การเคลือบอนุภาคละเอียดด้วยกรดสเตียริคโดยอาศัยการขยายตัวอย่างรวดเร็วของคาร์บอนไดออกไซด์เหนือวิกฤต

Coating of Fine Particles with Stearic acid Using Rapid Expansion of Supercritical Carbon Dioxide

นิพนธ์ต้นฉบับ

Original Article

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วารสารไทยเภสัชศาสตร์และวิทยาการสุขภาพ 2554;6(4):251-259

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Thai Pharmaceutical and Health Science Journal 2011;6(4):251-259

บทคัดย่อ

วัตถุประสงค์: เพื่อประยุกต์ใช้การขยายตัวอย่างรวดเร็วของสารละลายเหนือวิกฤต (อาร์อีเอสเอส) โดยใช้คาร์บอนไดออกไซด์เหนือวิกฤตที่ไม่มีตัวทำละลายร่วมในการเคลือบอนุภาคละเอียดของแป้งข้าวโพดด้วยกรดสเตียริค **วิธีการศึกษา:** ในกระบวนการเคลือบจะบรรจุคาร์บอนไดออกไซด์เหนือวิกฤตในภาชนะที่มีส่วนผสมของแป้งข้าวโพดและกรดสเตียริคเป็นเวลา 40 นาที ทิ้งให้ส่วนผสมเข้าสู่สภาพสมดุล 20 นาที ก่อนลดความดัน เพื่อให้สารละลายคาร์บอนไดออกไซด์เหนือวิกฤตขยายตัวอย่างรวดเร็ว ประเมินคุณลักษณะของผลิตภัณฑ์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (เอสอีเอ็ม) การวัดขนาดอนุภาค การดูดซับไอความชื้น ดิฟเฟอเรนเชียลสแกนนิงแคลอรีเมทรี (ดีเอสซี) และอินฟราเรดสเปกโทรสโกปีชนิดฟูเรียร์ทรานสฟอร์ม (เอฟที–ไออาร์) **ผลการศึกษา:** สามารถเคลือบอนุภาคแป้งข้าวโพดด้วยกรดสเตียริคโดยใช้คาร์บอนไดออกไซด์เหนือวิกฤตที่อุณหภูมิ 60 องศาเซลเซียสและความดัน 3000 ปอนด์ต่อตารางนิ้ว สารเคลือบห่อหุ้มอนุภาคแกนในระหว่างการลดความดันของสารละลายเหนือวิกฤต สามารถยืนยันว่ามีการเคลือบเกิดขึ้นโดยอนุภาคของแป้งข้าวโพด หลังกระบวนการเคลือบมีขนาดโตขึ้นตามสัดส่วนของกรดสเตียริคในส่วนผสม เทอร์โมแกรมจากดีเอสซีมีการดูดกลืนความร้อนที่อุณหภูมิ 57 องศาเซลเซียสซึ่งเป็นอุณหภูมิหลอมเหลวของกรดสเตียริค สเปกตรัมจากเอฟที–ไออาร์ปรากฏแถบการดูดกลืนรังสีอินฟราเรดของทั้งแป้งข้าวโพดและกรดสเตียริค ร้อยละโดยน้ำหนักที่เพิ่มขึ้นจากการดูดซับไอความชื้นของอนุภาคแป้งข้าวโพดที่ผ่านกระบวนการเคลือบต่ำกว่าอนุภาคแป้งข้าวโพดที่ไม่ได้เคลือบซึ่งสนับสนุนการมีชั้นเคลือบของกรดสเตียริคที่ช่วยป้องกันการดูดซับความชื้นของอนุภาคแป้งข้าวโพด ภาพถ่ายจากเอสอีเอ็ม ยืนยันการเคลือบอนุภาคแป้งข้าวโพด และแสดงอนุภาคเคลือบที่ไม่เกาะกลุ่มกันเมื่อใช้อัตราส่วนโดยน้ำหนักของอนุภาคแป้งข้าวโพดและกรดสเตียริค เท่ากับ 2.95:0.05 **สรุป:** สามารถประยุกต์ใช้การขยายตัวอย่างรวดเร็วของสารละลายเหนือวิกฤต โดยใช้คาร์บอนไดออกไซด์เหนือวิกฤตที่ไม่มีตัวทำละลายร่วมเพื่อเคลือบอนุภาคละเอียดของแป้งข้าวโพดด้วยกรดสเตียริค

คำสำคัญ: การเคลือบอนุภาคละเอียด, การขยายตัวอย่างรวดเร็วของสารละลายเหนือวิกฤต, แป้งข้าวโพด, กรดสเตียริค

