



Effect of Different Types of Modified Starches on Microencapsulation of Cajuput Oil

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Introduction

The essential oil from the twigs and leaves of Cajuput tree (*Melaleuca cajuputi* Powell) is endowed with the peculiar property to be a fragrance and flavoring agent. It has been widely used in aromatherapy, Thai spa and skin care products. It should be used in water and possesses mood lifting, sterilizing and can relieve muscle cramps, fever, nasal congestion¹. However, the cajuput oil evaporates easily and degenerated when it exposes heat, light or oxygen in the air. To minimize evaporation, increase shelf live and control release, which may increase the biological efficiency, the encapsulation of cajuput oil has been proposed for solving these problems².

In this study, the encapsulation of cajuput oil was carried out by spray drying into different types of modified starches. The efficiency of encapsulation was measured and the flavor release profiles from the microcapsules into water for spa bath was analysed by a validated GC-MS.

Methods

Materials. The cajuput oil was purchased from Tropicalife Co., Ltd. (Bangkok, Thailand). The encapsulating modified starches (M01-M04) were kind gifts from Siam Modified Starch Co., Ltd., and National Starch & Chemical Co., Ltd. All of modified starches were derived from tapioca base and involved the addition of lipophilic groups. M01 was modified without crosslinking process, while M02 was produced and combined with crosslinking treatment. Both of M03 and M04 were modified with low and high concentrations of n-octenyl succinic anhydride (OSA), respectively. The organic chemicals used in the analyses were of analytical grade.

Preparation of encapsulated cajuput oil powders. M01-M04 were used as encapsulating agents. The solution of encapsulating agent was prepared by dispersed 30 g of modified starch in 100 mL of warm distilled water and allowed to hydrate overnight. An emulsion of cajuput oil was formed by adding 3 g of cajuput oil into the solution and homogenized for 10 min. The emulsion was, then, spray dried by a Buchi Mini Spray dryer (B-191, Switzerland). The operational conditions of the spray drying were: air inlet temperature of 190±5°C, air outlet temperature of 130±5°C, feed rate of 5-7%, aspirator of 85% and air flow rate of 500 psi. The encapsulated powders were kept in airtight, self-seal pouches and stored in desiccators to prevent moisture absorption and lump formation until further studies.

Quantification of encapsulated 1,8-cineol in the powders. Encapsulated 1,8-cineol content of microcapsules was extracted according to the method of Wichienstein et al. (2012)³. 0.1 g of each of the spray-dried powders was dispersed in 8 ml of water, and then 4 ml of hexane was added, followed by violent mixing with a vortex mixer. The mixture was heating at 90°C for 30 min. with occasional mixing and then centrifuged at 4000 rev/min for 10 min. One microliter of supernatant was injected into gas chromatography (Trace GC Ultra, Thermo Electron Corporation, USA), equipped with an autosampler (AI 3000, Thermo Electron Corporation, USA) and a capillary column (ZB-5MSi, 30 m x 0.25 mm i.d., film thickness 0.25 µm, Phenomenex, USA). The chromatographic conditions were programmed heating from 60°C to 200°C at 6°C/min followed by 5 min under isothermal conditions. The injector was maintained at 250°C. Helium was the

carrier gas at 1.2 mL/min. The GC was fitted with a quadrupole mass spectrometer (MS) detector DSQ, Thermo Electron Corporation, USA). MS conditions were as follows: ionization energy 70 eV, electronic impact ion source temperature 250°C, Mass Spectra Libraries were used as references. Compounds were identified by matching their mass spectra and retention indexes with those reported in the libraries. Moreover, identification has been confirmed by injection of authentic sample of the compound. A quantitative analysis of encapsulated 1,8-cineol in the powders was carried out by external standard technique and calculated as the ratio of 1,8-cineol in the powder to 1,8-cineol in the feed liquid emulsion.

Surface oil content determination. 0.2 grams of each encapsulated powders were dispersed into 4 ml of hexane and then centrifuged at 4000 rev/min for 20 minutes. One microliter of supernatant was injected into GC-MS by using the conditions as described above. The results were the average of the triplicates in each sample. The retaining of oil on the powder surface was defined as the ratio of oil on the surface to the total oil in the powder.

Physicochemical properties of encapsulated cajuput oil powders. The angle of repose was determined by pouring a predefined mass of spray-dried powder through a funnel located at a fixed height on a graph paper, flat horizontal surface and measuring the height (h) and radius (r) of the conical pile formed. The tangent of the angle of repose is given by the h/r ratio. The moisture content and size distribution of the spray-dried powders were also studied. The powder moisture content was determined by a moisture analyzer with moisture balance (Sartorius Moisture balance, Germany) and particle size distribution was evaluated by using Light Diffraction Analyzer (LA950, Horiba, Japan). Each sample was analyzed in triplicates.

