CHAPTER 4

Encapsulation using spray drying and freeze drying, and characterization of white champaca (*Michelia alba D.C.*) extract using octenyl succinic anhydride

Abstract

The objective was to investigate effect of octenyl succinic anhydride (OSA) starch concentration toward rheological properties and characterization of *Michelia alba* D.C. (MAD) extract on encapsulation using spray drying and freeze drying. The changes of the volatile compounds of MAD from fresh, dry, extract, and encapsulated powder was also investigated and evaluated for main aroma characteristics using sensory descriptive analysis. The results showed that adding more OSA starch increased peak viscosity, breakdown and final viscosity. The moisture content, water activity and solubility of spray drying were lower than freeze drying. The microencapsulation efficiency of spray drying (92.62%) was higher than freeze drying (66.74%). Moreover, the high retention and lower occurrence of surface content of spray drying (0.54%) and freeze drying (2.40%). The sensory descriptive analysis was used to evaluate the characteristic aromas. Those were identified as linalool, verbenone, and 2-methyl butanoic acid. Those results were indicated higher stability of spray drying over freeze drying. Regardless of the decreasing of aroma intensity, the MAD encapsulated powder from spray drying also demonstrated potential to retain aroma by showing the decreased aroma intensity of main characteristic from MAD. Finally, the encapsulated powder from spray drying had more stability than freeze drying, so it is suitable process to encapsulate the MAD extract.

Keywords: *Michelia alba* D.C., encapsulation, octenyl succinic anhydride**,** rheological properties, spray drying, freeze drying

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4.1 Introduction

Michelia alba D.C. (MAD) or white champaca is a fragrant plant in the Magnoliaceae family. Originating from southern Asia, it has acclimatized in many regions of the world (Smitinand, 2001). The white elongated bell-shaped flowers have a strong sweet fragrance, bloom year round, and emit a powerful scent which can be detected several meters away. They have been used as sacred offerings or in garlands and their sweet aroma that make them an ideal ingredient for aromatherapy products (Bunyapraphatsara, 1996). There are various chemical constituents isolated from varieties of species from the genus Michelia, which are linalool, tetrahydrofuranol, steroids, and terpenoids. Volatile compounds from the flower of genus Michelia provide a pleasant fragrance to human olfactory sense and have potential application as a flavoring agent (Shang, Hu, Deng, & Hu, 2002). The MAD flowers contain aromatics that can be source of essential oils. It was provided pleasing aroma and flavour that has been shown to be effective to treat prostatitis and bronchitis (Chiang, Chen, Lin, T.-J., Shih, & Wen, 2012). In addition, there is a monoterpene alcohol, which is known as linalool, occurring naturally in MAD that can act as a flavoring agent; it is used in many industries that deal in flavors and contributes to the characteristic aroma natural products as well as beverages and sweets, for instance, tea and chocolates (Kumar *et al*.,

2012). In addition, *Michelia alba* D.C. is among the world's most famous fragrant flower as its aroma can be used in variety of expensive perfumes (Pensuk, Padumanond, & Pichaensoonthon, 2007).

In order to achieve the aroma, Scented plants are mostly dried before extracted. The preponderance of scented plants are marketed in dried form because of containing a high water content lead to deteriorative reaction that produced alterations in their composition, generally in their aroma which is an important quality factor that influences consumer acceptability of aromas and flavors (Díaz-Maroto, Vinãs, & Cabezudo, 2003). The fluctuations in the concentration of the aroma during drying process depend on numerous factors such as methods and variety of scented plants. Ibáñez *et al.* (1999) concluded that there were slightly changed of rosemary aroma between fresh sample and dried sample.

Extraction methods; solvent extraction soxhlet extraction, supercritical fluid extraction (SFE), distillation methods, including hydrodistillation (HD), stream distillation (SD), and vacuum distillation (VD), are conventional techniques that used for extracting aroma from scented plants for further analysis (Zhu *et al*., 2013). Solvent extraction commonly used is water, alcohol, petroleum ether and other organic solvents to extract aromatic materials from plant parts which contained crude extract, essential oils, resin gum and/or animal secrete fragrant substances. The selective extraction must be excluded unimportant components and selectively to desirable extract flavor substances (Zhu *et al*., 2013).

Gas chromatography–mass spectrometry (GC-MS) and gas chromatography flame ionization detector (GC-FID) are used for analysis of volatile organic compounds emitted from scented plants (Samuelsson, Nilsson, & Burvall, 2006). The combination of GC-MS, GC-FID, and a head space-solid phase microextraction (HS-SPME) is a suitable and sensitive for analysis of volatile compounds of natural products, spices, or aromatic plants (Huang *et al*., 2011). The evaluation of the sensory characteristics can be indicated from conventional descriptive sensory analysis. This technique involves

selection of terms and developments of the consensus descriptor (Civille & Lyon, 2001).

The interests of flavor and aroma stability had been increasing because of relationship with acceptability and qualities of foods. Many factors connected overall quality of food from aroma affect (Landy, Druaux, & Voilley 1995). Encapsulation is the techniques the material or mixture system entrapped other active ingredients inside. It is applied to retain flavor and aroma between storage periods in food products. It can protect flavor/aroma from undesirable interaction as well as increase flavor shelf-life and allow a controlled (Marcuzzo *et al*., 2012).

Spray drying and freeze drying are common methods applied to encapsulate bioactive components in a protective matrix. The properties of microcapsules obtained in these drying techniques can be influenced by emulsion or suspension properties, including the nature of oil phase, types of wall materials, ratio of wall to core, solid content, viscosity, stability and droplet size, and processing conditions (Chen, Zhong, Wen, McGillivray, & Quek, 2013). Spray drying of food emulsions has been used in the food industry since the late 1950s and is a well-established process to produce large amounts of material.

The wide application of spray drying in food is a result of its outstanding advantages, including the production of small-size and spherical-shape, free-flowing particles with narrow size distribution, giving good physical stability of finished products (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007). The relatively short drying time when compared with other drying processes, for instance drum drying, makes it relatively suitable for drying certain heat-sensitive materials, for instance, flavor. The advantages of spray-drying are continuous production, easy operation, low cost and wide choice of carrier material and equipment (Carneiro, Tonon, Grosso, & Hubinger., 2013). The drawback of this technique suggested that very volatile aromas called fresh top note can partially be lost during the process (Reineccius, 2006). Furthermore, some aromas were oxidized during the spray-drying

process because of their small size. Normally, spray-dried aromas are water-soluble which was desirable or not. Freeze drying is recognized as the best method for producing high-quality dried food products, although it is less attractive than spray drying due to high energy consumption and long processing time (Schwegman, 2009). As the drying process is conducted under vacuum and at temperatures lower than ambient temperature, freeze drying prevents oxidation and chemical modification of the products, making it especially attractive for drying heat-sensitive and bioactive components (Chen *et al*., 2013).

In this research, the properties of octenyl succinic anhydride starch (OSA starch) at different concentration were investigated along with comparison on spray-dried and freeze dried encapsulated powder properties. The results provided information of OSA starch and encapsulated powder properties that indicated the suitable OSA starch concentration and the process of encapsulating of MAD extract. The changes of the volatile compounds of MAD from fresh, dry, extract, and encapsulated powder were also set to investigate and evaluate the main characteristic aroma of MAD together with the changes of main aroma characteristics by conventional descriptive sensory analysis.

4.2 Materials and methods

4.2.1 Materials, references and standard aromas

The commercial OSA starch was purchased from National Starch & Chemical (Thailand), Co., Ltd. (Bangkok, Thailand). The MAD flower was purchased from flower orchard (Nakorn Pathom, Thailand). Those were collected at 5–8 am during June 2013. The 95% ethanol was purchased from Union Science Co., Ltd. (Chiang Mai, Thailand). All standards chemicals (2-methyl butyric acid, (-)-linalool, and (1s)-verbenone) were purchased from Sigma-Aldrich, Co., LLC. (MO, USA). Ground cinnamon and dried oregano were obtained from McCormick & Co., Inc., MD, USA. Fresh lemon was purchased from Rimping Supermarket (Chiang mai, Thailand). The analyzed organic chemicals were of analytical grade.