Abstract

Objective: The rapid expansion of supercritical solution (RESS) using carbon dioxide without cosolvent was applied for coating fine particles of corn starch with stearic acid. **Methods:** The coating process was performed by introducing supercritical carbon dioxide ($ScCO_2$) into a vessel containing mixture of corn starch and stearic acid for 40 min, then depressurizing the fluid after 20 min of equilibration. The products were characterized using scanning electron microscopy (SEM), particle size analysis, vapour sorption analysis, differential scanning calorimetry (DSC) and Fourier transform infrared (FT-IR) spectroscopy. **Results:** The results showed that coating of corn starch particles with stearic acid could be obtained by this process using $ScCO_2$ at temperature of 60 °C and pressure of 3000 psi. Deposition of the coating material onto the core particles occurred during depressurization of supercritical solution. The coating was evidenced by an increase in size of coated corn starch particles with increasing proportions of stearic acid in the mixture. DSC thermograms showed melting endotherm of stearic acid at 57 °C. FT-IR spectra exhibited combined absorption bands of both starting materials which implied the presence of unchanged stearic acid and corn starch in the coated products. Vapour sorption results showed lower percentage of mass increase of coated corn starch, as compared to that of uncoated one, indicating the presence of protective layer of stearic acid. SEM images confirmed coating of corn starch particles without agglomeration of the coated particles, which was achieved at corn starch to stearic acid weight ratio of 2.95:0.05. **Conclusion:** Film formation of stearic acid on corn starch particles could be accomplished via rapid expansion of supercritical solution (RESS) process without organic solvent.

Keywords: fine particle coating, rapid expansion of supercritical solution, corn starch, stearic acid

Introduction

Coating of pharmaceutical particles is often needed to modify surface properties of particles in order to improve its characteristics. Mainly, coated particles exhibit better flowability and wettability, mask the unpleasant taste of an ingredient, protect the drug against harsh environment, avoid incompatibility of the components in the dosage form and control the drug release characteristics. Coating techniques usually involve the application of organic solvent or aqueous based polymeric solution onto the surface of core particles, followed by solvent evaporation. Organic solvent coating encounters problems of excessive solvent exposure and residual solvent in the product. There are also drawbacks for aqueous coating, including slow drying rate, long processing time and degradation of the drug due to moisture. Alternative coating technologies are nonsolvent coatings, e.g. hot-melt coating[1] and dry powder coating[2]. Hot melt coating via a fluidized bed coater is associated with high temperature to melt a coating material and thus less desirable for heat sensitive substance. Dry powder coating relies on mechanical attachment forces between small guest particles and surface of host particles could be utilized. However, difficulties in formulating and controlling the qualities of film are experienced. In addition, these techniques often have problems of particle agglomeration when coating fine and/or cohesive particles.

Supercritical fluid technique has been introduced for particle engineering of pharmaceutical materials for over twenty years.[3] Many applications involve micronization, microencapsulation and production of micro- and nano-composite particles. The technique can be applied to coat fine particles. Tsutsumi et al (1995) developed a circulating fluidized bed coater with an internal nozzle by which supercritical fluid containing a coating material was expanded and the coating material was deposited onto the suspended bed of fine and cohesive particles.[4] Another approach in particle coating was investigated by using autoclave equipped with a rotating impeller, where a coating material was solubilized in supercritical carbon dioxide ($ScCO_2$) and an insoluble protein powder was dispersed in the solution. Controlled reduction of temperature and pressure of carbon dioxide phase caused a decrease in solubility of coating material which then being precipitated on the surface of protein particles[5-7]. Protein with a mean particle size of approximately 40 µm and greater could be coated by this technique. Coating of small particles could also be achieved by rapid expansion of supercritical solution (RESS). Matsuyama et al (2003) encapsulated an active ingredient by suspending the active ingredient in mixture of $ScCO_2$ and organic solvent containing dissolved polymer, then spraying the suspension through a nozzle to atmospheric pressure.[8]

In principle, the application of RESS technique as the coating method is possible when the coating material is dissolved while the core is insoluble in the supercritical fluid with or without cosolvent. The rapid expansion of the supercritical fluid through a nozzle resulted in the deposition of the coating material onto the surface of the core particles. Earlier work by Matsuyama et al. (2003) required ethanol as cosolvent to completely solubilize the coating material[8]. In the present study, rapid expansion of $ScCO_2$ without cosolvent could be applied in particle coating under low temperature condition. Corn starch were used as core particles. Stearic acid was used as a coating material. Basically, it was anticipated that stearic acid could be solubilized while corn starch was insoluble and dispersed in $ScCO_2$. Rapid depressurization of the dispersion would result in reduction of the solubilizing power of carbon dioxide, hence precipitation of stearic acid onto the surface of corn starch particles.