Release of flavor from encapsulated cajuput oil powders into water. In order to study the release characteristics of flavor from the spray-dried powders, the release of 1,8-cineol from encapsulated cajuput oil powders using different types of modified starches into water were evaluated. 200 mg of each spray-dried powders were placed in 20 mL of water and the residual amount of 1,8-cineol in the spray-dried powders was determined at prescribed time intervals (10, 30, 60, 90, 120 min) by the solvent extraction method described above.

Results and Discussion

Validation of Analytical Method. The encapsulated powders composed of M03 and cajuput oil were used for validation study. The accuracy of the method was evaluated by recovery assay, adding known amounts of each 1,8-cineol standard to a known amount of encapsulated powders, to obtain three different levels (80, 100, and 120%) of addition. Spiked amounts of standard ranged from 2.4-3.6 mg/mL. Each sample was analysed quantitatively in triplicate. No considerable differences had been found between recoveries at different spiked levels, which indicated good accuracy of the method. The obtained results of 1,8-cineol had shown recoveries between 99.85-101.12%, within the range of AOAC guidelines⁴. To assess the precision of the method, six replicates of the encapsulated powders were determined on the same day (intraday precision) and one time injection on five consecutive days (interday precision). The results showed acceptable precision with the developed GC-MS method. RSDs of Intra- and interassay were 1.5185 and 1.7620%, therefore, complying with the evaluation criterion of the Association of Official Agricultural Chemists (AOAC) guidelines. The linearity was determined using five concentrations of standard solutions of 1,8-cineol in the range of 0.30-14.96 mg/mL (n=3). The regression equations were found by plotting the peak area (y) versus the 1,8-cineol concentration (x) expressed in mg/mL. The results showed good linearity with calibration curves for $Y = 7E-08x + 0.1526$ and the correlation coefficient (r^2) was 0.999.

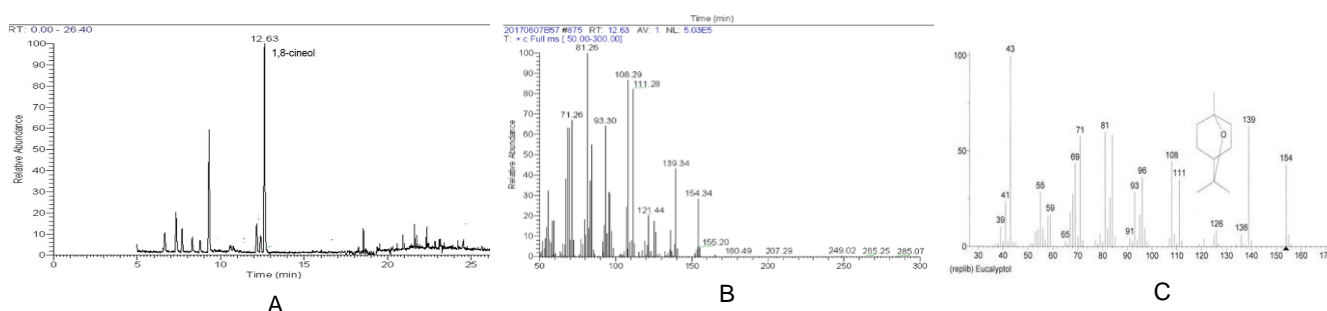


Figure 1: GC-MS chromatogram of encapsulated cajuput oil powders using M03 as wall material (A) and mass spectra of active ingredient, 1,8-cineol, obtained from experiment (B) and from libraries (C).

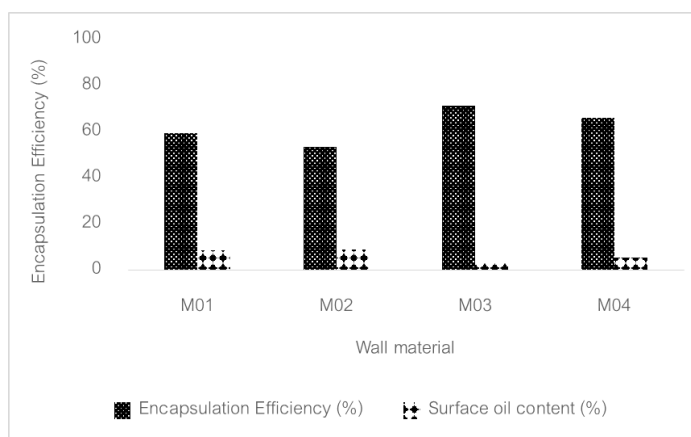


Figure 2: Effect of different types of wall materials (M01-M04) on the cajuput oil retention and the surface oil content.