4.2.2 MAD extract preparation

The MAD flower was rinsed through fresh water and then drained under cool shade. The washed MAD flower was separated, washed and left in cool shade to drain excesses water before taken through drying process. The fresh MAD petals were dried using tray dry hot air oven (464CHMU, NAVALOY Co., Ltd., Bangkok, Thailand) with temperature at 45±5°C for 24 hours. The dried MAD was ground using Hammer mill grinder (C31896, Armfield, Christy&Norris Ltd., England) with 0.5 mm mesh. All dried MAD was collected in vacuum foil packages and kept at -20°C. The MAD extract was prepared from the dried MAD petals in solvent extraction using 70% v/v ethanol under 30°C for 12 hr with sample and solvent ratio at 1:10. After time lapse, the solvents was filtered and drained. The evaporated filtrate under reduce pressure at the 40°C (R-200, Buchii, Switzerland) was weighed and contained in amber vial less than 4°C for further experiment (Paibon *et al*., 2011; Samakradhamrongthai Thakeow, Kopermsub, Chansakoaw, & Utama-ang, 2012).

4.2.3 Investigation on rheological properties of OSA starch

The OSA starch solution ratio variation of starch in water at 0.25:1, 0.50:1, 0.75:1, 1:1, 1.25:1, 1.5:1, and 2:1 were investigated to find out the suitable ratio of mixture between water and the OSA starch for encapsulation. The rheological properties of OSA starch were analyzed using a rapid viscosity analyzer (RVA-4D, Newport Scientific Pty. Ltd., NSW, Australia). The 2 g of OSA sample was prepared in deionized water of volume 25 ml. The initial speed of stirring in RVA was 960 rpm for 10 sec, followed by 160 rpm for the remainder of the analysis. The condition of RVA was started at 50°C with ramping rate at 15°C/min, advancing to 90°C. The temperature was detained at 90°C for 10 min and dropped to 30°C in 5 min, and then detained again at 30°C for 10 min (Song, He, Ruan, & Chen, 2006). After that, the suitable time for dispersing flavor in the emulsion was investigated. The suitable concentration of the OSA starch using rheological analysis condition as described above compared with the analysis condition using the holding time at 90°C for 25 min.

4.2.4 Preparation of MAD encapsulated powder using spray drying and freeze drying

The suitable OSA starch concentration was selected to prepare encapsulated powder. The aqueous phase was prepared by dissolving the OSA starch at a suitable selected ratio (1:1 of starch in water) in deionized water at 50°C while stirring for 30 min until the solution temperature reached 90°C. The MAD extract was added into solution at 10% w/w of dry shell material and stirred vigorously. The solution was left to stand at room temperature for 30 min to confirm a complete dispersion (Samakradhamrongthai, 2011; Ades, Kesselman, Ungar, & Shimoni, 2012; Carneiro *et al*., 2013).

The emulsion were dehydrated using spay drying and freeze drying. The spray dryer (March Cool Industry Co., Ltd., Bangkok, Thailand) was operated at an inlet temperature of 150°C, outlet temperature of 50°C with blower speed at 50 rpm. The spray-dried powder was gathered from the collect chamber. The freeze drying of emulsion was performed on freeze dryer (Model 7948030, Labconco, USA). The emulsion was frozen dried at -20°C immediately after preparation. The frozen sample was then dried in freeze dryer for 48 hr at -45°C under pressure of less than 0.120 mbar. The freeze-dried products were ground using mortar and pestle after drying. All encapsulated powder samples were directly weighed and stored in desiccators at 25°C for further analysis.

4.2.5 Physical properties of encapsulated powder

Yield recovery. The microcapsules obtained from spray drying were directly weighed for each tests and stored in desiccators for further analysis. Yield recoveries (%Y) of spray drying have been calculated using Eq. (4.1).

$$\%Y = (\text{mass of collected solid} / \text{mass of solid in the feed}) \times 100 \qquad (4.1)$$

Moisture content. Five grams of encapsulating powder were dried in hot air oven (FD 115, Serial 08-836864, Binder, Germany) at 105°C until reaching constant weight. Afterwards, samples were weighed and the moisture contents were calculated (AOAC, 2000, NO. 934.01).

Water activity. One gram of encapsulated powder was analyzed with water activity analyzer (AquaLab LITE, DECAGON Devices Inc., USA). All samples were kept in sealed packages prior the analysis. The sample was poured into a tested plastic cup with a cover before the analysis.

Color measurement. The color was analyzed using Hunter LAB (Colorquest XE, Hunter Lab, USA). The light source was Illuminant D65. The CIELab color values were used with *L** (Lightness), *a** (negative value means green and positive value means red), *b** (negative value means blue and positive value means yellow). All samples were measured in triplicate.

Solubility. The solubility of the encapsulated powders was examined according to the method described in Fernandes, Borges, & Botrel. (2014) research. The quantity of 2.5 g of powder was dissolved in 250 ml of boil water in 600 ml beaker for 5 min. The aqueous solution was filtered all solution with dried and weighted on filter paper No.1 (Whatman™ No. 1, Buckinghamshire, UK). The filter paper was dried in hot air oven at 105°C for 24 hr. The solubility (%) was calculated as the percentage of dried supernatant in relation to the amount of powder.

4.2.6 Encapsulation efficiency (%EE)

The encapsulation efficiency of encapsulated powder was analysed followed method from Carneiro *et al*. (2013) with modification. The MAD extract was trapped in the microcapsule and adhered on the surface; therefore, to examine the microencapsulation efficiency, the quantities of surface and total content of MAD extract were determined. Five grams of encapsulated powder from spray drying and

freeze drying were soaked in 50 ml of absolute ethanol using magnetic stirrer at 50 rpm. The mixing time for surface content was 5 min while the mixing time for total content was 15 min. The extracted solvent was transferred to Büchner funnel with 125 mm diameter filter paper (Whatman^{TM} No. 4, Buckinghamshire, UK) which was dried in hot air over for 24 hr and then weighted before use. The filtrates of extracted solvent was taken to evaporate and eliminate all the solvent using rotary evaporator (V800, Buchi, Switzerland) at 40°C with pressure at 175 mbar for ethanol and 72 mbar for water. After the evaporation, the pear-shaped evaporating flask with extract was taken to get rid of excessed moisture using hot air over (FD 115, Serial 08836864, Binder, Germany). The residue in pear-shaped evaporating flask was then weighed determined for extracted filtrate (applied from Ades *et al*., 2012 and Samakradhamrongthai, 2011). The quantities were reported as mean and standard deviation of triplicate measurements. EE was calculated according to Eq. (4.2)

$$EE = [(\text{Total extract content (g)} - \text{surface extract content (g)})/\text{Total extract content (g)}] \times 100 \quad (4.2)$$

4.2.7 Morphology of microcapsules

The microstructures obtained from spray and freeze drying were examined using scanning electron microscope (SEM, JSM5410-LV, JEOL, Japan). The samples were placed on the SEM stubs using a two sided-adhesive tape and subsequently coated with gold using an electrically conductive of 60 kV in a vacuum chamber. Photographs were taken at an excitation voltage of 10 kV (Borrmann, Pierucci, Leite, & Leão, 2013).

4.2.8 Glass transition temperature (T_g)

The encapsulated powders were stored at 25% relative humidity (3% moisture content) in a desiccator for 24 hr prior to the glass transition temperature (T_g) measurement. Then the samples were weighed (5±0.2 mg) in an aluminium pan and sealed. The measurement was conducted by differential scanning calorimeter (Diamond DSC, Perkin Elmer, Inc., OH, USA) using a liquid nitrogen cooling system (Intracool

2P, TA instruments, NC, USA). The operating conditions were as follows: nitrogen flow rate at 20 ml/min and temperature ramping from 20°C to 120°C at the rate of 10°C/min. A sealed empty aluminum pan was used as reference. All measurements were performed in triplicate (Chen *et al*., 2013).

4.2.9 X-Ray diffraction (XRD)

The formation of the encapsulated powder from spray drying and freeze drying were verified using XRD. The experiment was carried out by a Miniflex II Desktop X-ray Diffractometer equipped with a graphite crystal monochromator (Miniflex II, Rigaku Corp., Japan) providing the Cu Kα radiation (λ = 0.154 nm). The diffractograms were obtained under the condition of 40 kV and 30 mA with scanning angle 2θ set from 5 - 30° with a scanning rate of 0.02°/sec. The crystalline nature of the complexes was determined by the position of the XRD peaks (Sit, Misra, & Deka, 2013).