Materials and Methods

Materials

Corn starch (Purity® 21A, National Starch & Chemical Co., Thailand) was obtained as a gift sample from Siam Medicare Co., Ltd. (Bangkok, Thailand). Stearic acid was supplied by Natural Oleochemicals Sdn. Bhd. (Johor, Malaysia) and passed through 80 mesh sieve before use. Liquefied carbon dioxide with purity of 99.5% was purchased from Thai Industrial Gases Public Co., Ltd. (Samut Prakarn, Thailand). All other chemicals and reagents used were of pharmaceutical or analytical grade.

Coating process

Coating fine particles was carried out by RESS technique. The schematic diagram of the apparatus is shown in Figure 1. Accurately weighed corn starch and stearic acid at various ratios with a total weight of 3.0 g were mixed and filled into a 10 ml extraction vessel (Supercritical fluid extractor, Model SFE-400, SUPELCO INC., Bellefonte, Pennsylvania, USA). Liquefied carbon dioxide was charged to a thermal pump in which it was heated and compressed to certain temperature and pressure above the critical temperature (31.1 °C) and pressure (1070.4 psi), transforming to $ScCO_2$. The $ScCO_2$ obtained was then delivered and allowed to circulate in the extraction vessel for 40 min before a valve between the pump and the vessel was closed. The dispersion in the vessel was equilibrated for further 20 min. The extraction vessel was then vented manually by opening a valve of the extraction vessel to the atmospheric pressure, inducing a phase change of $ScCO_2$ to gaseous carbon dioxide. The products were kept in the extraction vessel at an ambient temperature for 24 h before collected and stored in a desiccator for further characterization.

To investigate an appropriate temperature and pressure of $ScCO_2$ for coating, the pressures and temperatures were varied as presented in Table 1. The weight ratio of corn starch to stearic acid of 2:1 was used and the coating procedure was carried out as described above. At a selected temperature and pressure, the effect of corn starch to stearic acid weight ratios on coating was investigated by varying amounts of core and coating materials as presented in Table 2.

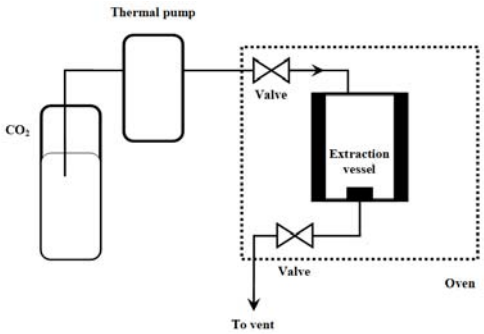


Figure 1 Schematic diagram of the apparatus setup in the present study.

Table 1 Temperatures and pressures of $ScCO_2$ employed to investigate coating conditions using weight ratio of corn starch to stearic acid of 2:1

Temperature (°C)	Pressure (psi)
40	1500
40	3000
40	4500
50	1500
50	3000
50	4500
60	1500
60	3000
60	4500

Table 2 Weight ratios of corn starch and stearic acid used in RESS process with $ScCO_2$ temperature of 60 ºC and pressure of 3000 psi

Corn starch (g)	Stearic acid (g)
2.20	0.80
2.40	0.60
2.60	0.40
2.80	0.20
2.85	0.15
2.90	0.10
2.95	0.05

Characterization of Coated Particles

Morphology Observation

The morphology and surface appearance of uncoated and coated corn starch particles were examined by scanning electron microscopy (SEM; Model JSM-5410LV, JEOL Ltd., Tokyo, Japan). Scanning electron photomicrographs of the samples were obtained at magnifications of x500 and x7500.

Particle Size Analysis

Particle size and size distribution of uncoated and coated corn starch particles were measured by laser light scattering technique (Model Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK). The powder samples were suspended in 2% w/v Tween 80 aqueous solution. The value of mean volume diameter was an average from three measurements.

Apparent Density Analysis

The amount of uncoated and coated corn starch of approximately 0.5 - 1.0 g was weighed into a micro cell. The apparent density of uncoated and coated corn starch was determined using helium gas displacement pycnometry (Model Ultrapycnometer 1000, Quantachrome Instruments, Florida, USA). The value of apparent density was an average from five determinations.

