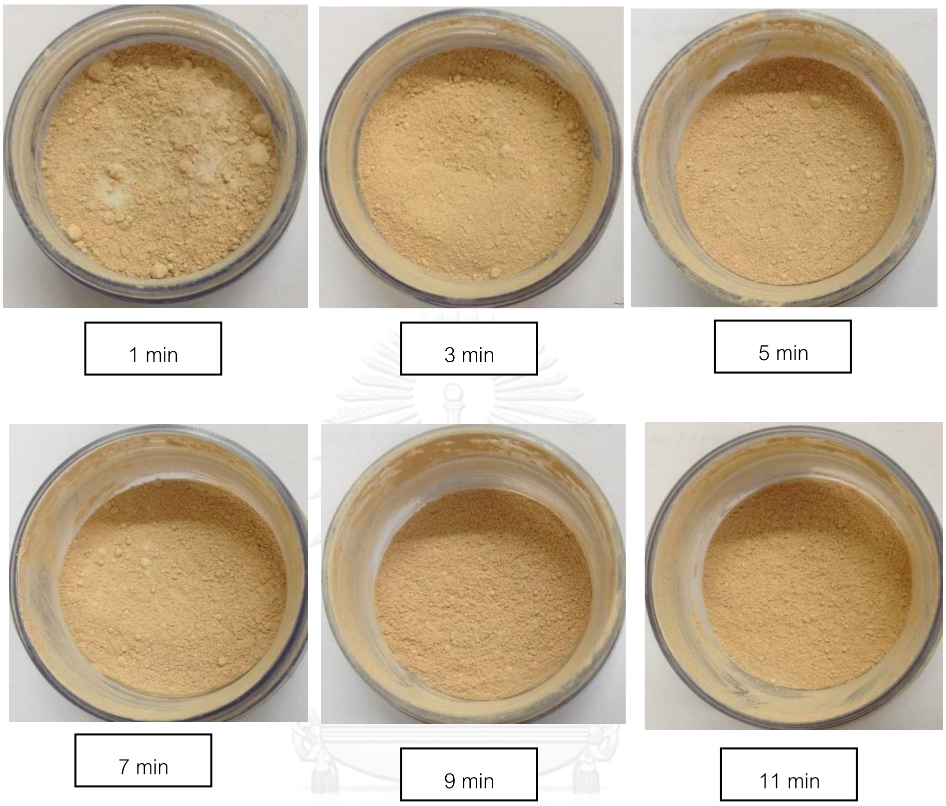


Figure 23 Physical appearance of loose face powder containing water-entrapped silica particles prepared with multiple step of different mixing time.

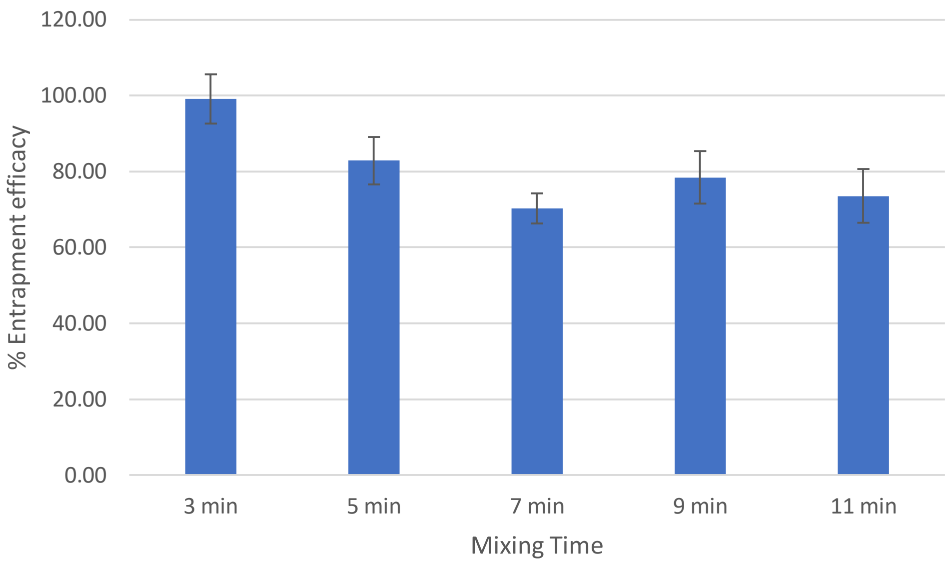


Figure 24 The water entrapment efficiency of loose face powder containing water-entrapped silica particles prepared with multiple step in different mixing time (mean ± SD, n=3).

Table 7 Cooling burst sense score of loose face powder containing water-entrapped silica particles prepared with multiple step at different mixing time (n=3).

Mixing time	Cooling burst sense score		
	N 1	N 2	N3
5 min	+++	+++	+++
7 min	++	++	+
9 min	+	+	-
11 min	-	+	-

The number of + represents the effect of cooling burst sense after applied on the area behind the palms by blush brush

+: Feel a bit cooling burst

++: Feel cooling burst

+++: Cooling burst obviously

-: No cooling burst

The suitable method of preparation of loose face powder containing water-entrapped silica particles would be the multiple step process. Firstly, basic loose face powder was prepared with high shear mixer. Water-entrapped silica particles was separately produced before transferring into basic loose face powder within tumble mixer. The mixing time of 5 minutes would be preferred.

Generally, water-entrapped silica particles could be added into basic loose face powder with no upper limit. However, the optimal level of water-entrapped silica particles should be determined. It was the lowest amount of R812S used due to the less toxicity but might provide the maximum cooling burst sense. In addition, the final product needed to be a dry powder form with free flow property. Therefore, 10 to 40% by weight of water-entrapped silica particles were proposed and studied. All levels of water-entrapped silica particles used provided the final product that found to be the free flowing and dry powder, no aggregation and good color uniform. At the highest level of water-entrapped silica particles used (40%), water was equivalent to 38.8% by weight that seemed to be very high level of liquid but the final product still be in the dry form. It showed the efficiency of water encapsulation of this system that could keep and not released all liquid to the formulation and make it into a paste-like appearance.

Lower level of water-entrapped silica particles incorporated (10 and 20%) gave the product that spilled over and not adhered on the skin after applied. The encapsulated water seemed not to be released after applied that could be evaluated from no cooling burst sense. Meanwhile, the loose face powder containing 30% and 40% of water-entrapped silica particles showed the sensibleness of cooling that meant to the water easily released after applied onto the skin (Table 8). They also provided better adhesion with no over wet appearance on the skin. Therefore, loose face powder containing 30% and 40% of water-entrapped silica particles were chosen and further characterized.

Table 8 Cooling burst sense score of loose face powder containing water-entrapped silica particles (n=3).

Water-entrapped silica particles : Basic loose face powder	Cooling burst sense score		
	N 1	N 2	N3
10:90	-	+	-
20:80	+	-	+
30:70	++	+++	+++
40:60	+++	+++	+++

The number of + represents the effect of cooling burst sense after applied on the area behind the palms by blush brush

+: Feel a bit cooling burst

++: Feel cooling burst

+++: Cooling burst obviously

-: No cooling burst

The loose face powder containing 30% and 40% of water-entrapped silica particles provided the high level of water encapsulation of 85.17±5.31% and 84.23±7.50% (Figure 25) (Appendix H). They were no significantly different. It was clearly demonstrated that most of the water added in water-entrapped silica particles was preserved after blended with basic loose face powder.

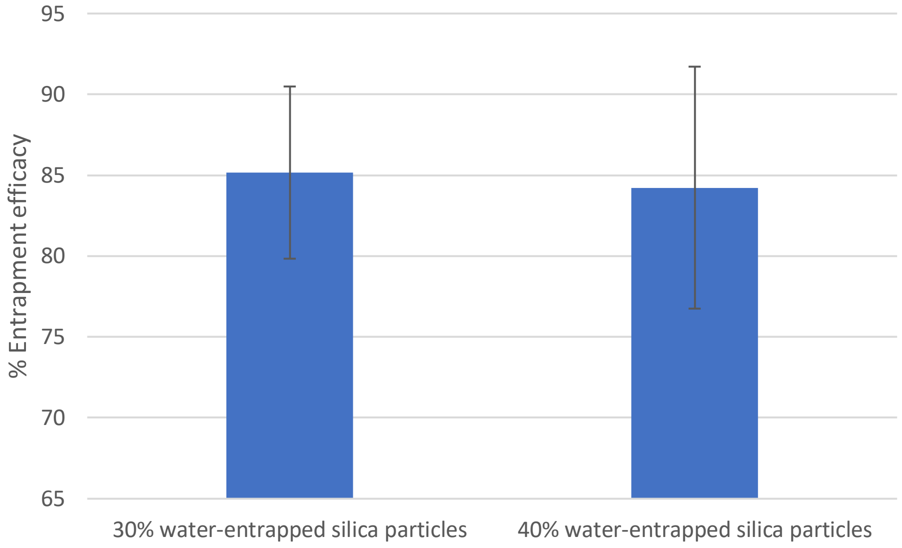


Figure 25 The water entrapment efficiency of loose face powder containing 30% and 40% of water-entrapped silica particles (mean ± SD, n=3).