4.2.10 Characterization of volatile compounds from MAD extract and microencapsulated powder using gas chromatography

The volatile compounds were analyzed using gas chromatography-flame ionization detector (GC-FID). The volatile compounds were identified with the headspace of each sample, using solid phase microextraction technique (SPME). The 85 μm Carboxen™/Polydimethylsiloxane StableFlex™ type fiber (Car/PDMS, Supelco, USA) was used. The Car/PDMS fiber was exposed for 60 sec in the headspace of a septum-capped vial containing 2 g of samples. Subsequently, the fiber was directly injected into an injection port of a gas chromatograph (GC-2010, 05853, Shimadzu Corp., Japan) The FID was operated with sampling rate at 40 msec and air flow rate of 400 ml/min, 230°C source temperature. The GC was operated on DB-WAX column (30 m x 0.53 mm, i.d., 1.50 μm film thickness) (Model 125-7333, Agilent Technologies, Inc., USA), and helium is used as a carrier gas at a flow rate of 50.0 ml/min. The temperature program was started with an initial temperature of 40°C, then heated up to 250°C at 7°C/min and held for 5 min at 250°C. The MS is operated in the electron

impact mode with electron energy of 70 eV and scan over range 20–300 amu, the source temperature being 230°C. The obtained mass spectra are preliminarily interpreted comparing with those of Enhance chemstation version D00.00.38 (Agilent Technologies), the Mass spectral search library of the National Institute of Standards and Technology (NIST, Gaithersburg, USA). The relative content of identified volatile compounds was calculated from effective carbon number (ECN). The weight of compound was calculated based on one µl of injected hexanal solution which used as standard reference to plot calibration curve. The relative amount was calculated from constant ratio of hexanal as followed the method of Scanlon & Willis. (1985) and Samakradhamrongthai. (2011) with slightly modification.

4.2.11 Comparison of volatile compounds from fresh, dried, extract, and encapsulated MAD sample using gas chromatography

The volatile compounds were analyzed using GC-FID. The volatile compounds were identified with headspace of each sample using static head space technique. Five µL of equilibrium air from all samples were manually injected and analyzed using the condition followed the method from 4.2.10.

4.2.12 Sensory descriptive analysis

The aroma profile of four samples (fresh MAD, dried MAD, MAD extract, and MAD encapsulated powder) was conducted and evaluated using generic descriptive analysis (Meilgaard, Civille, & Carr, 2007).The dried MAD petal was used as a warm up sample and to describe the term of aroma characteristic and determined level of intensity of each characteristic. The prepared standard references were used for intensity analysis of trained panel. The trained panels were selected by screening questionnaire and odor matching test. All trained panels were research official and graduate students from Division of product development technology, Faculty of Agro-Industry, Chiang Mai University. They were five males and five females. The subjects were selected by screening questionnaire and odor matching test (ASTM, 2013). The references and

standards aroma for odor matching on MAD aroma were prepared using dried parsley (3.75 g), dried oregano (1.00 g), Pandan flavor (4.00 g), 2-methyl butanoic acid (0.50 g), linalool (1.50 g), dried rosemary (3.00 g), cinnamon (5.00 g), verbenone (1.00 g), dried MAD flower (10.00 g), lemon zest (7.50 g), and dried thyme (1.00 g). The meeting session was taken place at the sensory evaluation laboratory (Sensory evaluation and consumer testing unit, Faculty of Agro-Industry, Chiang Mai University, Chiang Mai, Thailand) and took about 2 hr per session (10 sessions). In each session, the trained panels had evaluation of aroma with references which selected by trained panels then rated the intensity of each aroma characteristics.

4.2.13 Statistical analysis

All data were collected in triplicate. The data regarding the samples from spray drying and freeze drying were presented as mean values±standard deviations and analyzed using t-test statistic. Analysis of variance (ANOVA) was performed using the Duncan's multiple range test (DMRT; SPSS Inc., IBM Corp., Chicago, IL, USA). All statistical analysis was conducted at significant level at 95% ($p < 0.05$). (SPSS 17.0 SPSS Inc., IBM Corp., Chicago, IL, USA)

4.3 Results and discussion

4.3.1 Rheological properties of OSA starch slurry at different concentrations

The rheological properties of the OSA starch at different concentrations were obtained by a rapid viscosity analyzer (RVA). The major RVA parameters were peak viscosity, breakdown viscosity, setback viscosity, and final viscosity. The viscosity curves reveal an increase in the peak viscosity (71.00–1193.33 cP), breakdown viscosity (32.67–687.00 cP), and final viscosity (42.00–2031.00 cP). This study showed that the degree of changes in the rheological properties of the OSA starch depend on the increasing percentages of the OSA starch as demonstrated in Table 4.1.

The peak viscosity of the OSA starch increased because of the increase in the swelling volume of the OSA starch and the hydrophilic interaction (Chen *et al*., 2013). The massive OSA groups on the starch molecules reasoned to restructure as a result of steric interference and resulted in repulsion toward simplifying to increase the swelling volume (Lawal, 2012). The breakdown viscosity was different between the peak viscosity and the minimum viscosity during heating. A higher value of the breakdown viscosity indicated that the resistances shear force decreasing during heating. Jiranuntakul, Puncha-arnon, & Uttapap (2014) reported that starch was usually disrupted during heating, resulting to reduce its viscosity.

The results as regarding to the breakdown viscosity show an increase in the breakdown viscosity — a finding which is in contrast to the nature of starch. This proves that an increase in the OSA starch provides more shear force resistance to starch complex. The setback viscosity of the OSA starch ratio at 0.25:1–1:1 was observed to be decreasing, which showed a decreasing retrogradation from −27.00 cP to −93.33 cP, whereas the retrogradation of the OSA starch which was higher than 1:1 was started to be increasing.

This demonstrated that an increasing of the OSA starch decreased the degree of retrogradation of the starch complex and provided more strength of force within those complexes. The higher setback viscosity created the occurrence of recrystallization of gelatinization starches, which indicates inappropriate OSA starch concentration (Silaket *et al*., 2014). The result suggested that OSA starch at ratio of 1:1 was suitable to create suitable gelatinization for this experiment.

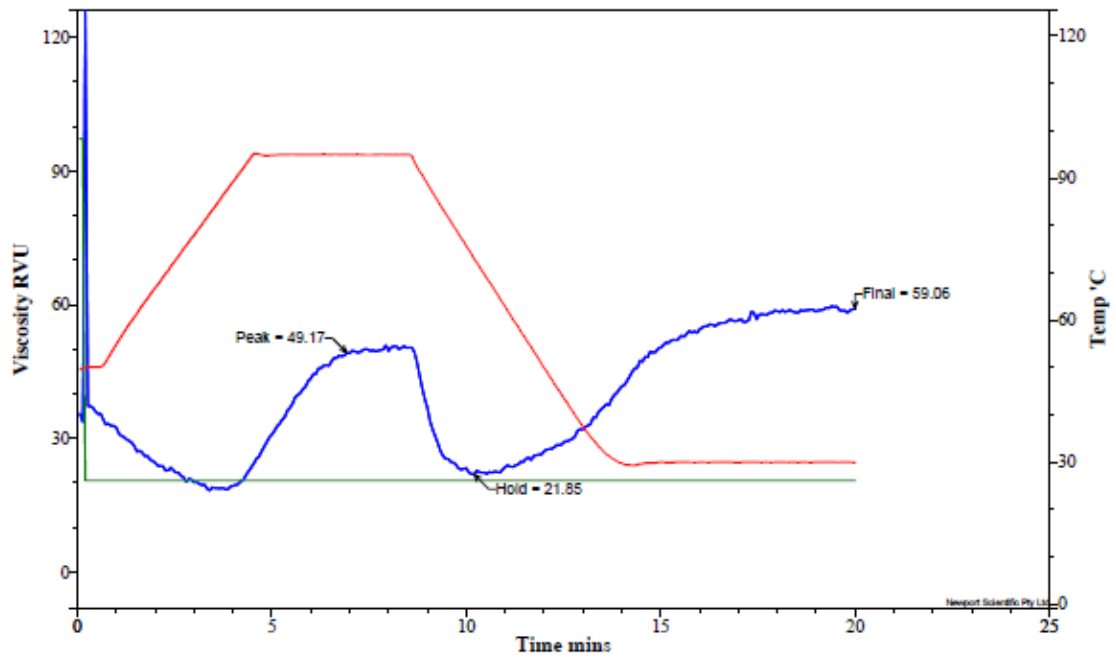
In addition, the suitable time for dispersing flavor in emulsion was investigated using OSA starch:water ratio at 1:1 which was the maximum concentration to create suitable setback viscosity. The result revealed that holding time after the temperature reaches 90°C provided different rheological properties of the OSA starch. The decreased temperature can create the setback immediately which decreased the length of time for infusing the aroma or flavor into the emulsion. There was about 10 min when holding the temperature at 90°C to infuse the aroma or flavor into the emulsion before the OSA starch started to create the set back (Fig. 4.1).