Vapour Sorption Analysis

The water vapour sorption of uncoated and coated corn starch was determined gravimetrically using a Dynamic Vapour Sorption apparatus (Model DVS INTRINSIC, Surface Measurement Systems Ltd., London, United Kingdom). Approximately 5 mg of samples were accurately weighed into a stainless steel pan and positioned on the arm of the microbalance. Prior to each experiment, the sample was purged with dry nitrogen for 1 h in order to ensure 0% relative humidity and stabilize the sample mass. The sample was then exposed to 75% relative humidity at 25 ºC. The system was considered to reach equilibrium if the rate of change in mass was less than 0.002%. The percentage of mass increase was an average from three measurements.

Differential Scanning Calorimetry (DSC)

Thermal properties of stearic acid, uncoated and coated corn starch, and the physical mixtures of corn starch and stearic acid with varied weight ratios were investigated using differential scanning calorimeter (Model DSC822^e, METTLER TOLEDO, Schwerzenbach, Switzerland). Approximately 5 mg of samples were accurately weighed into a 40 µl aluminum pan. The sample pans were hermetically sealed and placed in the sample holder with an empty pan as reference. The samples were heated from 25 to 250 °C at a heating rate of 5 °C/min under a nitrogen atmosphere at a flow rate of 60 ml/min.

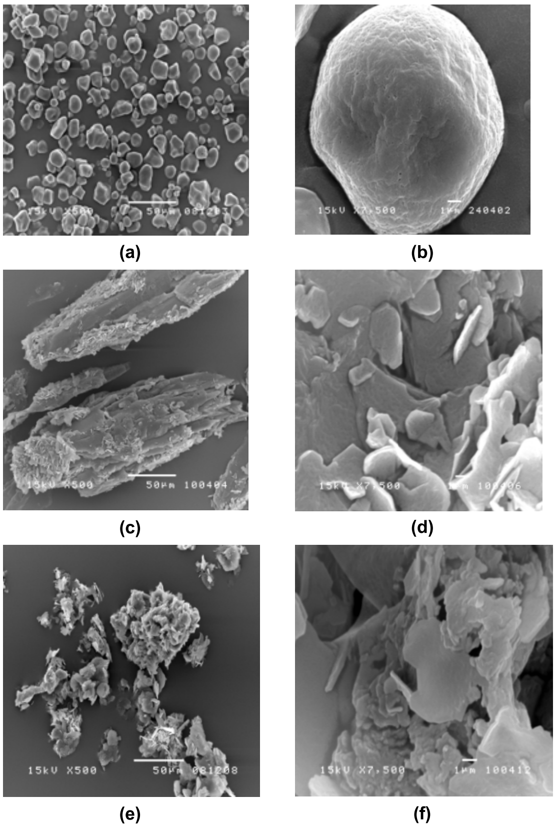
Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectra of stearic acid, uncoated and coated corn starch, and the physical mixtures of corn starch and stearic acid with varied weight ratios were determined by FT-IR spectrometer (Model Spectrum One, Perkin Elmer Ltd., Massachusetts, USA). The powder samples were blended with potassium bromide and compressed. The FT-IR spectra were investigated ranging from 4000 to 450 cm^{-1}.

Results and Discussions

Corn starch particles with mass median diameter of 16.27 µm were used as the core material. Stearic acid was employed as the coating material which could be solubilized in ScCO$_2$.[9] When the condition applied was above stearic acid melting point, it was liquefied and solubilized in ScCO$_2$. Corn starch should remain intact. Subsequent depressurization of the ScCO$_2$ phase to the atmospheric pressure would lead to the precipitation and/or deposition of congealed stearic acid on the surface of corn starch particles. The former phenomenon may be explained that the ScCO$_2$ acting as solvent, transformed to gaseous carbon dioxide, solubilized stearic acid became saturated and eventually precipitated onto the surface of core particles. For the latter, evaporation of gaseous carbon dioxide caused a decrease in the temperature inside the vessel, resulting in molten stearic acid to be congealed and deposited on the solid core. Rapid depressurization of the ScCO$_2$ phase would expedite the rate of precipitation and/or congealing of stearic acid and minimize agglomeration. However, stearic acid may be precipitated or congealed as free small particles and evacuated along with gaseous carbon dioxide through the vent of the vessel. An appropriate weight ratio of corn starch and stearic acid should be optimized for film formation and avoidance of agglomeration.