In term of the particle size and size distribution, they were found to be in good agreement with microscopic observation (Figure 26). The particulate diameters of both concentrations of water-entrapped silica particles were in the range of approximately 20 to 260 µm. They showed the mean and SD of 85.01 ± 0.52 µm and 84.26 ± 4.49 µm. for 30% and 40% water-entrapped silica particles, respectively (Figure 27). However, the flow character of both formulations were in the categories of very poor flow (%CI of 38.97±0.81% and 34.67±2.09% for 30% and 40% water-entrapped silica particles) (Figure 28) (Appendix I). They were not similar to the result of pure water-entrapped silica particles. Eventhough the average particle size and size distribution of loose face powder containing water-entrapped silica particles were closely related to water-entrapped silica particles particle, the flowability were different. It was according to fact that the water released from the destroying of water-entrapped silica particles structure during mixing process was absorbed with other ingredients of basic loose face powder. The particle of such ingredient that absorbed the released water had more moisture and more adhesion between particles. It would provide less gliding and flowability.

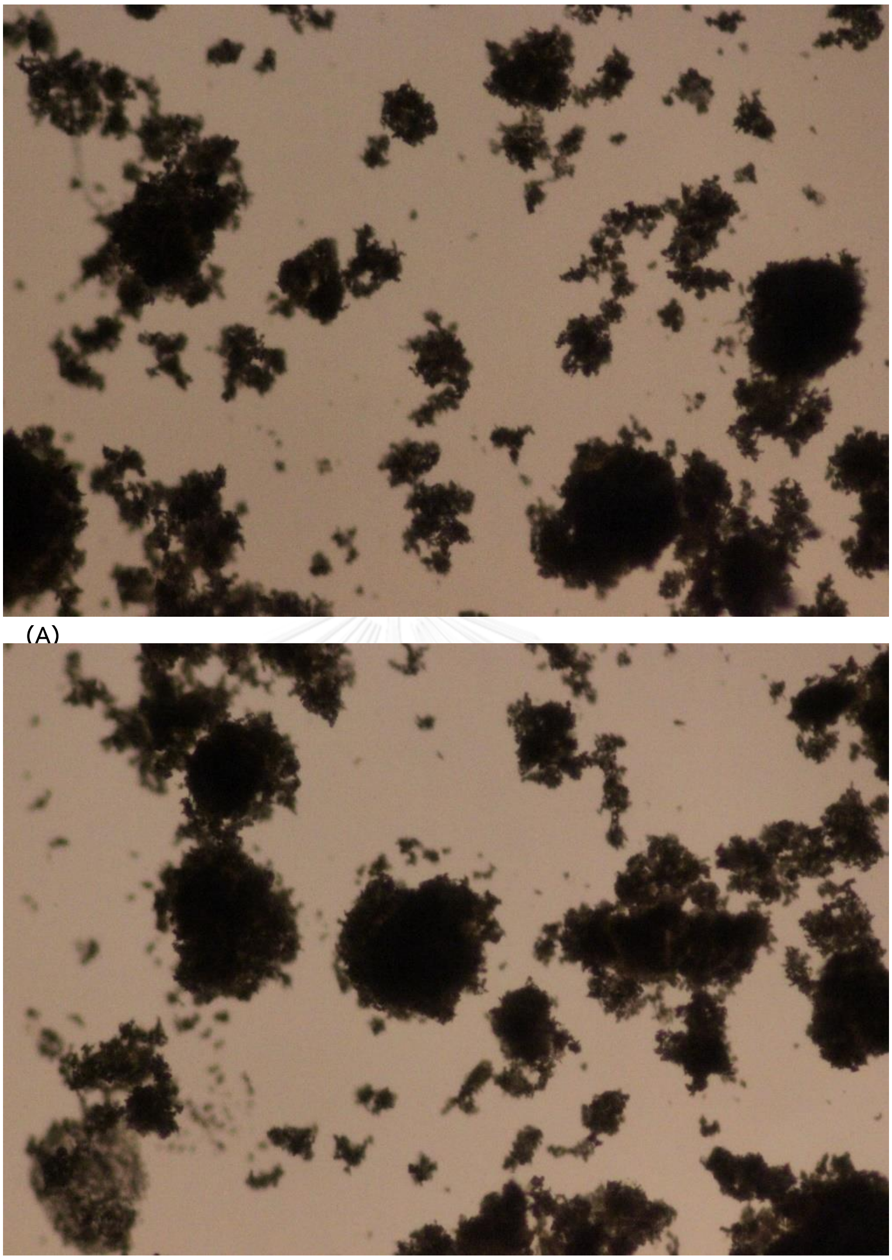
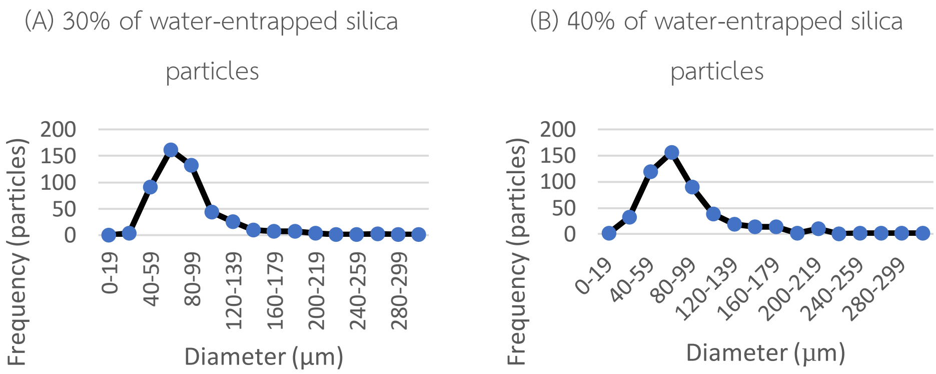


Figure 26 The microscopic observation of loose face powder containing different amounts of water-entrapped silica particles: (A) 30% of water-entrapped silica particles and (B) 40% of water-entrapped silica particles.



(A) 30% of water-entrapped silica particles

(B) 40% of water-entrapped silica particles

Figure 27 Particle size and size distributions of loose face powder containing different amounts of water-entrapped silica particles.

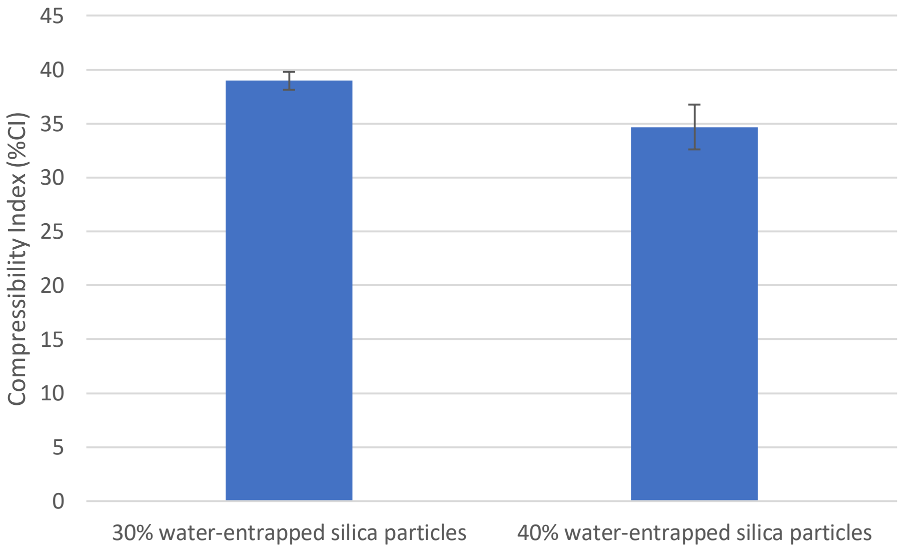


Figure 28 The compressibility index of loose face powder containing 30% and 40% of water-entrapped silica particles (mean ± SD, n=3).

Loose face powder containing water-entrapped silica particles should have the oil absorption property due the intrinsic property of basic loose face powder ingredient including the existence of R812S in the formulation even it presented in water-entrapped silica particles form. To prove that water-entrapped silica particles structure might impact on oil absorption property, the positive control of each formulation was fabricated. The difference between the positive control and formulations of both water-entrapped silica particles levels were significant ($p < 0.05$) (Figure 29) (Appendix J). The capacity of oil absorption of the positive control was higher than that of the formulation. It was due to the fact that the positive control was composed of all the same components and quantity ratio as formulation except water, it would show the highest absorption capacity themselves. While the formulation contained water-entrapped silica particles would release the water because water-entrapped silica particles was broken during testing from the spatulation process. The released water would be reabsorbed from the remained ingredients in the formulation. The capacity of such ingredients would then reduce and eventually result in less oil absorption capacity. Oil absorption studies also indicated no significant difference of the oil absorption capacity between 30% and 40% water-entrapped silica particles. When calculate the amount of R812S presented in 30% and 40% water-entrapped silica particles, they were found to be 0.9 and 1.2% by weight that were not drastically different. Therefore, the oil absorption capacity considerably depended on the ingredients of basic loose face powder such as talc. In conclusion, the loose face powder containing water-entrapped silica particles at 30% and 40% by weight were then subjected to stability investigation.