The findings of this experiment revealed that the ratio of the OSA starch:water for encapsulation had an effect on the rheological properties, which proves that the degree of changes in the rheological properties of the OSA starch depends on the increasing of OSA starch. However, it has to be taken into consideration that the starch solution ratio for this study was OSA starch:water at 1:1 which did not create the undesirable retrogradation. The concentration range of the selected ratio was 0.25:1–1:1, which was used in the microencapsulation of the MAD extract.

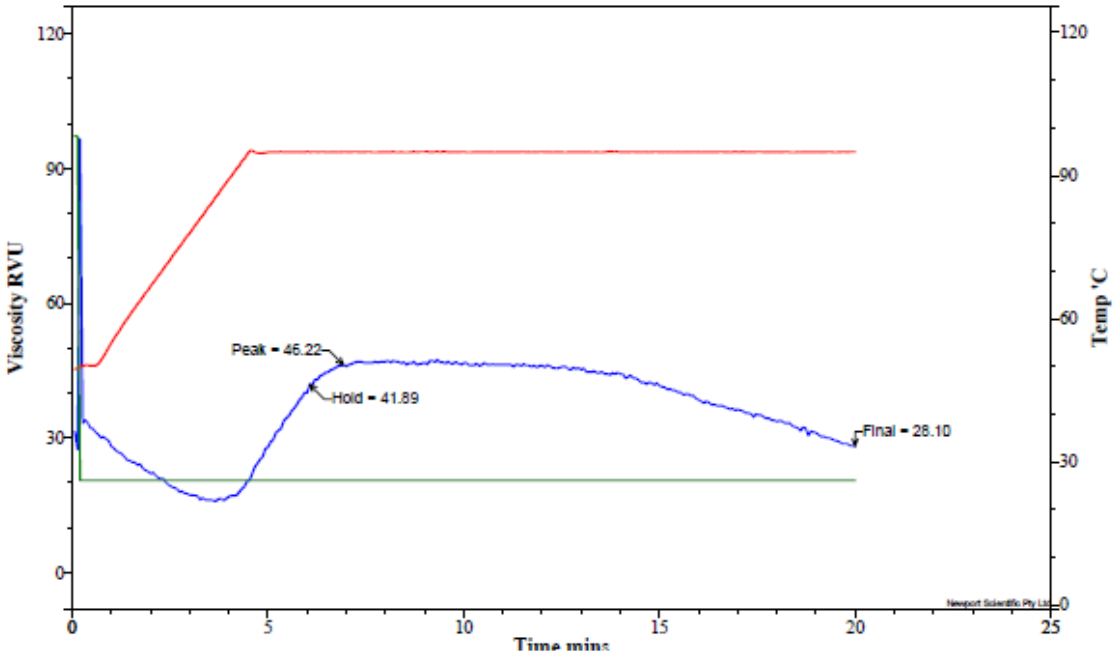
Table 4.1 The rheological properties of different percentages of OSA starch

OSA starch: water ratio	Peak (cP)	Trough (cP)	Breakdown (cP)	Set back (cP)	Final viscosity (cP)	Peak Time (min)	Pasting Temperature (°C)
0.25:1	71.00±1.00g	36.33±0.58g	32.67±2.52g	-27.00±1.00c	42.00±2.65g	3.97±0.04c	92.12±0.21g
0.50:1	112.67±1.53f	55.67±2.08f	60.67±0.58f	-60.00±1.00d	53.00±1.53f	6.54±0.65b	92.65±0.10f
0.75:1	273.67±1.53e	100.00±1.00e	176.00±1.00e	-83.67±1.15e	185.00±2.52e	6.99±0.01a	93.06±0.06**e**
1:1	293.67±3.21d	104.67±3.41d	195.00±5.57d	-90.00±2.00f	212.00±1.73d	7.00±0.00a	93.33±0.10d
1.25:1	422.33±2.52c	144.67±1.53c	280.33±8.72c	-93.33±2.08f	322.00±2.51c	7.00±0.00a	94.20±0.03c
1.5:1	672.00±2.65b	298.00±2.00b	376.67±1.53b	68.00±2.00b	743.00±1.15b	7.00±0.00a	94.74±0.06b
2:1	1191.33±2.31a	516.33±1.53a	687.00±2.00a	835.67±5.13a	2031.00±1.53a	7.00±0.00a	95.58±0.04a
p-value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Note: The different letters in the same row mean significant difference ($p \leq 0.05$)



(a)



(b)

Fig. 4.1 The rheological properties of the OSA starch, comparing the (a) extended hold time and (b) non-extended hold time.

4.3.2 Characterization of MAD extract encapsulation

The OSA starch ratio at 1:1 was use in this experiment to screen suitable process of encapsulation on MAD extract. The yield recovery of freeze drying was higher than spray drying at 50.01% and 22.42%, respectively (Table 4.2) which conformed to results reported by Santo, Lima, Torres, Oliveira, & Ponsano (2013), who studied the comparison of spray drying and freeze drying to obtain powder *Rubrivivax gelatinousus* biomass. The findings showed that spray drying had lower in moisture content, water activity, and mass recovery, whereas there was no significant difference in yield recovery. The lower yield of spray drying resulted from adhesiveness of slurry solid, and it has been responsible for the lower yield recovery in the case of spray drying which caused the product to adhere on collecting chamber, leading to losses during process (Islam, Edrisi, & Langrish, 2013). However, moisture content, water activity and solubility of spray drying were lower than freeze drying which indicated high stability of encapsulated powder as suggested in the research of Rosa, Tsukada, & Freitas (2006). These parameters pointed to the fact that the spray drying method was more effective at eliminating water which can be explained by the extreme interaction between microcapsule and the hot air in the chamber (Rosa, Tsukada, & Freitas, 2006). The lower moisture content registered by the spray-drying technique demonstrated more effective for encapsulation than freeze drying (Santo *et al*., 2013). The spray-dried product exhibited higher color value of lightness (L^*), whereas red (a^*) and yellow (b^*) color values were lower. These results demonstrated that the spray-dried powder was lighter, less red, and less yellow, which means that it had more saturated color than the freeze-dried powder. These differences were because of the higher temperature and pressure that changed the color of the final product (Fellows, 2006). In addition, the lightness, red color and yellow color suggested that the spray-dried powder provided higher consistency of slurry prior to the encapsulation process. Additionally, another factor that explained the differences in the color value was the difference in the water content of the encapsulated powders since the drying process modifies microcapsule surfaces, fluctuating its reflectiveness and color (Fellows, 2006).