Figure 2 displays photomicrographs of the starting materials, i.e. corn starch particles, stearic acid and processed stearic acid by RESS process with ScCO$_2$ at 60 °C and 3000 psi. Corn starch particles exhibited an uneven surface, while stearic acid appeared as flakes. It was observed that flakes of stearic acid became smaller and morphologically altered after RESS process (Figure 2e and 2f). This demonstrated that stearic acid was solubilized and/or melted in ScCO$_2$ when processed at the temperature of 60 °C and pressure of 3000 psi. The result suggested that



(a) (b)
(c) (d)
(e) (f)

Figure 2 Scanning electron photomicrographs of uncoated corn starch particles (a-b), stearic acid passed through 80 mesh sieve (c-d) and stearic acid obtained from RESS process using ScCO$_2$ at 60 ºC and 3000 psi (e-f), taken at magnifications of x500 and x7500.

coating of corn starch particles may occur if stearic acid was precipitated and/or congealed efficiently from $ScCO_2$ at an appropriate amount and rate.

Table 3 Effects of temperature and pressure of $ScCO_2$ on coating characteristics when using the weight ratio of corn starch to stearic acid of 2 : 1

Conditions		Appearance of the products
Temp (°C)	Pressure (psi)	
40	1500	Similar appearance to that of the raw materials
40	3000	Presence of stearic acid flakes
40	4500	Presence of stearic acid flakes
50	1500	Absence of stearic acid flake
50	3000	Absence of stearic acid flake
50	4500	Absence of stearic acid flake
60	1500	Absence of stearic acid flake
60	3000	Absence of stearic acid flake
60	4500	Absence of stearic acid flake

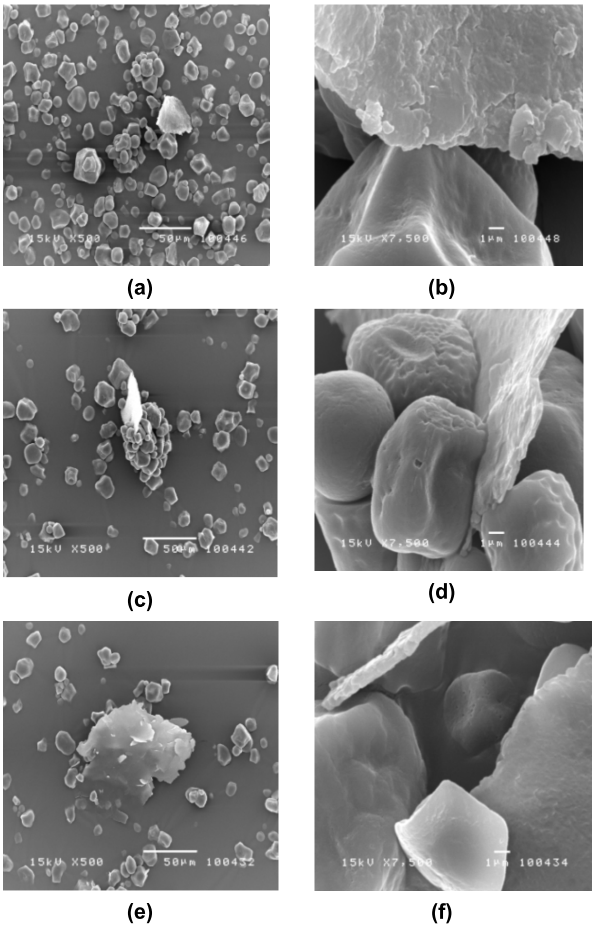

(a) (b)
(c) (d)
(e) (f)

Figure 3 Scanning electron photomicrographs of the coated products with corn starch to stearic acid weight ratio of 2:1 processed under the $ScCO_2$ temperature of 40 ºC and varied pressures of 1500 psi (a-b), 3000 psi (c-d) and 4500 psi (e-f), taken at magnifications of x500 and x7500.