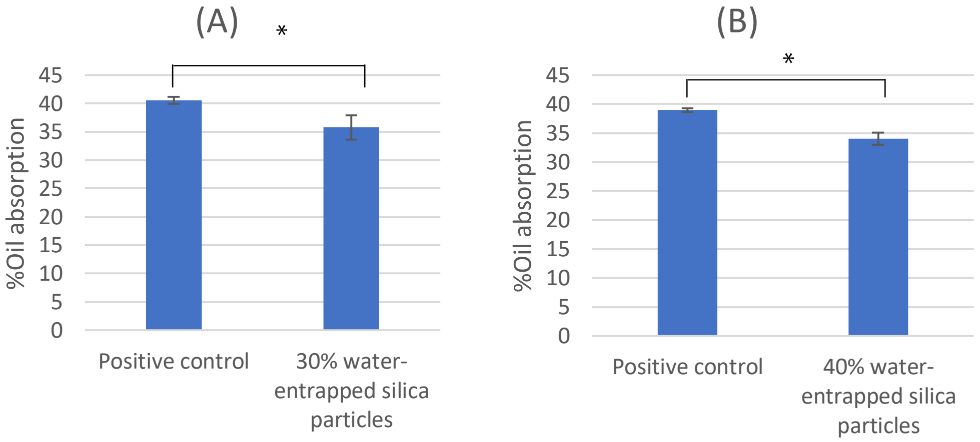


Figure 29 Oil absorption capacity of loose face powder containing 30% and 40% of water-entrapped silica particles compared with the positive control (mean ± SD, n=3).

4. Stability of loose face powder containing water-entrapped silica particles

Loose face powders containing 30% and 40% of water-entrapped silica particles could keep the existed water-entrapped silica particles within the final product. Furthermore, they provided the appearance of good color uniform powder and also gave a burst cooling sense after applied on skin. The feeling after applied the final product was dusty with no wet appearance including good adhesion. However, there was some of moist particle adhering on the inner surface wall of mixer during and after processing. It should be the result of the broken of water-entrapped silica particles by powder collision which would eventually release some of encapsulated water. The free water migrated and was reabsorbed by other components of basic loose face powder. Then moist particle was generated.

Loose face powder in this study was filled in a plastic container (plastic jar). Hence, the moisture permeation across the plastic wall of container would be an important consideration. To prove the suitability of the plastic jar as a product container, only water-entrapped silica particles produced were filled in plastic jar and subjected under 40±2 °C / 75±5 % RH for 1 and 3 months. The result indicated that %EE at first and third month of storage were not show any significantly different

(Figure 30) (Appendix K). The flow property of formulation before and after storage were found to be passable to fair flow which could be seen in Figure 31 (Appendix L). The particle size were not also significantly different after storage (Figure 32). Therefore, plastic jar container could be used as the suitable container and closure system for storing loose face powder containing water-entrapped silica particles in the stability study.

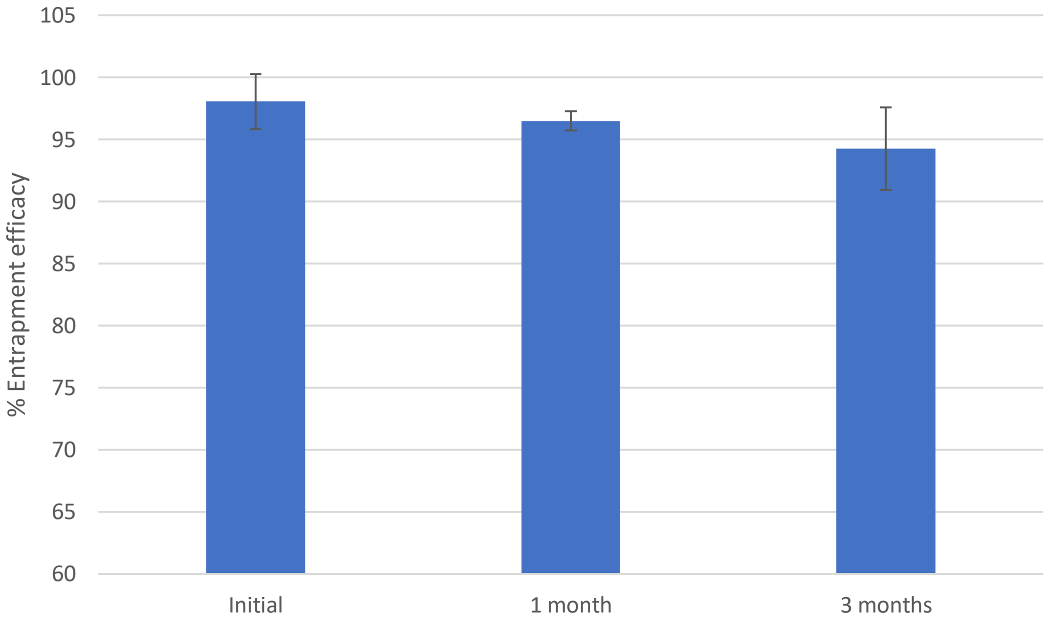


Figure 30 Water entrapment efficiency of water-entrapped silica particles prepared with 3% of R812S in plastic jar after storage the conditions (mean ± SD, n=3).

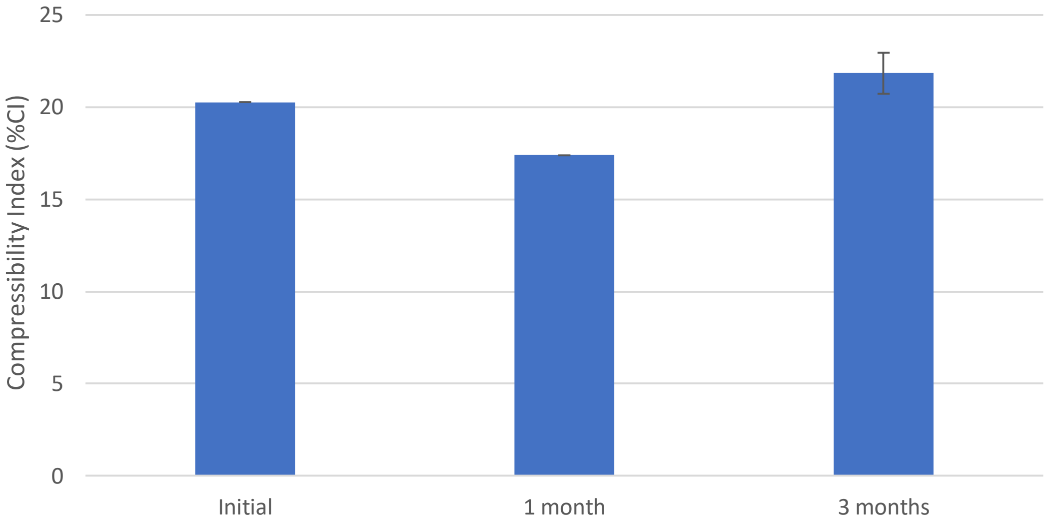


Figure 31 The compressibility index of water-entrapped silica particles prepared with 3% of R812S in plastic jar after the storage conditions (mean ± SD, n=3).

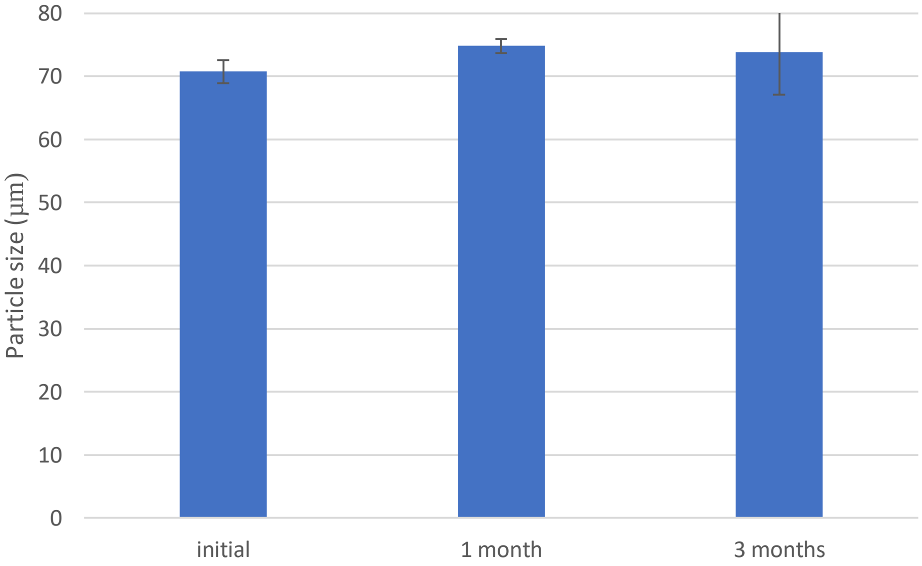


Figure 32 The particulate diameter of water-entrapped silica particles prepared with 3% of R812S in plastic jar after the storage conditions (mean ± SD, n=3).

In term of stability studies of loose face powder containing water-entrapped silica particles, the physical appearance of final product which was kept under 40±2 °C / 75±5 % RH for a period of 3 months are shown in Table 9. An unacceptance of physical appearance was remarkably seen from 30% water-entrapped silica particles formulation at the third month. Small aggregation scattered throughout the final product was detected including some of moist free particle adhering on the wall of plastic jar. In addition, cooling burst sense obviously decreased when applied on the skin (Table 10). The low %EE of water (18.04±7.36%) was observed and well agreed with the less cooling burst sense above (Figure 33) (Appendix M). On the other hand, loose face powder containing 40% water-entrapped silica particles showed the better physical appearance. The less number of lumpy and free moist particle were found in dry uniform powder. The cooling burst sense after applied was relatively higher than that of 30% water-entrapped silica particles formulation. The %EE was found to be 71.11±6.54% that showed no significant difference compared with initial condition.