Table 4.2 Comparison of encapsulated powder from spray drying and freeze drying

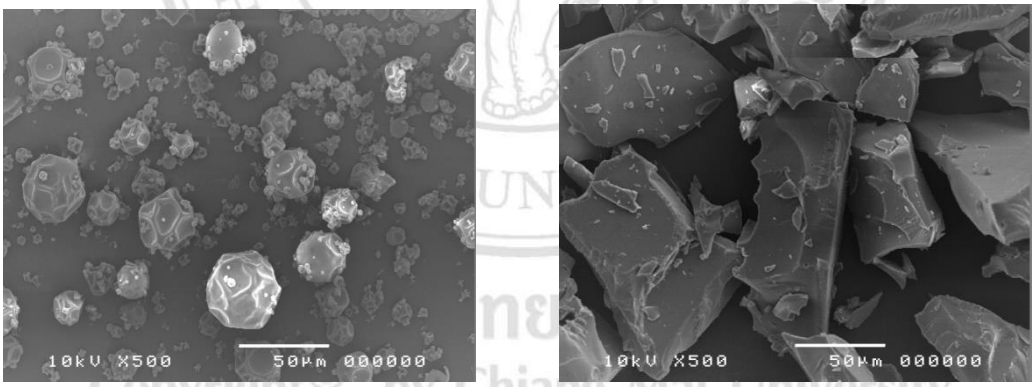
Properties of encapsulated powder	Spray Drying	Freeze Drying
Yield recovery (%)	22.42±0.55b	50.01±0.18a
Moisture content (%)	0.70±0.08b	1.28±0.01a
Water activity (a_w)	0.610±0.004b	0.656±0.007a
Color value		
L*	87.93±0.34a	72.84±0.23b
a*	3.35±0.07b	9.45±0.36a
b*	14.38±0.27b	21.58±0.76a
Solubility (%)	81.89±0.70b	98.67±0.07a
Surface content (%)	0.54±0.03b	2.4±0.06a
Extract recovery (%)^{ns}	73.61±2.91	72.25±1.50
Encapsulation efficiency (%EE)	92.62±0.45a	66.74±1.19b
T_g (°C)	75.20±0.93a	70.65±0.50b

Note: [1]Mean values and standard deviation. [a,b]Letters in the same row with different superscripts mean differ significantly ($p<0.05$) by the t-test.
[ns] means non-significant difference ($p \leq 0.05$)

The encapsulation efficiency (%EE) of spray drying was higher than that of freeze drying, and these were 92.62% and 66.74%, respectively, whereas the observed surface content of spray drying (0.54%) was lower than that of freeze drying (2.40%). (Table 4.2). The disparity in the values of the encapsulation efficiency is indicative of the higher retention of volatile compounds during drying. This indicated that spray drying can create microcapsules in the film-forming shell at the last stage of drying, resulting in high incidence of entrapment of extract content which leads to low content of surface content (Dickinson, 2003). On the other hand, freeze drying promotes droplet-to-droplet interaction in the emulsion until the drying stage, which causes freeze drying to consume more time than spray drying, resulting in inconsistency in the entrapment of the extract of the freeze-dried encapsulated powder which leads to low incidence of entrapment of extract content and, thereby, high surface content. Moreover, the encapsulated constituents can be released through powder porous causing from sublimated ice crystals during the drying stage (Chen *et al*., 2013). These results suggested that spray drying has higher stability in encapsulation than freeze drying.

4.3.3 Morphology of encapsulated powder

The microstructure of encapsulated powder from spray and freeze drying showed differences (Fig. 4.2). The spray-dried powder showed a spherically regular shape with shallowed dent of shrinkage which happened during early stage of drying and cooling. These results are conformed to Sahin-Nadeem, Torun, & Ozdemir (2011) investigation. In contract to the freeze-dried powder was more likely to develop irregular crystalline-like shape with sharper edges, broken glass-like surface and brittle texture due to lyophilized process (Chen *et al*., 2013). The asymmetrical shape usually resulting from homogenization of core material in matrix solution created irregular crystalline-like shape before lyophillization (Desai & Park, 2007). The asymmetrical crystal happened when the sample was frozen between (−90) and (−40)°C and then dried by direct sublimation under low pressure and reduced temperature (between (−90)°C and (−20)°C). After drying, The brittle matrix obtained can be broken or ground into smaller pieces (Saikia, Mahnot, & Mahanta, 2015).



(a) (b)

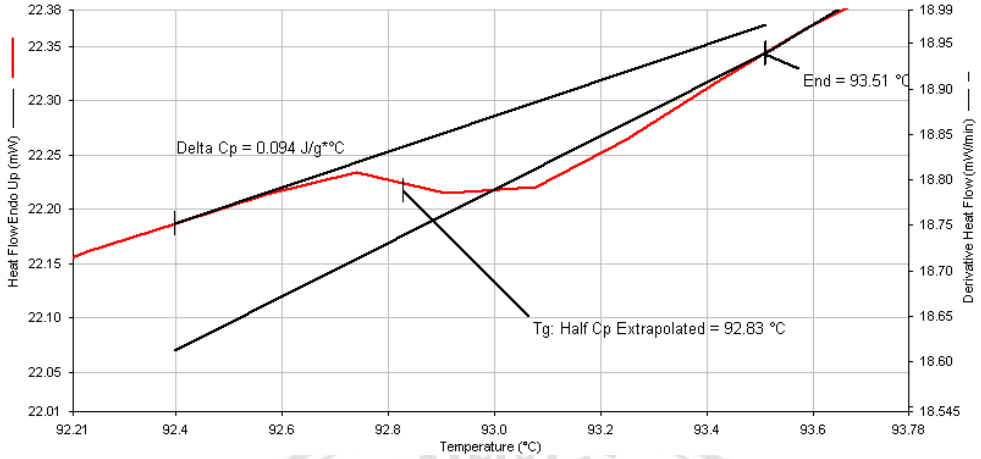
Fig. 4.2 The SEM micrographs of microencapsulation of MAD flower extract using (a) spray drying and (b) freeze drying.

4.3.4 Glass transition temperature (T_g) of spray-dried and freeze-dried encapsulated powders

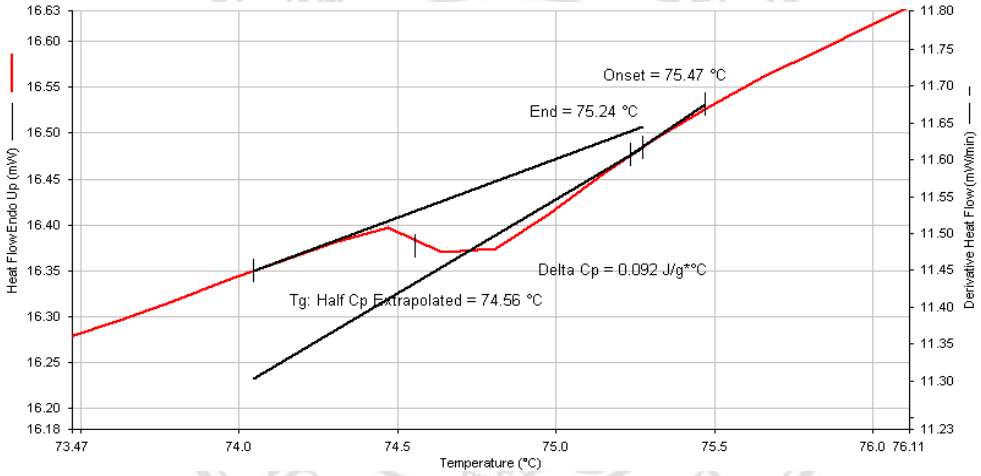
The results showed that the T_g was significant difference between the drying methods and non-processed OSA starch. The T_g from encapsulated powder from spray drying and freeze drying was 75.20°C and 70.65°C which were lower than OSA starch (92.83°C), which was conformed to the result obtained by Chen *et al*. (2013) that T_g of freeze-dried powder was lower than spray-dried powder.

This suggested that spray drying provided higher stability under processing conditions. The value of T_g obtained from the analyses of the encapsulated powder from spray drying and freeze drying was above 70°C, which indicated that the material transformed to rubbery state when temperature of sample reached over 70°C and can be stored under temperature 70°C at 25% ambient relative humidity and moisture content at 3% as an inclination toward Anwar & Kunz (2011) investigation on comparison of the stabilisation from spray drying and freeze drying on fish oil microcapsules.