Table 1: Properties of encapsulated cajuput oil powders after spray drying using different modified starches (M01-M04) as wall materials.

Wall Materials	Moisture content (%)	α (°)	Size distribution (μm)
M01	1.5	15.9 ± 1	4.29 ± 0.05
M02	2.5	34.82 ± 1	33.5 ± 2.14
M03	0.6	30.65 ± 2	15.64 ± 2.74
M04	0.4	25.01 ± 1	14.23 ± 1.22

Effect of different types of wall materials on the cajuput oil encapsulation. The amount of flavor retention and surface oil was determined using validated GC-MS method (Figure 1). The surface oil content in the spray-dried powders is the main parameter affecting the stabilization against oxidation, since oil droplets on the surface of spray-dried powders can be easily oxidized and may be less protected against atmospheric oxygen. The modified starch with low OSA concentration, M03, indicated higher 1,8-cineol retention than the other wall materials. Furthermore, the surface 1,8-cineol content of M03 powders was very low and was independent on the oil content of the powder, as illustrated in Figure 2. Similar results were also reported in previous study⁵. On the other hand, M02 powders showed higher surface oil content than the M03 powders at the same amount of oil loaded. That might be explained by the breakdown of emulsion particles during atomization and the emulsifying properties of each type of wall material on the oil retention and the surface oil content.

Physicochemical properties of encapsulated cajuput oil powders. The moisture contents of spray-dried powders were in the range of 0.4-2.5% as shown in Table 1. The moisture content of natural dry powder should not over 12% for prevention from bacterial growth on the product. According to USP 36-NF 31⁶, the flowability of powder can indicate by angle of repose. The powder is defined as excellent, good, fair and poor at the angle repose of $<30^\circ$, $31-35^\circ$, $35-40^\circ$ and $>40^\circ$, respectively. The M02 and M03 powders showed good flowing property, while M01 and M04 showed excellent flowing property. All powder samples displayed particle diameter values between 4.29 ± 0.05 and $33.5 \pm 2.14 \mu\text{m}$.

Flavor release profiles from the microcapsule into water. The release profile of cajuput oil was influenced by the type of encapsulating agent as demonstrated in Figure 3. First, the M03 powders showed markedly slower release of the oil than the other powders resulting in sustained flavor release. Then, after the initial period, the flavor release dramatically increased and all of flavor released from the powders within 180 min. That might be explained by different changes of matrix structures after adsorbing of water in the wall materials. The water begins to penetrate the surface wall of the spray-dried particle, cracks and subsequent release of the flavor.

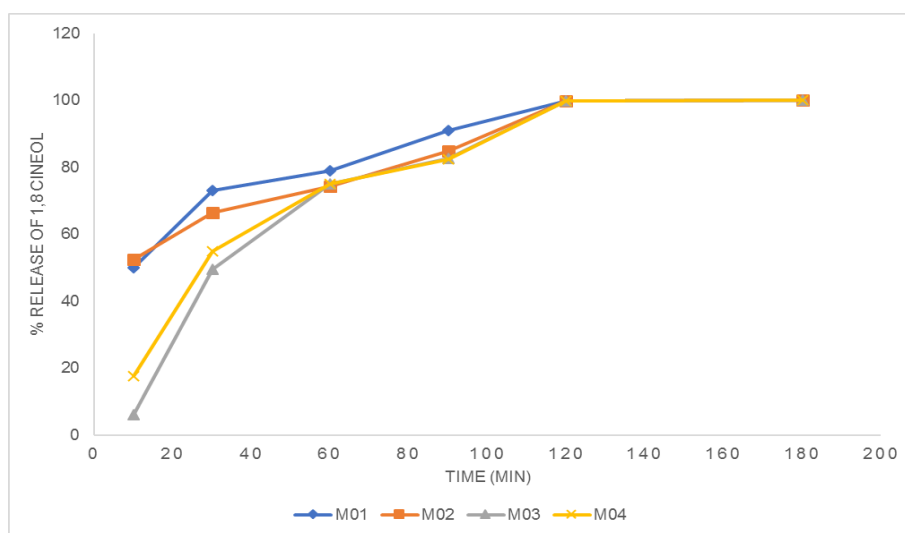


Figure 3: The release characteristics of encapsulated cajuput oil powders from different types of modified starches.

Conclusion

The retention of cajuput oil was influenced by the type of encapsulating agent. M03 was found to be a superior encapsulating agent over M01, M02 and M04. The type of encapsulating agent also affected to the release behavior of encapsulated oil.

References

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