At the first month of stability, a few small aggregations were found in 30% water-entrapped silica particles formulation while 40% water-entrapped silica particles was negligible. Both formulations provided the acceptable cooling burst sense but still lower than that of freshly prepared (Table 10). It might demonstrate the existence of water-entrapped silica particles in the final product. The %EE are shown in Figure 33, they were found to be 63.91±6.04 and 79.19±6.60 for 30% and 40% water-entrapped silica particles formulation. All data well correlated to cooling sense above. It should be noted that even low %EE (60%) was measured but cooling burst sense was perceived. They also showed the good adhesion with no wet appearance. In term of flowability, the particle size with size distribution and the %CI showed no significantly difference after storage for both formulations (Figures 34 and 35). They were fallen in the group of very poor flow character (Appendix N). In conclusion, both formulations were stable in short term period even at accelerated condition. However, the higher the level of % water-entrapped silica particles the better the formulation in case of longer stability time period. It was due to the key parameters of high temperature and storage time. Upon accelerated condition, the heat was accumulated into the product and directly impacted on the evaporation of encapsulated water in water-entrapped silica particles. The remaining of water would be low in case of lower proportion of water-entrapped silica particles (30% water-entrapped silica particles) due to the lower water loading (as a result of lower amount of water-entrapped silica particles) in the formulation. Whilst the high loading of water from higher amount of water-entrapped silica particles in formulation was less influenced from temperature.

Table 9 Physical appearance of loose face powder containing water-entrapped silica particles after storage under 40±2 °C / 75±5 % RH (n=3).

Water-entrapped silica particles : Basic loose face powder	1 month			3 months		
	N1	N2	N3	N1	N2	N3
30:70	-	+	+	++	++	++
40:60	-	+	-	+	-	+

The number of + represented the number of the particle aggregation in the sample.

+: A few small aggregation of the particle

++: Small aggregation of the particle throughout the sample including some of moist free particle adhering on the wall of plastic jar

+++: Large aggregation of the particle including some of moist free particle adhering on the wall of plastic jar

-: Unchanged sample

Table 10 Cooling burst sense score of loose face powder containing water-entrapped silica particles after storage under 40±2 °C / 75±5 % RH (n=3).

water-entrapped silica particles : Basic loose face powder	1 month			3 months		
	N1	N2	N3	N1	N2	N3
30:70	++	++	+++	+	+	++
40:60	+++	+++	++	++	++	+

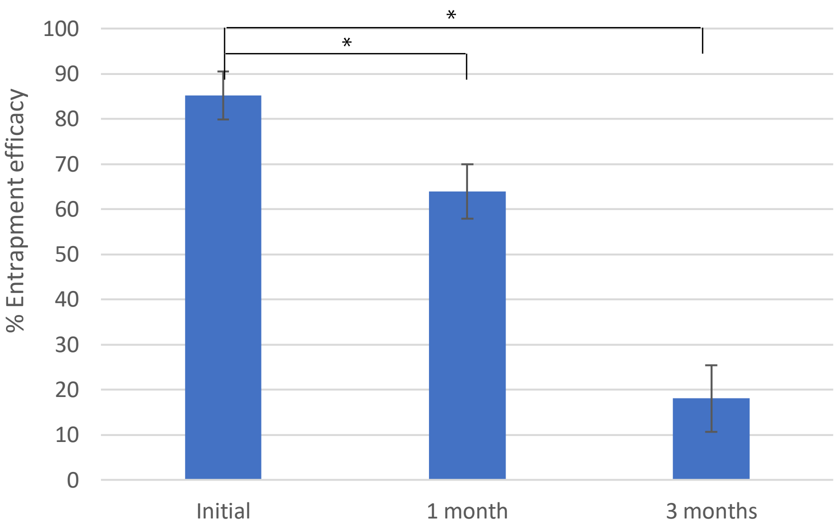
The number of + represents the effect of cooling burst sense after applied on the area behind the palms by blush brush

+: Feel a bit cooling burst

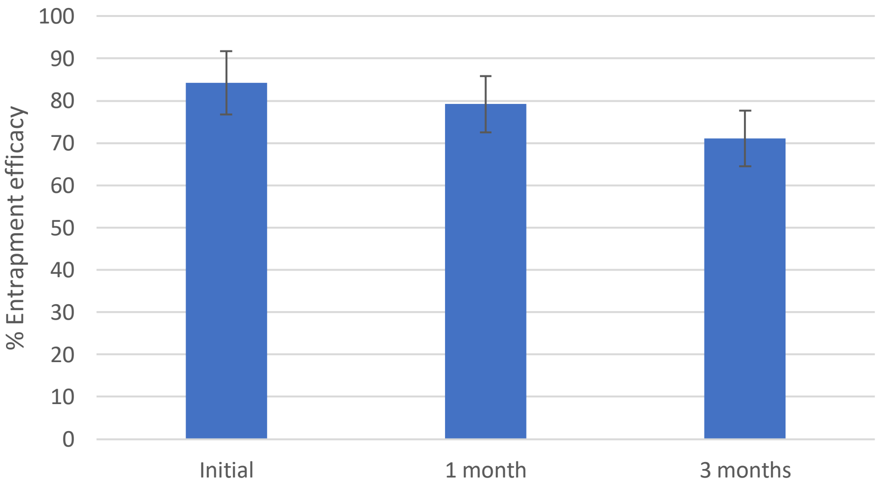
++: Feel cooling burst

+++: Cooling burst obviously

-: No cooling burst

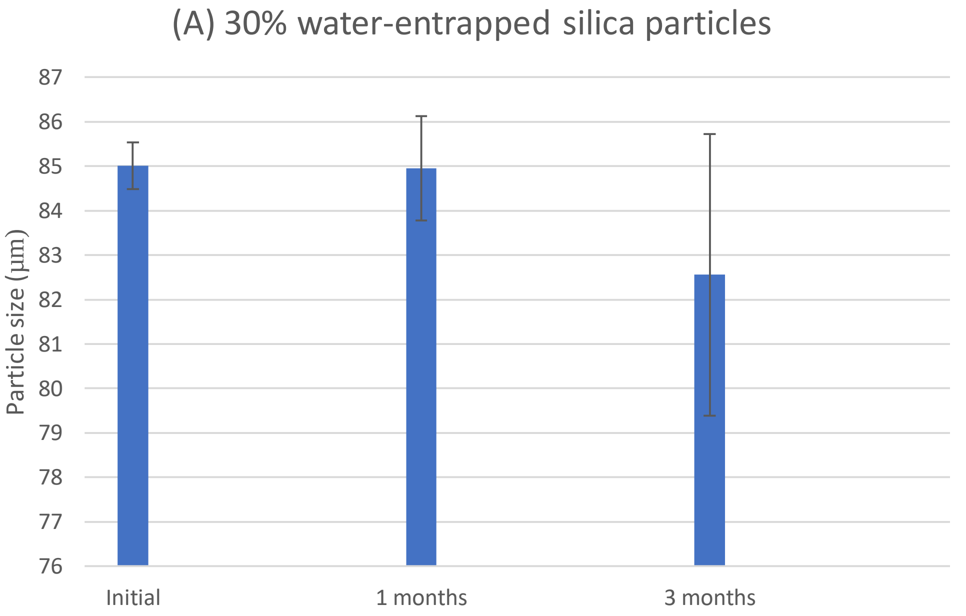


(A) 30% water-entrapped silica particles



(B) 40% water-entrapped silica particles

Figure 33 Water entrapment efficiency of loose face powder containing after the storage condition (mean ± SD, n=3).