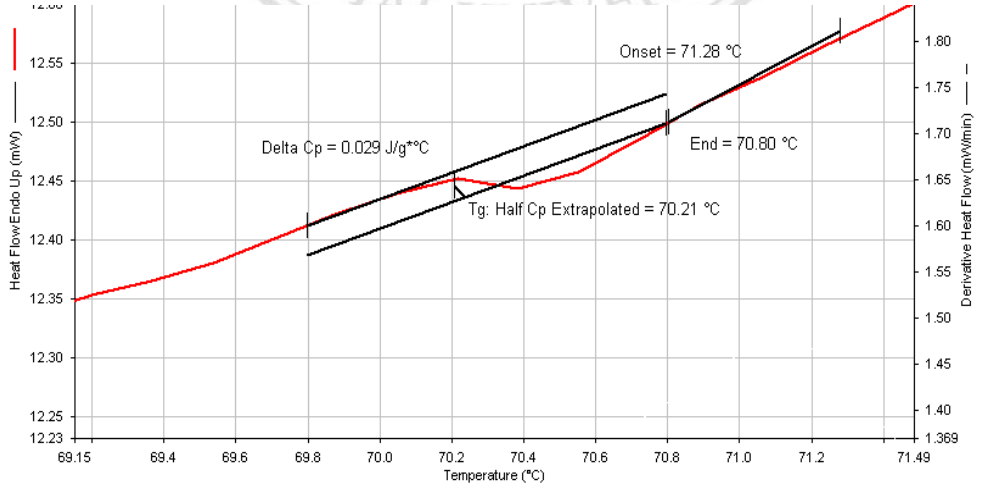
These results demonstrated that encapsulated powder from spray drying provided higher stability than encapsulated powder from freeze drying and was a suitable process to encapsulate extract from MAD.



(a)



(b)



(c)

Fig. 4.3 The differential scanning calorimetry of (a) non-processed OSA starch, (b) spray-dried encapsulated powder, and (c) freeze-dried encapsulated powder.

4.3.5 Comparison of spray-dried and freeze-dried encapsulated powders using X-ray diffraction

The changes of degree of crystallinity of samples were analyzed using X-ray diffraction. The diffraction patterns were compared to know V-type polymorphs also with diffraction patterns of OSA starch itself. The results of XRD analysis showed that all samples were in amorphous form (Fig. 4.4). The non-processed OSA starch had a typical diffraction which Bragg angles of 2θ for A-Type diffraction (11°, 15°, 17°, 18°) and B-Type diffraction (11°, 15°, 17°, 22°). The mixing of diffraction angle suggested that non-processed OSA starch used in this experiment had C-Type crystallinity diffraction which mixed between A-Type and B-Type diffraction (Buléon *et al*., 1997; Buléon, Coloma, Plancot, & Ball, 1998). The encapsulated powder from spray drying (Fig. 4.4b) and freeze drying (Fig. 4.4c) created complexes of the OSA starch and the MAD extract, resulting in V-type polymorphs which provided the Bragg angles of 2θ for V_7-type (13° and 18°), V_{6h}-type (8° and 20°) (Takeo, & Kuge, 1969; Le bail, Rondeau, & Buléon, 2005); also, there were C-type crystalline pattern (11°, 15°, and 23°) of the OSA starch which remained unchanged. This indicated that the OSA starch did not form complexes with the MAD extract completely. The freeze-dried encapsulated powder exhibited less amorphous form provided Bragg angles of 2θ at 11°, 15°, and 17° and higher form provided Bragg angles of 2θ at 13°, 18°, and 20° than the spray-dried encapsulated powder, which indicated that the spray-dried encapsulated powder had stability to retain extract over freeze-dried encapsulated powder.

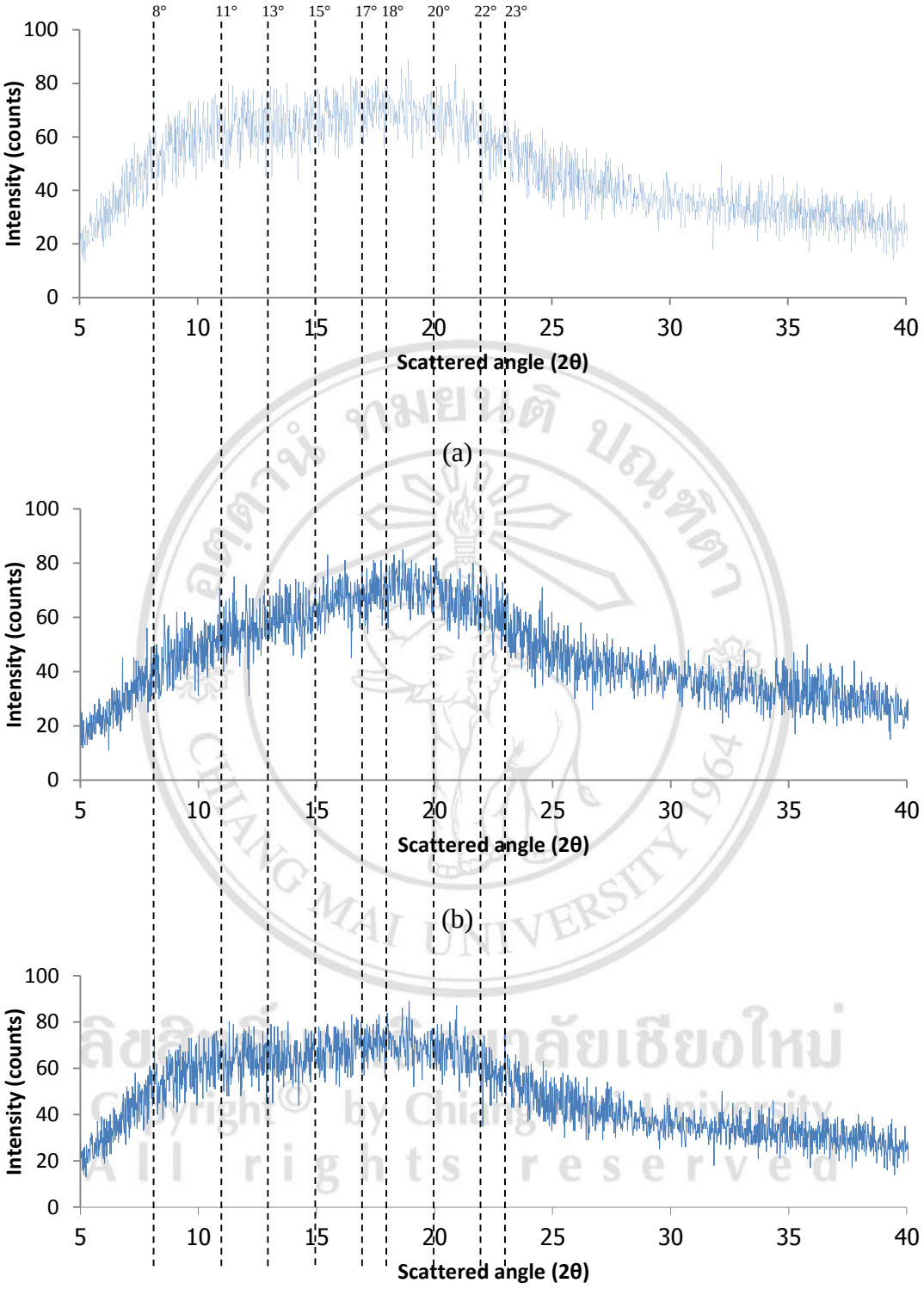


Fig. 4.4 X-ray diffraction scans of (a) non-process OSA starch, (b) spray-dried encapsulated powder and (c) freeze-dried encapsulated powder.

4.3.6 Comparison of volatile compounds from MAD extract and microencapsulated powder

The volatile compounds of the MAD extract were compared to the MAD spray-dried encapsulated powder and the freeze-dried encapsulated powder. The results showed that detected volatile compounds from MAD extract, MAD freeze-dried powder and MAD spray-dried powder were quite similar. There were detected compounds as 9, 6, and 4 compounds, respectively (Table 4.3).

The MAD extract showed a high percentage of 2-methyl butanoic acid (2.0124 µg/ml) and lilac aldehyde (0.0051 µg/ml), follow by linalool (0.0297 µg/ml) and verbenone (0.0226 µg/ml), whereas in the MAD dried powder only lilac aldehyde, linalool, verbenone, and terpendiol were detected. The MAD extract showed the presence of characteristic odors of MAD, which were 2-methyl butanoic acid and linalool (Pensuk *et al*., 2007; Kumar *et al.,* 2012). Therefore, there were lower molecular weight volatile compounds that were undetectable in the MAD freeze-dried powder and the MAD spray-dried powder. Those volatile compounds were lost during the entrapment from encapsulation (Penbunditkul *et al*., 2012). Interestingly, there was one significant change of an increase in an aroma compound: terpendiol was detected to increase in quantity from the extract to the encapsulation powder. The higher volatile compounds from MAD freeze-dried powder and spray-dried powder such as phenyl ethyl alcohol, lilac aldehyde, linalool, verbenone, and terpendiol were detected because of there were more space on SPME fiber to attached since the lower molecular weight volatile compounds evaporated through drying process. The observation of this incident was reported in Penbunditkul *et al*. (2012) research, as well as volatile hydrophobic compounds were considerably lost during the encapsulation and the drying process. Besides, Samavati, Emam-Djomeh, Mohammadifar, Omid, & Mehdinia (2011) also reported that compounds with higher relative volatility possessed lower retention aroma release.