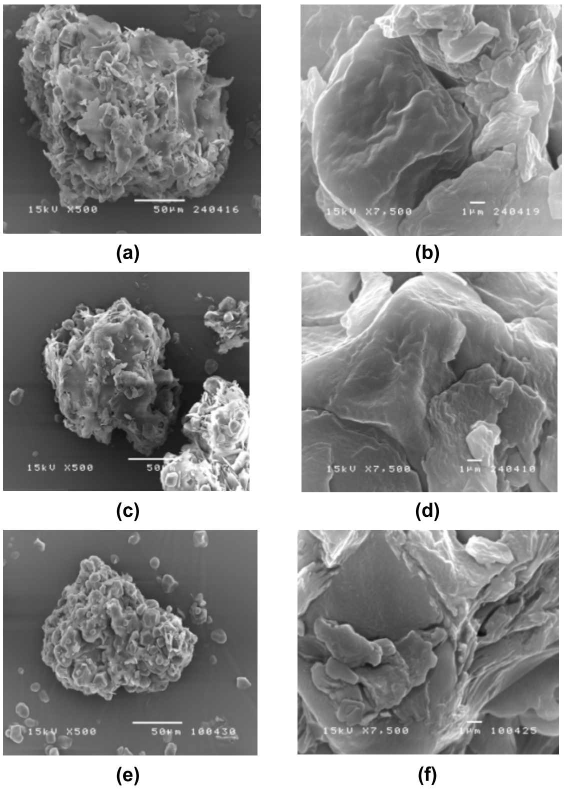

(a) (b)
(c) (d)
(e) (f)

Figure 4 Scanning electron photomicrographs of the coated products with corn starch to stearic acid weight ratio of 2:1 processed under the $ScCO_2$ temperature of 50 ºC and varied pressures of 1500 psi (a-b), 3000 psi (c-d) and 4500 psi (e-f), taken at magnifications of x500 and x7500.

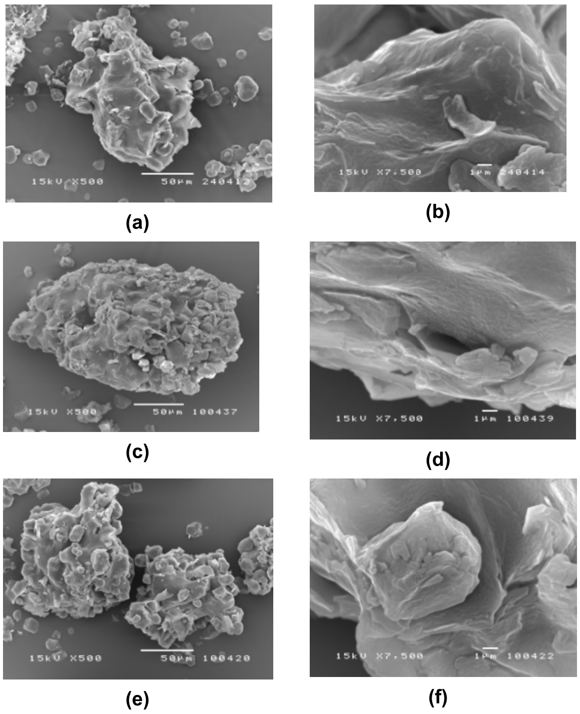

(a) (b)
(c) (d)
(e) (f)

Figure 5 Scanning electron photomicrographs of the coated products with corn starch to stearic acid weight ratio of 2:1 processed under the $ScCO_2$ temperature of 60 ºC and varied pressures of 1500 psi (a-b), 3000 psi (c-d) and 4500 psi (e-f), taken at magnifications of x500 and x7500.

Preliminary investigation was performed at 40, 50 and 60 °C with varying pressures between 1500-4500 psi using weight ratio of corn starch and stearic acid at 2:1. The appearance of the processed products was observed using SEM as summarized in Table 3 and depicted in Figures 3-5. By visual observation, it was found that at the temperatures of 50 and 60 °C and pressures between 1500-4500 psi, the process gave a white caked product without flake of stearic acid. The SEM images of the products (Figures 4-5) exhibited agglomerates of the particles. However, at the temperature of 40 °C with pressure of 3000 psi and above, flakes of stearic acid remained in the mixtures (Figures 3 c-d, e-f). On the other hand, at the pressure of 1500 psi, no difference was observed in the product compared to the initial powder mixture of corn starch and stearic acid. This result suggested that stearic acid had limited solubility in $ScCO_2$ at 40 °C with the pressure levels studied. It has been reported that increasing either temperature or pressure would lead to an increase in the solute solubility in $ScCO_2$. The solute solubility in $ScCO_2$ would be higher, when the processing temperature is closer to the melting point of solute[6]. Accordingly, it was expected that the amount of stearic acid could be solubilized and/or completely transformed to liquid state in $ScCO_2$ at the temperature near its melting temperature (56.3-60.8 ºC) of 50 ºC and pressure of 1500 psi.