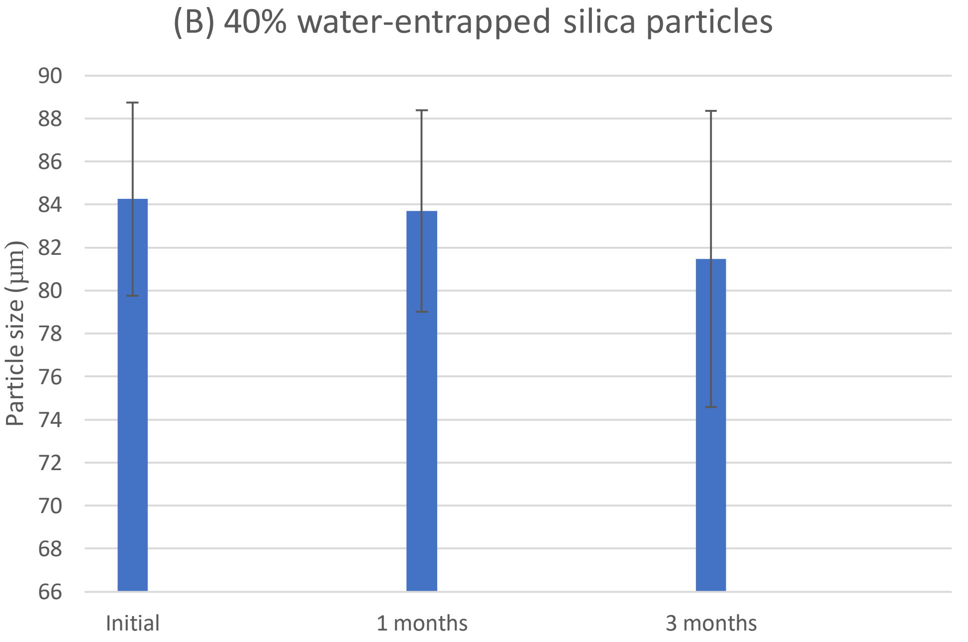
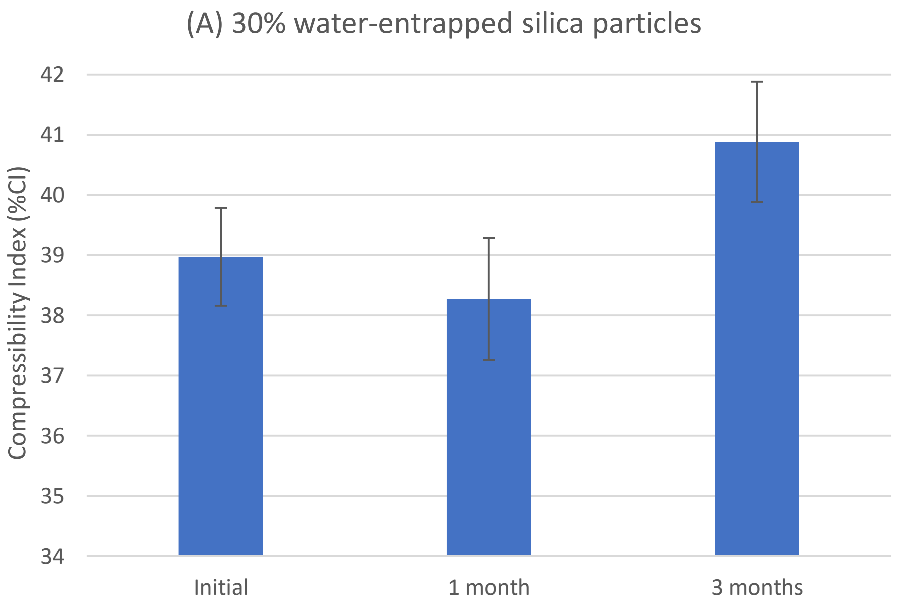


Figure 34 The particulate diameter of loose face powder containing water-entrapped silica particles after the storage condition (mean ± SD, n=3).



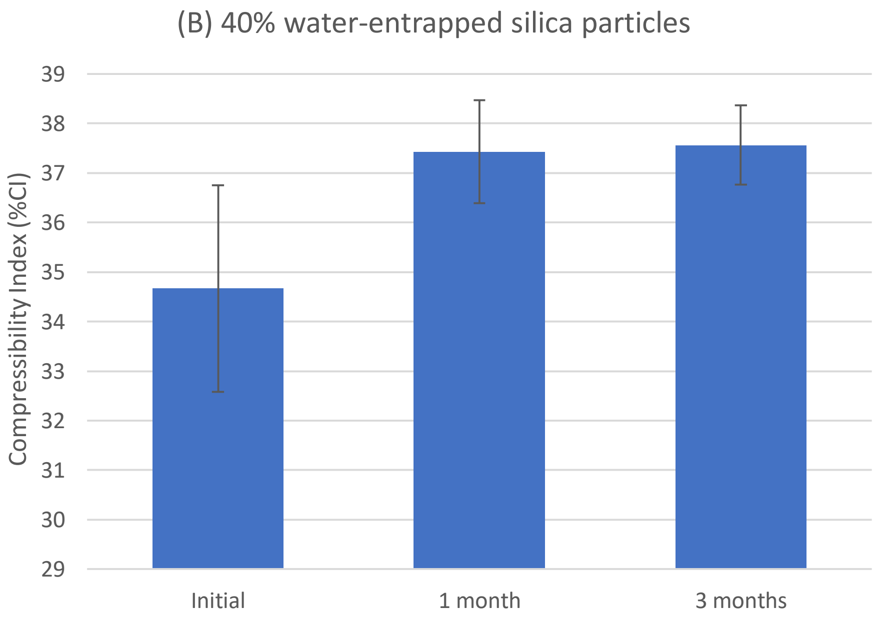


Figure 35 The compressibility index of loose face powder containing water-entrapped silica particles after the storage condition (mean ± SD, n=3).

Another property of loose face powder containing water-entrapped silica particles, oil absorption property, was further investigated. The oil absorption capacity of both formulations was nearly identical (Figure 36) (Appendix O). It would be the result of different amount of R812S. The component of basic loose face powder between two formulations was different for 10% by weight while the amount of R812S was very slightly different for 0.3% by weight. Larger difference of amount of basic loose face component was not hence a pivotal role on oil absorption capacity but the different quantity of R812S was a key role. It gave more impact on oil absorption capacity. The stability studies showed that oil absorption capacity at the longer stability time was definitely increased. It might concern with the evaporation of water as ascribed earlier. When the final product lose more water, the sample at the same weight would be composed of more solid particles which could then relatively absorb oil higher.

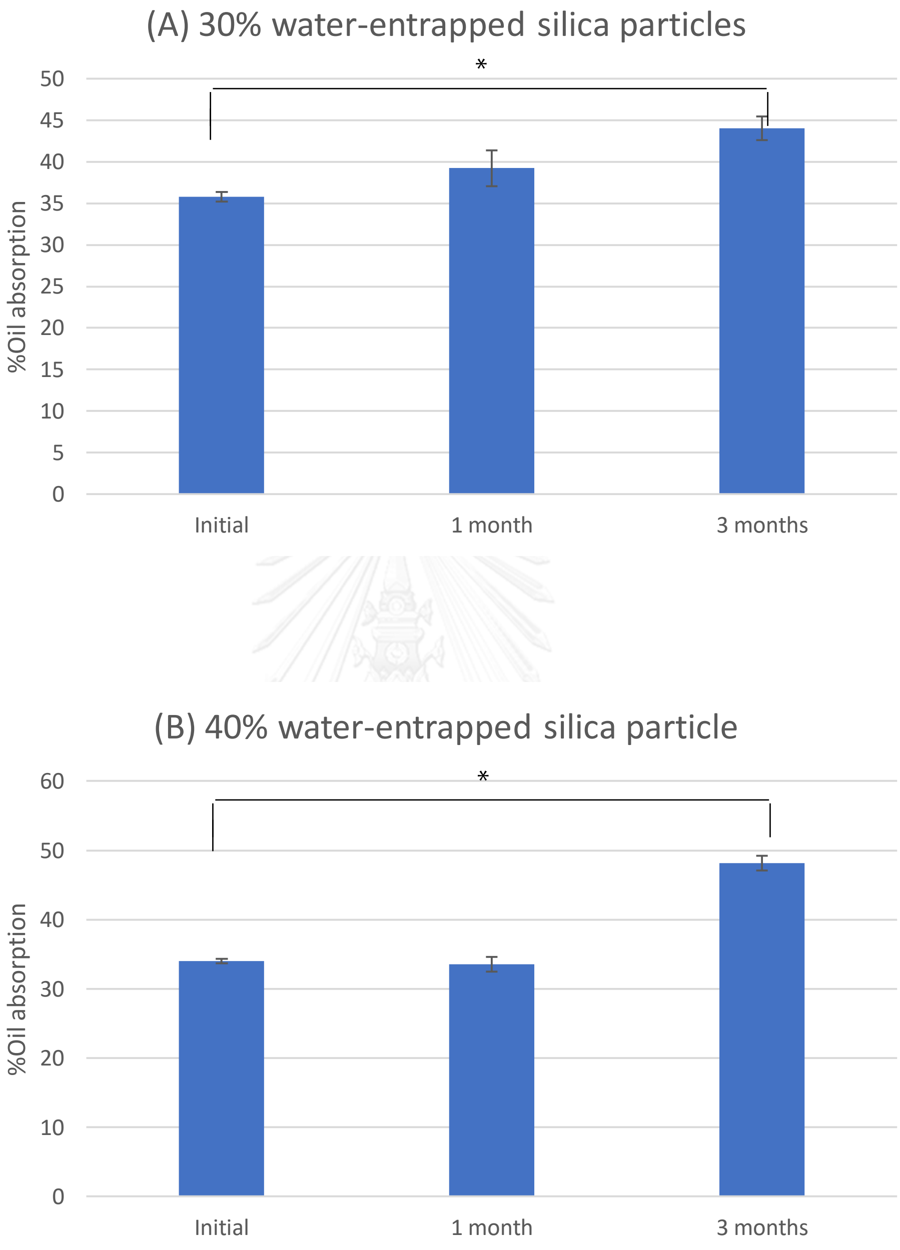


Figure 36 Oil absorption capacity of loose face powder containing water-entrapped silica particles after the storage condition (mean ± SD, n=3).