These results explain the greater ability of low molecular weight compounds to evaporate (Reineccius, 1988; Goubet, Le Quere, & Voilley, 1998), and also to entrap

inside the hydrophobic cavity created from the conformation of the polysaccharide structure (Bylaite, Adler-Nissen, & Meyer, 2005). Similar findings were discovered in many other studies also that there was a decrease in the quantity of volatile compounds during the drying process, as stated in the researches of Laohakunjit &Noomhorm (2004), Bhattacharjee, Kshirsagar, & Singhal. (2005), and Yahya, Lu, Santos, Fryer, & Bakalis (2010). The encapsulation process also reveals a decrease in the aroma from the MAD extract. All the detected aromas, except terpendiol, were observed to have decreased. The MAD encapsulated powder showed a decrease in the amount of the aroma content, which suggests that volatile compounds are restored better by microencapsulation. The analyzed surface content was also observed (data not shown) and it showed that the percentage of surface content had become, which proved that there was good maintenance of aromatic substances inside the microcapsules, as stated in the research of Janiszewska & Witrowa-Rajchert (2007).

Table 4.3 Identified volatile compounds and relative content from MAD extract, MAD freeze-dried powder and MAD spray-dried powder using SPME technique

Compounds	Relative content (µg/ml)		
	MAD extract	**MAD Freeze-dried powder**	**MAD Spray-dried powder**
2-methyl butanoic acid	2.0124±0.0304	Not detected	Not detected
terpinolene	0.0053±0.0001	Not detected	Not detected
diethyl malonate	0.0047±0.0001	Not detected	Not detected
phenyl ethyl alcohol	0.0123±0.0002b	0.0147±0.0001a	Not detected
lilac aldehyde	0.0051±0.0001b	0.0063±0.0001a	Not detected
linalool	0.0297±0.0001a	0.0038±0.0001b	0.0026±0.0001c
verbenone	0.0226±0.0001a	0.0058±0.0001b	0.0013±0.0001c
terpendiol	0.0153±0.0001a	0.0037±0.0001b	0.0037±0.0001b
menthoglycol	0.0125±0.0002b	0.0037±0.0001c	0.0179±0.0001a

Note: The different letters in the same row mean significant difference ($p \leq 0.05$)

4.3.7 Chemical characteristics of volatile compounds of fresh, dried, extract, and encapsulated MAD

There was similarity of chemical characteristics of volatile compounds from all four samples. Nine volatile compounds from MAD were identified as shown in Table 4.4. The fresh MAD showed the highest intensity of volatile compounds with sweet/floral characteristic which were linalool (209.56±0.14 µg/ml), phenyl ethyl alcohol (175.73±2.72 µg/ml), lilac aldehyde (28.63±2.52 µg/ml) and diethyl malonate (35.26±1.03 µg/ml) followed by volatile compounds with piney/citrus characteristic which were terpendiol (4.88±0.50 µg), menthoglycol (0.72±0.01 µg/ml) and 2-methyl butanoic acid (0.37±0.02 µg/ml) The dried MAD showed the highest intensity of volatile compound with floral/fruity characteristic as identified as linalool (11.51±0.03 µg/ml), followed by phenyl ethyl alcohol (3.88±0.07 µg/ml), terpinolene (2.81±0.02 µg), and diethyl malonate (1.38±0.05 µg/ml). MAD extract showed that there were high amount of verbenone (4.35±0.28 µg/ml), followed by phenyl ethyl alcohol (4.86±0.05 µg/ml), and diethyl malonate (3.41±0.07 µg/ml) with small amount of linalool (0.86±0.02 µg/ml) and 2-methyl butanoic acid (0.16±0.01 µg/ml). The MAD extract showed the present of characteristic aromas of MAD which were 2-methyl butanoic acid and linalool (Pensuk *et al*., 2007) after drying and evaporating process. The drying and extraction processes can cause the lower molecular weight compounds such as diethyl malonate, phenyl ethyl alcohol and lilac aldehyde to evaporate before others. These results explained that the greater ability of low molecular weight compounds to evaporate during drying and extraction processes (Goubet *et al*., 1998; Reineccius, 1988). The findings were also discovered in many studies that there was a decreasing of volatile compounds during drying and extraction process as stated in researched of Laohakunjit & Noomhorm (2004), Bhattacharjee *et al*. (2005) and Yahya *et al*. (2010). The MAD encapsulated flavor powder showed decreasing amount of all detected volatile compound by 60% which suggested that volatile compounds were restored better by microencapsulation. The content of capsulated aromatic compounds was ranged from 38 to 40%. The analyzed surface content was observed (data not shown). There were in the amount of lower than 2% of their content in the staring feed of

extract. This proves good maintenance of aromatic substances inside microcapsules as stated in research of Janiszewska & Witrowa-Rajchert (2007).

In conclusion, the fresh MAD showed the highest intensity of volatile compounds of floral characteristic whereas dried MAD and MAD extract showed higher intensity of volatile compounds of spice characteristic. There was the decreasing of volatile compound during drying and extraction process which mostly happened to volatile compound with lower molecular weight. In contrast, the microencapsulation process also showed the decreasing of volatile compounds but this was happened because of the entrapment of extract into the microcapsule.

Table 4.4 Identified volatile compounds and relative content of volatile compound from fresh, dry, extract, and encapsulated MAD using static head space technique

Compounds	Relative content (µg/ml)			
	Fresh MAD	**Dried MAD**	**MAD extract**	**MAD encapsulated powder**
2-methyl butanoic acid	0.37±0.02a	0.26±0.01b	0.16±0.01c	0.10±0.01d
terpinolene	0.26±0.01b	2.81±0.02a	0.27±0.01b	0.17±0.01c
diethyl malonate	35.26±1.03a	1.38±0.05d	3.41±0.07b	2.14±0.04c
phenyl ethyl alcohol	175.73±2.72a	3.88±0.07b	4.86±0.05b	3.05±0.03b
lilac aldehyde	28.63±2.52a	0.52±0.42b	0.28±0.01b	0.18±0.01b
linalool	209.56±0.14a	11.51±0.03b	0.86±0.02c	0.54±0.01c
verbenone	0.05±0.01d	0.77±0.02c	4.35±0.28a	2.75±0.20b
terpendiol	4.88±0.50a	0.45±0.02b	0.12±0.01b	0.08±0.01b
menthoglycol	0.72±0.01a	0.22±0.01b	0.01±0.01c	0.01±0.01c

Note: The different letters in the same row mean significant difference ($p \leq 0.05$)

4.3.8 Aroma profiling of fresh, dried, extract, and encapsulated MAD using descriptive analysis technique

The trained panels were discussed from term and definition of fresh MAD, dried MAD, MAD extract, and MAD encapsulated powder (spray drying). The session of evaluation was conducted for two hr per session of five sessions. The first and second sessions were about perception. The trained panels were asked to sniff all samples, and coffee bean was used to cleanse aroma between sniff. The order of aromas was presented as floral, spice, and citrus, respectively. The aromas were detected in similar perception but in different level of intensity that might occurred from differences of panelist aroma perception (Murugan, Thiyagarajan, & Ramesh, 2007).

The aromas were perceived in order of perception in all four samples. There were two aromas (floral and citrus) which that can be detected in samples which conform to research of Pensuk *et al*. (2007) that revealed two main volatile compounds of MAD which were linalool and 2-methyl butanoic acid. Those two volatile compounds provided aroma characteristics as floral and citrus. Moreover, there is one character that trained panel detect from all sample which described as spice. The Floral was perceived immediately when panels inhaled, followed by spice and citrus. These three aromas acted as main character of MAD. The perception of floral was perceived prior to spice and citrus in all four samples. The aromas were perceived from light to heavy characteristic. The light characteristic was dominated for sweet or floral whereas heavy characteristic was dominated for wood, earthy or spice (Loewer, 1998).