To ensure that stearic acid would be liquefied during processing, the $ScCO_2$ temperature of 60 °C and pressure of 3000 psi were selected for further investigation. Appropriate weight ratios of corn starch to stearic acid were also selected to provide good quality of coating. Weight ratios of corn starch and stearic acid were varied as presented in Table 2. By visual observation of the products obtained, reduction of powder cohesiveness and agglomeration was found when stearic acid proportion was decreased. The photomicrographs of powder morphology after RESS processing are displayed in Figure 6. Excessive amount of stearic acid would induce agglomerate formation or non-uniform coatings as shown in Figure 6 (a-d). Discrete coated particles were obtained when the proportion of stearic acid was reduced below 7% by weight of the solid mixture (Figure 6 (e - j)). Smooth film of stearic acid could be formed with the weight ratio of corn starch to stearic acid of 2.95 to 0.05 or using stearic acid 1.7% by weight of the solid mixture.

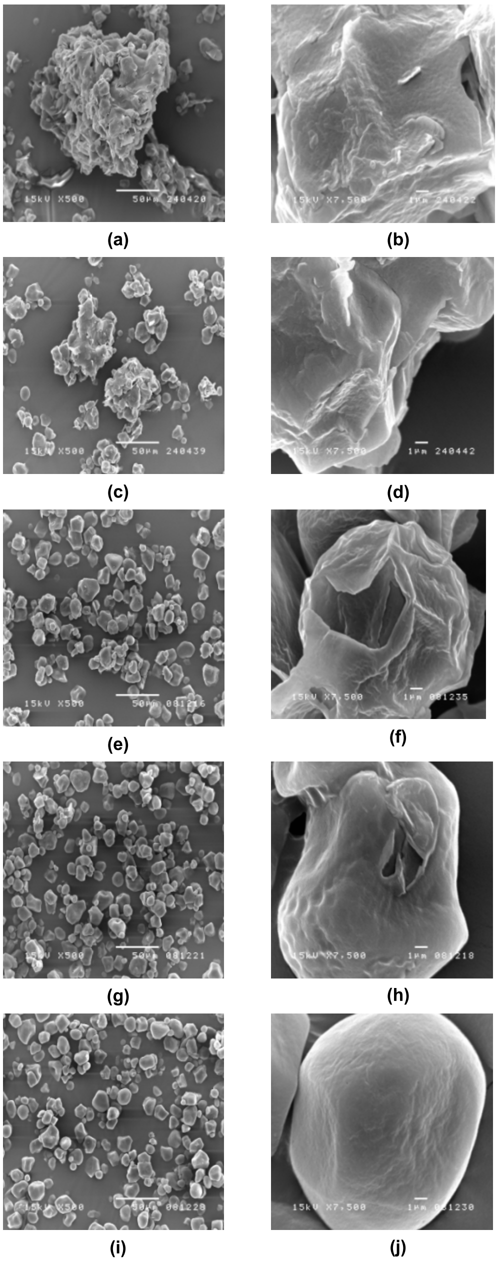


Figure 6 Scanning electron photomicrographs of the coated products obtained by RESS process with $ScCO_2$ temperature of 60 ºC and pressure of 3000 psi using the varied weight ratios of corn starch to stearic acid at 2.20 : 0.80 (a-b), 2.60 : 0.40 (c-d), 2.80 : 0.20 (e-f), 2.90 : 0.10 (g-h) and 2.95 : 0.05 (i-j), taken at magnifications of x500 and x7500**.**

The particle size and size distribution of uncoated and coated corn starch are summarized in Table 4. The uncoated corn starch was relatively smaller and had a narrower size distribution as compared to the coated corn starch. The results were consistent with the images from SEM as shown in Figures 2 (a - b) and 6 (e - j). The uncoated corn starch particles had the volume mean diameter (*D* [4, 3]) of 16.73 ± 0.02 µm, whereas the coated corn starch particles exhibited slightly larger volume mean

Table 4 Particle size analysis [average (SD)] of uncoated samples and coated samples obtained by RESS process with $ScCO_2$ temperature of 60 °C and pressure of 3000 psi

Sample	Ratio of corn starch to stearic acid	*d* (*v*, 0.1) μm	*d* (*v*, 0.5) μm	*d* (*v*, 0.9) μm	*D* [4, 3] μm	Span
Coated corn starch	2.80 : 0.20	9.18 (0.14)	16.56 (0.15)	32.62 (0.56)	19.35 (0.13)	1.56 (0.01)
	2.90 : 0.10	8.91 (0.17)	16.33 (0.10)	29.93 (0.24)	18.00 (0.19)	1.41 (0.02)
	2.95 : 0.05	8.66 (0.12)	16.29 (0.02)	26.76 (0.02)	16.75 (0.01)	1.56 (0.00)
Uncoated corn starch	-	8.34 (0.01)	16.27 (0.01)	26.73 (0.03)	16.73 (0.02)	1.13 (0.00)