CHAPTER V
CONCLUSIONS

Shear force and water addition method were the pivotal parameters on the formation of water-entrapped silica particles containing encapsulated water. High shearing force with the pouring of whole water at once was successfully carried out in order to fabricate the prototype water-entrapped silica particles with R812S:DI water ratio of 5:95. The ratio of R812S and DI water directly affected on the formation of water-entrapped silica particles. Lower level of R812S used with a plenty of water (1:99) could not provide water-entrapped silica particles formation but the unstable mousse like solid with separation of water was found. However, higher level of R812S used had good potential of water-entrapped silica particles formation with high %EE. Water-entrapped silica particles produced could encapsulate almost of water added internally and provided a physical appearance of free flowing powder including the particle size range of 20 to 200 µm. Water-entrapped silica particles structure was found to be a core shell like structure. The encapsulated water could therefore be released after applied small pressure or force. It would be the result of the sensitive loose network of R812S shell that was broken easily with less mechanical force applied. Five percent of R812S used in water-entrapped silica particles preparation would provide more free R812S particles that resulted in more electrostatic effect. They were then attached together and led to poor flowabillity. Typically, water-entrapped silica particles was physically unstable when facing with mild to moderate stimuli such as mechanical or temperature. Developed water-entrapped silica particles comprised of 2 to 4% R812S in this studies were not tolerated under severe condition throughout 6 months. Water squeezing was mostly observed. Water-entrapped silica particles fabricated with 2% R812S could not preserve the occupied water in water-entrapped silica particles structure that could be seen from water separation. In turn, 3 and 4% by weight of R812S in water-entrapped silica particles formulation seemed to be the good candidates for further development as a part of loose face powder.

Development of loose face powder that would intend to carry on some of water-entrapped silica particles was performed. The major problem of this product development was “How to blend two components between basic loose face powder with water-entrapped silica particles homogeneously and retain the structure of water-entrapped silica particles”. The method with mild mixing force like tumble mixer was appropriate to make this product that almost of water-entrapped silica particles incorporated could retaine their structure and later release water droplet after applied by blush brush. However, mixing time was another critical process parameter and should be optimized. Five minutes of mixing with tumble mixer showed an acceptable final product in terms of good free flowing dry powder and high %EE including the cooling burst sense after applied. In addition, the determination of suitable quantity of water-entrapped silica particles incorporated in loose face powder product was carried out. The higher water-entrapped silica particles amount generally provided the more encapsulated water that led to more cooling burst sense and moisturizing effect. However, it might not be in the form of dry powder because large quantity of water in water-entrapped silica particles would wet entire particles until paste like appearance formed. The loose face powder with 40% water-entrapped silica particles had all acceptable properties which conformed with the specified criteria. It could be filled in plastic jar and showed the acceptable stability of at least one month under the accelerated condition. It showed the capacity of oil absorption in comparable with the positive control formulation without water-entrapped silica particles.

In conclusion, loose face powder containing water-entrapped silica particles with encapsulated water might be one of the most promising cosmetic product for adhering with the special function of cooling sense and moisturizing effect.

These studies could be used as a rough guideline for further development of the powder cosmetic containing water-entrapped silica particles. Nevertheless, the stability of water-entrapped silica particles should be concerned for further study. It could not permanently encapsulate the inner core of liquid due to the force sensitive shell. When temperature and humidity was changed over storage time, the core shell structure could not retain the water inside. Thus, increasing the strength of the shell structure and/or more viscosity of the inner liquid core structure might be further investigated.

REFERENCES

American Society for Testing and Materials (ASTM). Standard test method for oil absorption of pigments by spatula rub-out: D 281-95. Annual Brook of American Standard Testing Methods. 06.012002.

American Society for Testing and Materials (ASTM). Standard test methods for determining average grain size using semiautomatic and automatic image analysis: E1382-97. Annual Brook of American Standard Testing Methods. 03.012010.

Cabot Corporation. เอกสารข้อมูลความปลอดภัย DMD Treated Fumed Silica. 2015.

Evonik industries. Successful use of AEROSIL® fumed silica in liquid systems. Technical Information 1279: 3.

Fassih A, Park F, San Y, Mead B. Anhydrous powder-to-liquid particles. 2014;Paten US20140170195 A1.

Fielden KE, Newton JM, Obrien P, Rowet RC. Thermal Studies on the Interaction of Water and Microcrystalline Cellulose. Journal of Pharmacy and Pharmacology. 1988;40:674-8.

Forny L, Pezron I, Saleh K, Guigon P, Komunjer L. Storing water in powder form by self-assembling hydrophobic silica nanoparticles. Powder Technology. 2007;171(1):15-24.

Forny L, Saleh K, Pezron I, Komunjer L, Guigon P. Influence of mixing characteristics for water encapsulation by self-assembling hydrophobic silica nanoparticles. Powder Technology. 2009;189(2):263-9.

Igarashi K, Sagara K, Egawa J. A new water-in-powder technology: A novel structure for creating unique cosmetic product. International journal of cosmetic science. 2008;42(4):313-8.

Lahanas KM, Vrabie N, Santos E, Miklean S. Powder to liquid compositions. 2001;Paten US6290941 B1.

Lemine OM, Alyamani A. FE-SEM Characterization of Some Nanomaterial. Scanning Electron Microscopy. 2012:463-72.

Makeupforever. (2016). Retrieved from http://www.makeupforever.com/th/th-th/make-up/face/powder/poudre-hd?sku=6675

Saleh K, Forny L, Guigon P, Pezron I. Dry water: From physico-chemical aspects to process-related parameters. Chemical Engineering Research and Design. 2011;89(5):537-44.

Sivamani RK, Jagdeo JR, Elsner P, Maibach HI. Cosmeceuticals and active cosmetics. Boca Raton: CRC Press; 2015.

The United States Pharmacopeial Convention. USP 34/NF 29. 1. Maryland: United Book Press; 2010. p. 688-91.

Yoichiro T, Junichiro E. Whitening powder. 1998;Paten EP0855177 A2.

Yoichiro T, Yuriko T, Shinji K. Water-containing powder composition, process for producing the same, and cosmetic preparation containing the powder composition. 2002;Patent EP1206928 A1.

อรัญญา มโนสร้อย. เครื่องสำอาง. 2. พิมพ์ครั้งที่ 1 ed. กรุงเทพมหานคร: โอเดียนสโตร์; 2533.

APPENDICES

APPENDIX A

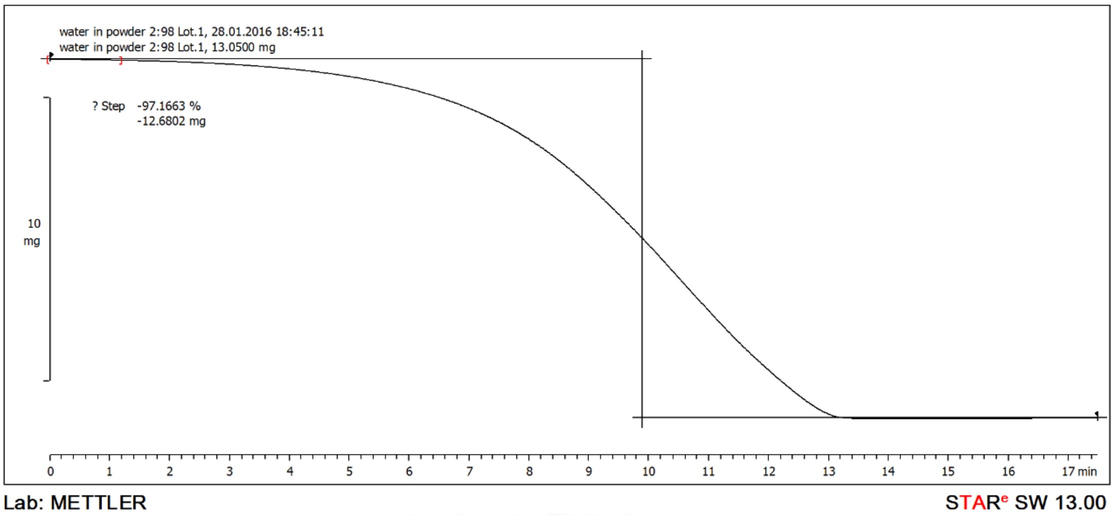


Figure 37 TGA of water-entrapped silica particles produced with 2% of R812S.

APPENDIX B

Table 11 The water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water (mean ± SD, n=3).

R812S:Water	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE
5:95				
N 1	12.85	12.21	11.86	97.14
N 2	13.05	12.40	12.21	98.52
N 3	12.92	12.27	12.08	98.44
4:96				
N 1	12.92	12.40	12.37	99.75
N 2	13.00	12.48	12.33	98.80
N 3	12.88	12.36	12.24	99.02
3:97				
N 1	12.93	12.54	12.41	99.17
N 2	13.05	12.66	12.52	98.91
N 3	12.97	12.58	12.41	98.64
2:98				
N 1	13.05	12.79	12.68	99.16
N 2	13.01	12.75	12.56	98.50
N 3	13.03	12.77	12.41	97.19

APPENDIX C

Table 12 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water (mean ± SD, n=3).