Thereafter, from session two the trained panels were asked to compare and match aroma to the referenced aroma samples. The result showed that aroma released from sample were similar with different intensity. All sample had aromas that matched fresh MAD, cinnamon powder, dried oregano, lemon zest, linalool, 2-methyl butanoic acid and verbenone. The fresh MAD showed strong intensity of aroma from linalool whereas dried MAD showed strong intensity of cinnamon powder, followed by linalool, 2-methyl butanoic acid and lemon zest. The MAD extract showed medium intensity of

linalool and cinnamon powder, followed by weak intensity of 2-methyl butanoic acid, lemon zest and fresh white champaca (Table 4.5).

The result from trained panels' decision was compared to aroma and flavor lexicon (Civille & Lyon, 2001). The conclusion of terms and definitions from all four samples were described. The two main aromas from all samples which were floral and citrus were concurred from trained panels to be linalool and 2-methyl butanoic acid while the other main aroma that detected as spice was referred to verbenone (Table 4.6). From term and definition, the reference samples of linalool and 2-methyl butanoic acid and verbenone were selected. The standard aromas were prepared for evaluating and discussing for the intensity. The line scale was used to discuss intensity range from weak, medium and strong (Meilgaard *et al*., 2007).

Table 4.5 Comparing aroma between standard references and fresh MAD, dried MAD, and MAD extract (with 70% Ethanol) and MAD encapsulated powder samples

Reference aroma sample	**Fresh MAD**	**Dried MAD**	**MAD extract**	**MAD encapsulated powder**
fresh MAD	+++	++	+	++
cinnamon powder	+	+++	++	-
dried Oregano	+	+++	++	+
lemon zest	+	++	+	+
linalool	+++	++	++	+
2-methyl butanoic acid	+	++	+	+
verbenone	+	++	++	+

Note: +++ = strong intensity, ++ = medium intensity and + = weak intensity

Table 4.6 Term and definition and reference sample of character aromas

Term	definition	reference sample
Floral	aromatic associated with materials that have a sweet aroma and related to flower scent	linalool
Spice	aromatic associated with materials that related to spics and savory aroma	verbenone
Citrus	aromatic associated with fermented citrus (fermented and citrus)	2-methyl butanoic acid

For the third session, the trained panels were inquired to rate intensity of prepared standard references and adjusted intensity for all three levels. The standard references were prepared in three levels of intensity. Those aromas were diluted differently as in low, medium and high; 2-methyl butanoic acid was used for Citrus characteristic, linalool was used for floral characteristic, verbenone was used for spice characteristic. The aroma intensity from all four samples was rated using prepared standard aroma as references. The intensity of linalool, verbenone, and 2-methyl butanoic acid was initiated from low, medium, and high as shown in Table 4.7.

Table 4.7 The threshold intensity level of linalool, verbenone and 2-methyl butanoic acid

Standard reference	Molecular weight (g/mol)	Aroma intensity (mm.)		
		Low (µl/ml)	Medium (µl/ml)	High (µl/ml)
linalool	102.13	25.00 mm. (500µl/ml)	68.00 mm. (1000µl/ml)	120.00 mm. (2000µl/ml)
verbenone	150.22	12.00 mm. (100µl/ml)	44.00 mm. (400µl/ml)	75.00 mm. (800µl/ml)
2-methyl butanoic acid	154.25	26.00 mm. (200µl/ml)	77.00 mm. (100µl/ml)	107.00 mm. (3000µl/ml)

*Aroma sample applied from Civille & Lyon (2001) with intensity level on scale 150 mm. Weak intensity = 12.5 and Strong intensity = 137.5

There were a decreasing of the aroma intensity of floral and citrus in fresh MAD, dried MAD, MAD extract and MAD encapsulated powder whereas spice aroma from dried MAD was higher than fresh MAD. The spice character appeared to be stronger than other characters which happened from drying process as suggested from Loewer (1998) research. After extraction process, there was decreasing of all aromas. This is due to the process involving solvent that can dilute aromas intensity also some of the volatile compounds with lower molecular weight can be evaporated through the evaporation process as the following findings from Table 4.4 and Table 4.5 along with the research from Baranauskiene, Bylaite, Zukauskaite, & Venskutonis (2007) and Rowan (2011). The effect the drying, extracting, and encapsulation process toward MAD main aroma intensity can be evaluated by descriptive analysis as shown in Fig. 4.5. The MAD encapsulation powder also showed decreasing of aroma intensity from MAD extract. The deceasing of aroma can be explained from the comparison result discussed previously Table 4.3. The encapsulation process also affected toward moisture content, water activity, color value (*a** and *b**), solubility and surface content to be lower while encapsulation efficiency demonstrated to be higher. These findings suggested that the spray drying can retain aroma from MAD better than freeze drying.

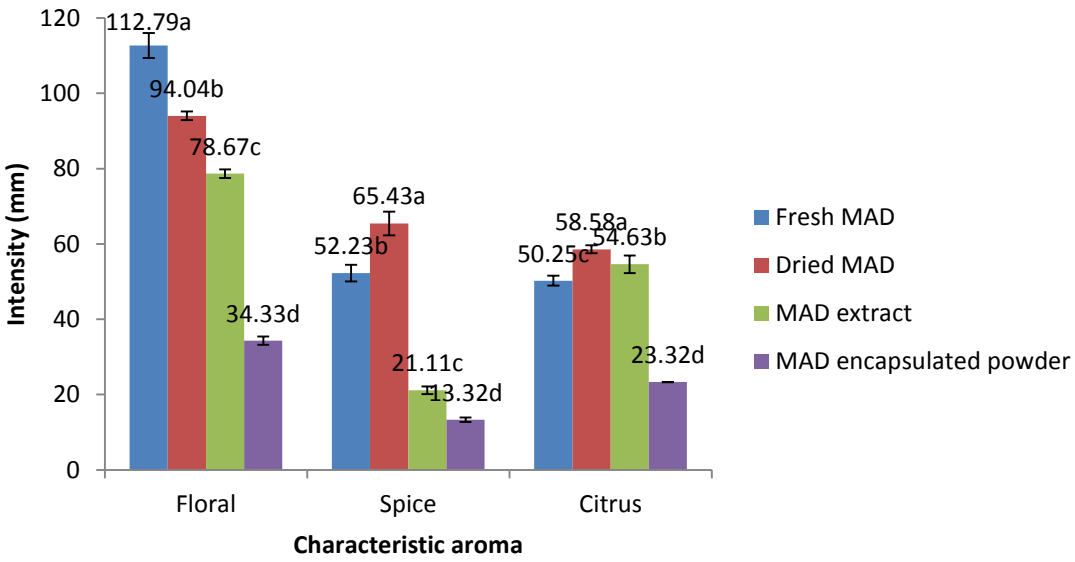


Fig. 4.5 The aroma intensity of fresh MAD, dried MAD, MAD extract, and MAD encapsulated powder.

4.4 Conclusion

The findings of this research revealed that the ratio of OSA starch:water for encapsulation had affected on the rheological properties which showed that the degree of changes in rheological properties depend on the increasing of OSA starch. However, the suitable ratio of OSA starch:water for this study was 1:1 that starch did not create excessive retrogradation. The selected ratio was used in microencapsulation of MAD extract. The yield recovery of spray drying microencapsulation was lower than freeze drying. Therefore, the microencapsulation efficiency of the spray drying was higher than freeze drying. In addition, the moisture content, water activity and solubility of spray drying were lower which indicated higher stability. The change of microstructure, including color value and surface content from different drying method, serves as indicators for stability of encapsulated powder. The aroma identification showed that 2-methyl butanoic acid, terpinolene, diethyl malonate, phenyl ethyl alcohol, lilac aldehyde, linalool, verbenone, terpendiol, and menthoglycol can be detected. The sensory descriptive sensory showed that there were three main characteristic aromas of MAD which were floral, spice, and citrus, in order of perception. There was a potential of encapsulation process that can entrap and retain aroma from MAD. This showed that microencapsulation was one of the suitable processes to retain active ingredient such as main aroma compound until expenditure on any activity. All inclusive, spray drying produced powder with superior properties and exhibited better protection towards the core materials.

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