R812S:Water	Density		%CI
	d_{bulk}	d_{tapped}	
5:95			
N 1	0.47	0.59	20.34
N 2	0.47	0.59	20.34
N 3	0.45	0.59	23.73
4:96			
N 1	0.51	0.67	23.88
N 2	0.53	0.67	20.90
N 3	0.53	0.67	20.90
3:97			
N 1	0.59	0.74	20.27
N 2	0.59	0.74	20.27
N 3	0.61	0.77	20.78
2:98			
N 1	0.67	0.80	16.25
N 2	0.69	0.80	13.75
N 3	0.69	0.80	13.75

APPENDIX D

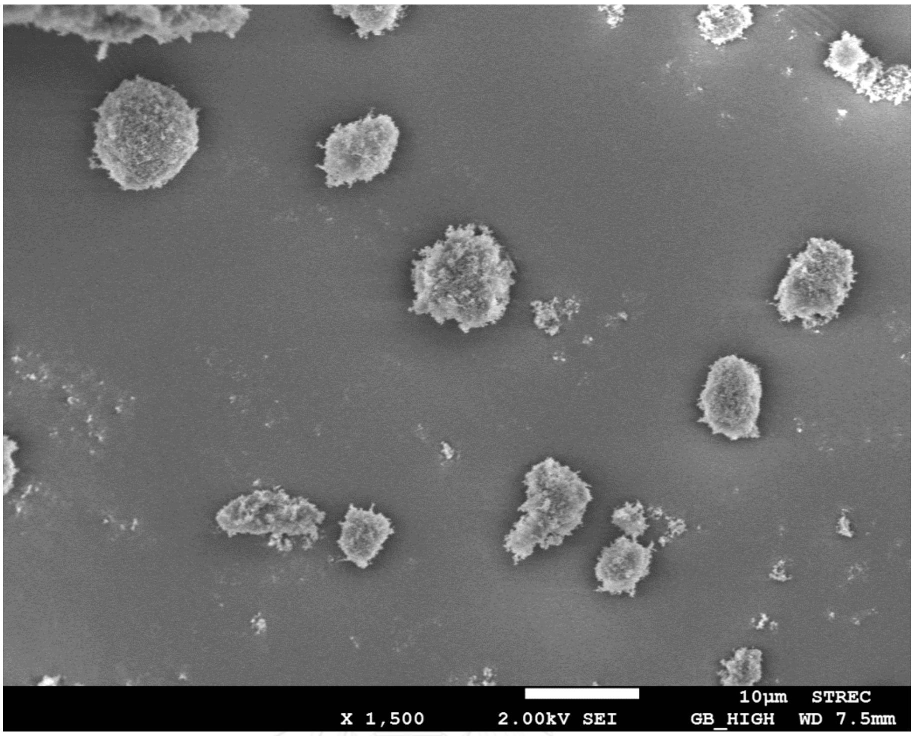


Figure 38 FE-SEM micrograph of particle size of water-entrapped silica particles produced with 2% of R812S.

APPENDIX E

Table 13 Water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water at initial (mean ± SD, n=3).

R812S:Water	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE
4:96				
Lot. 1	13.00	12.48	12.25	98.16
Lot. 2	13.00	12.48	12.27	98.32
Lot. 3	13.02	12.50	12.31	98.48
3:97				
Lot. 1	13.01	12.62	12.49	98.97
Lot. 2	13.02	12.63	12.49	98.89
Lot. 3	13.00	12.61	12.49	99.05
2:98				
Lot. 1	13.03	12.77	12.61	98.75
Lot. 2	13.00	12.74	12.67	99.45
Lot. 3	13.01	12.75	12.66	99.29

Table 14 Water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water after storage in different conditions at 1 month (mean ± SD, n=3).

R812S:Water	1 month											
	Ambient				30°C/75%RH				40°C/75%RH			
	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE
4:96												
N 1	13.06	12.54	11.93	95.14	13.02	12.50	12.12	96.96	13.02	12.50	12.00	96.00
N 2	13.03	12.51	12.17	97.28	13.12	12.59	12.14	96.43	13.00	12.48	12.32	98.72
N 3	13.02	12.50	12.05	96.40	13.19	12.66	12.27	96.92	13.07	12.55	12.24	97.53
3:97												
N 1	13.11	12.72	12.32	96.86	13.14	12.75	12.46	97.73	13.01	12.62	12.35	97.86
N 2	13.03	12.64	12.34	97.63	13.10	12.71	12.19	95.91	13.01	12.62	12.15	96.28
N 3	13.04	12.65	12.24	96.76	13.06	12.67	12.36	97.55	13.01	12.62	12.52	99.21
2:98												
N 1	13.03	12.77	12.38	96.95	13.17	12.91	12.71	98.45	13.02	12.76	12.61	98.82
N 2	13.05	12.79	12.65	98.91	13.25	12.98	12.69	97.77	13.02	12.76	12.29	96.32
N 3	13.03	12.77	12.29	96.24	13.25	12.98	12.73	98.07	13.05	12.79	12.37	96.72

Table 15 Water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water after storage in different conditions at 3 months (mean ± SD, n=3).

R812S:Water	3 months											
	Ambient				30°C/75%RH				40°C/75%RH			
	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE
4:96												
N 1	13.08	12.56	12.33	98.17	13.02	12.50	11.63	93.04	13.12	12.59	12.33	97.93
N 2	13.01	12.49	12.19	97.60	12.96	12.44	11.97	96.22	13.08	12.56	12.40	98.73
N 3	13.08	12.56	12.06	96.02	13.19	12.66	11.96	94.47	13.12	12.59	12.38	98.33
3:97												
N 1	13.01	12.62	12.28	97.31	13.11	12.72	11.80	92.77	13.01	12.62	12.43	98.49
N 2	13.15	12.76	12.24	95.92	13.22	12.82	12.40	96.72	13.11	12.72	12.50	98.27
N 3	13.08	12.69	12.17	95.90	13.03	12.64	12.03	95.17	13.06	12.67	12.45	98.26
2:98												
N 1	13.04	12.78	12.64	98.90	13.17	12.91	12.36	95.74	13.02	12.76	12.51	98.04
N 2	13.10	12.84	12.44	96.88	12.97	12.71	12.30	96.77	13.07	12.81	12.61	98.44
N 3	13.02	12.76	12.28	96.24	13.03	12.77	12.35	96.71	13.13	12.87	12.68	98.52

Table 16 Water entrapment efficiency of water-entrapped silica particles produced with different ratios between R812S and DI water after storage in different conditions at 6 months (mean ± SD, n=3).

R812S:Water	6 months											
	Ambient				30°C/75%RH				40°C/75%RH			
	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE
4:96												
N 1	13.16	12.63	12.37	97.94	13.22	12.69	12.22	96.30	13.13	12.60	12.52	99.37
N 2	13.17	12.64	12.44	98.42	13.24	12.71	11.97	94.18	13.08	12.56	12.42	98.89
N 3	13.12	12.59	12.37	98.25	13.14	12.61	11.63	92.23	13.27	12.74	12.48	97.96
3:97												
N 1	13.03	12.64	12.29	97.23	13.35	12.95	12.56	96.99	13.21	12.81	12.53	97.81
N 2	13.06	12.67	12.42	98.03	13.13	12.74	12.32	96.70	13.21	12.81	12.59	98.28
N 3	13.22	12.82	12.64	98.60	13.14	12.75	12.40	97.25	13.07	12.68	12.56	99.05
2:98												
N 1	13.17	12.91	12.19	94.42	13.19	12.93	12.08	93.43	13.16	12.90	12.69	98.37
N 2	13.21	12.95	12.51	96.60	13.25	12.98	12.46	95.99	13.01	12.75	12.58	98.67
N 3	13.19	12.93	12.19	94.28	13.25	12.98	12.55	96.69	13.04	12.78	12.34	96.56

APPENDIX F

Table 17 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water at initial (mean ± SD, n=3).

R812S:Water	Density		%CI
	d_{bulk}	d_{tapped}	
4:96			
N 1	0.51	0.67	23.88
N 2	0.53	0.67	20.90
N 3	0.53	0.67	20.90
3:97			
N 1	0.59	0.74	20.27
N 2	0.59	0.74	20.27
N 3	0.61	0.77	20.78
2:98			
N 1	0.67	0.80	16.25
N 2	0.69	0.80	13.75
N 3	0.69	0.80	13.75

Table 18 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water in different conditions at 1 month (mean ± SD, n=3).

R812S:Water	1 month								
	Ambient			30°C/75%RH			40°C/75%RH		
	Density		%CI	Density		%CI	Density		%CI
	d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}	
4:96									
N 1	0.51	0.67	23.88	0.54	0.67	19.40	0.54	0.67	19.40
N 2	0.53	0.67	20.90	0.53	0.67	20.90	0.56	0.69	18.84
N 3	0.53	0.67	20.90	0.54	0.67	19.40	0.54	0.69	21.74
3:97									
N 1	0.59	0.74	20.27	0.59	0.74	20.27	0.59	0.74	20.27
N 2	0.59	0.74	20.27	0.59	0.77	23.38	0.59	0.74	20.27
N 3	0.61	0.77	20.78	0.59	0.74	20.27	0.59	0.74	20.27
2:98									
N 1	0.67	0.80	16.25	0.69	0.80	13.75	0.69	0.80	13.75
N 2	0.69	0.80	13.75	0.69	0.80	13.75	0.69	0.80	13.75
N 3	0.69	0.80	13.75	0.67	0.80	16.25	0.67	0.80	16.25

Table 19 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water in different conditions at 3 months (mean ± SD, n=3).

R812S:Water	3 months								
	Ambient			30°C/75%RH			40°C/75%RH		
	Density		%CI	Density		%CI	Density		%CI
	d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}	
4:96									
N 1	0.54	0.69	21.74	0.56	0.69	18.84	0.56	0.69	18.84
N 2	0.53	0.67	20.90	0.54	0.67	19.4	0.54	0.69	21.74
N 3	0.53	0.69	23.19	0.54	0.67	19.4	0.53	0.69	23.19
3:97									
N 1	0.59	0.74	20.27	0.61	0.77	20.78	0.57	0.74	22.97
N 2	0.59	0.74	20.27	0.59	0.74	20.27	0.57	0.74	22.97
N 3	0.59	0.74	20.27	0.59	0.74	20.27	0.57	0.74	22.97
2:98									
N 1	0.69	0.80	13.75	0.69	0.83	16.87	0.71	0.83	14.46
N 2	0.69	0.80	13.75	0.69	0.80	13.75	0.69	0.83	16.87
N 3	0.69	0.83	16.87	0.67	0.80	16.25	0.69	0.83	16.87

Table 20 The compressibility index of water-entrapped silica particles produced with different ratios between R812S and DI water in different conditions at 6 months (mean ± SD, n=3).

R812S:Water	6 months								
	Ambient			30°C/75%RH			40°C/75%RH		
	Density		%CI	Density		%CI	Density		%CI
	d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}	
4:96									
N 1	0.54	0.69	21.74	0.53	0.63	15.87	0.54	0.69	21.74
N 2	0.53	0.69	23.19	0.53	0.67	20.90	0.54	0.69	21.74
N 3	0.54	0.69	21.74	0.53	0.65	18.46	0.53	0.67	20.90
3:97									
N 1	0.59	0.74	20.27	0.57	0.71	19.72	0.59	0.74	20.27
N 2	0.59	0.74	20.27	0.59	0.74	20.27	0.60	0.77	22.08
N 3	0.59	0.74	20.27	0.59	0.74	20.27	0.60	0.77	22.08
2:98									
N 1	0.67	0.80	16.25	0.69	0.80	13.75	0.69	0.80	13.75
N 2	0.69	0.83	16.87	0.67	0.80	16.25	0.67	0.80	16.25
N 3	0.71	0.87	18.39	0.67	0.80	16.25	0.67	0.80	16.25

APPENDIX G

Table 21 The water entrapment efficiency of loose face powder containing water-entrapped silica particles prepared with multiple step in different mixing time (mean ± SD, n=3).

Mixing time (min)	Sample weight (g)	W_t (g)	W_s (g)	% EE
3 min				
N 1	0.497	0.192836	0.1868720	96.91
N 2	0.513	0.199044	0.2118177	106.42
N 3	0.498	0.193224	0.1817202	94.05
5 min				
N 1	0.518	0.200984	0.1783474	88.74
N 2	0.512	0.198656	0.1656320	83.38
N 3	0.497	0.192836	0.1473108	76.39
7 min				
N 1	0.495	0.192060	0.1385505	72.14
N 2	0.496	0.192448	0.1405664	73.04
N 3	0.496	0.192448	0.1265296	65.75
9 min				
N 1	0.499	0.193612	0.1673147	86.42
N 2	0.496	0.192448	0.1425504	74.07
N 3	0.518	0.200984	0.1502718	74.77
11 min				
N 1	0.504	0.195552	0.1593144	81.47
N 2	0.498	0.193224	0.1315218	68.07
N 3	0.510	0.197880	0.1405560	71.03

APPENDIX H

Table 22 The water entrapment efficiency of loose face powder containing 30% and 40% of water-entrapped silica particles (mean ± SD, n=3).

Water-entrapped silica particles:Basic loose face powder	Sample weight (g)	W_t (g)	W_s (g)	% EE
30:70				
N 1	0.497	0.144627	0.1279775	88.49
N 2	0.500	0.145500	0.128000	87.97
N 3	0.501	0.145791	0.115230	79.04
40:60				
N 1	0.499	0.193612	0.1749993	90.39
N 2	0.499	0.193612	0.1673147	86.42
N 3	0.497	0.192836	0.1463168	75.88

APPENDIX I

Table 23 The compressibility index of loose face powder containing 30% and 40% of water-entrapped silica particles (mean ± SD, n=3).

Water-entrapped silica particles:Basic loose face powder	Density		%CI
	d_{bulk}	d_{tapped}	
30:70			
N 1	0.44	0.71	38.03
N 2	0.43	0.71	39.44
N 3	0.43	0.71	39.44
40:60			
N 1	0.48	0.71	32.39
N 2	0.48	0.74	35.14
N 3	0.47	0.74	36.49

APPENDIX J

Table 24 Oil absorption capacity of loose face powder containing 30% and 40% of water-entrapped silica particles compared with the positive control (mean ± SD, n=3).

Water-entrapped silica particles:Basic loose face powder	Oil usage (g)	%Oil absorption
Positive control		
N 1	0.411	41.1
N 2	0.399	39.9
N 3	0.406	40.6
30:70		
N 1	0.370	37
N 2	0.333	33.3
N 3	0.371	37.1
Positive control		
N 1	0.391	39.1
N 2	0.386	38.6
N 3	0.392	39.2
40:60		
N 1	0.330	33
N 2	0.339	33.9
N 3	0.351	35.1

APPENDIX K

Table 25 Water entrapment efficiency of water-entrapped silica particles prepared with 3% of R812S in plastic jar after storage the conditions (mean ± SD, n=3).

R812S:Water	Initial				1 month				3 months			
	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE	Sample weight (mg)	W_t (mg)	W_s (mg)	% EE
3:97												
N 1	12.9793	12.589921	12.54	99.60	13.1595	12.764715	12.43	97.38	13.1394	12.745218	12.00	94.15
N 2	13.1192	12.725624	12.61	99.09	13.0493	12.657821	12.15	95.99	13.2895	12.890815	11.73	91.00
N 3	13.0691	12.677027	12.11	95.53	13.1795	12.784115	12.29	96.13	12.9897	12.600009	12.30	97.62

APPENDIX L

Table 26 The compressibility index of water-entrapped silica particles prepared with 3% of R812S in plastic jar after the storage conditions (mean ± SD, n=3).

R812S:Water	Initial			1 month			3 months		
	Density		%CI	Density		%CI	Density		%CI
	d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}	
3:97									
N 1	0.59	0.74	20.27	0.57	0.69	17.39	0.53	0.67	20.90
N 2	0.59	0.74	20.27	0.57	0.69	17.39	0.51	0.65	21.54
N 3	0.59	0.74	20.27	0.57	0.69	17.39	0.50	0.65	23.08

APPENDIX M

Table 27 Water entrapment efficiency of loose face powder containing water-entrapped silica particles after the storage condition (mean ± SD, n=3).

Water-entrapped silica particles:Basic loose face powder	Initial				1 month				3 months			
	Sample weight (g)	W_t (g)	W_s (g)	% EE	Sample weight (g)	W_t (g)	W_s (g)	% EE	Sample weight (g)	W_t (g)	W_s (g)	% EE
30:70												
N 1	0.497	0.144627	0.1279775	88.49	0.498	0.144918	0.1001976	69.14	0.518	0.150738	0.0220668	14.64
N 2	0.500	0.145500	0.12800	87.97	0.511	0.148701	0.0851837	57.29	0.502	0.146082	0.0189756	12.99
N 3	0.501	0.145791	0.11523	79.04	0.501	0.145791	0.095190	65.29	0.506	0.147246	0.0390126	26.49
40:60												
N 1	0.499	0.193612	0.1749993	90.39	0.504	0.195552	0.1689912	86.42	0.499	0.193612	0.1299895	67.14
N 2	0.499	0.193612	0.1673147	86.42	0.498	0.193224	0.1419798	73.48	0.500	0.19400	0.152600	78.66
N 3	0.497	0.192836	0.1463168	75.88	0.501	0.194388	0.1510014	77.68	0.500	0.19400	0.131	67.53

APPENDIX N

Table 28 The compressibility index of loose face powder containing water-entrapped silica particles after the storage condition (mean ± SD, n=3).

Water-entrapped silica particles:Basic loose face powder	Initial			1 month			3 months		
	Density		%CI	Density		%CI	Density		%CI
	d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}		d_{bulk}	d_{tapped}	
30:70									
N 1	0.44	0.71	38.03	0.43	0.71	39.44	0.40	0.69	42.03
N 2	0.43	0.71	39.44	0.43	0.69	37.68	0.40	0.67	40.30
N 3	0.43	0.71	39.44	0.43	0.69	37.68	0.40	0.67	40.30
40:60									
N 1	0.48	0.71	32.39	0.44	0.69	36.23	0.42	0.67	37.31
N 2	0.48	0.74	35.14	0.44	0.71	38.03	0.40	0.65	38.46
N 3	0.47	0.74	36.49	0.44	0.71	38.03	0.41	0.65	36.92

APPENDIX O

Table 29 Oil absorption capacity of loose face powder containing water-entrapped silica particles after the storage condition (mean ± SD, n=3).

Water-entrapped silica particles:Basic loose face powder	Initial		1 month		3 months	
	Oil usage (g)	%Oil absorption	Oil usage (g)	%Oil absorption	Oil usage (g)	%Oil absorption
30:70						
N 1	0.370	37	0.398	39.8	0.385	38.5
N 2	0.333	33.3	0.376	37.6	0.479	47.9
N 3	0.371	37.1	0.403	40.3	0.458	45.8
40:60						
N 1	0.330	33	0.332	33.2	0.471	47.1
N 2	0.339	33.9	0.348	34.8	0.515	51.5
N 3	0.351	35.1	0.327	32.7	0.459	45.9

VITA

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