10 % of sample smaller than this value, *d* (*v*, 0.1)

50 % of sample smaller and 50% of sample larger than this value (the mass median diameter), *d* (*v*, 0.5)

90 % of sample smaller than this value, *d* (*v*, 0.9)

The volume mean diameter, *D* [4, 3]

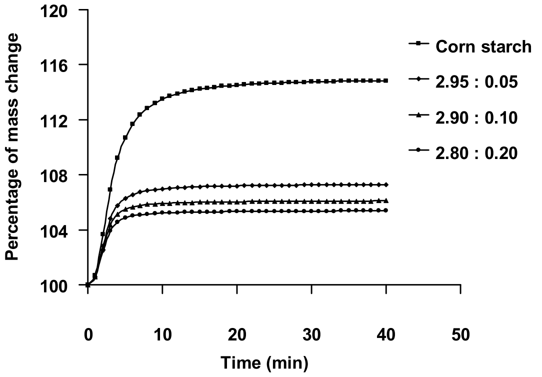
Table 5 Apparent density of uncoated corn starch and coated corn starch obtained by RESS process with the $ScCO_2$ temperature of 60 °C and pressure of 3000 psi.

Sample	Ratio of corn starch to stearic acid	Apparent density (g/cm^3)
Coated corn starch	2.80 : 0.20	1.45
	2.90 : 0.10	1.48
	2.95 : 0.05	1.50
Uncoated corn starch	-	1.50

diameter of 19.35 ± 0.13, 18.00 ± 0.19, and 16.75 ± 0.01 μm, at weight ratios of corn starch to stearic acid of 2.80: 0.20, 2.90: 0.10 and 2.95: 0.05, respectively. This could be deduced that stearic acid was deposited on the corn starch particles. In addition, the apparent density of uncoated corn starch was found to be slightly higher as compared to that of coated corn starch. This might be due to the presence of stearic acid which had lower density (0.83 - 1.01 g/cm^3) than pure corn starch.

The percentages of mass change of uncoated and coated corn starch determined after exposure to relative humidity of 75 % at 25 °C are shown in Figure 7. The percentage of mass increase of uncoated and coated corn starch before exposure to relative humidity values of 75 % was designated as 0 %. The results showed that the percentage of mass increase of uncoated corn starch was 115.06±0.05 %, corresponding to a reported equilibrium moisture content for corn starch of approximately 14-15 % at 25 °C/75 % relative humidity[10]. The coated corn starch showed lower percentages of mass increase as compared to that of the uncoated corn starch. The degree of mass increase was in accordance with the proportion of stearic acid in the product. With greater proportion of stearic acid coated on the particles, the lower percentage of mass increase would be observed. Similar results were found for the time needed to reach moisture equilibrium. Uncoated corn starch needed the longest time to be saturated with moisture. Based on the results obtained, the coated corn starch was unfavorable for moisture sorption due to the hydrophobic character of stearic acid film formed on the surface of corn starch particles. The greater proportions of stearic acid would form thicker film and provided better protection against moisture. The finding showed a significant improvement in moisture resistance of corn starch particles via the surface modification using RESS process.

Figure 7 The percentage of mass change after exposure to relative humidity of 75% at 25 °C of uncoated corn starch and coated corn starches obtained by varying the weight ratios of corn starch to stearic acid and processed at the $ScCO_2$ temperature of 60 °C and pressure of 3000 psi.



DSC thermograms of uncoated and coated corn starch, stearic acid, and the physical mixtures of corn starch and stearic acid at different weight ratios are shown in Figure 8. The DSC thermogram of uncoated corn starch showed endothermic peak due to dehydration at 92.66 °C. Stearic acid showed single sharp endothermic peak at 58.35 °C which corresponded to its melting point. The melting point of stearic acid was reported to be 57 - 60 °C[10]. The coated corn starche samples showed the combined water loss endothermic peak of corn starch and melting endotherm of stearic acid approximately at 91 - 93 °C and 57 °C, respectively (Figure 8 (a - c)). DSC thermograms of the physical mixtures of corn starch and stearic acid are shown in Figure 8 (d - f). DSC thermograms of the coated samples and the physical mixtures of corn starch and stearic acid with varied ratios had a similar pattern. In addition to the results from SEM of coated particles which showed the absence of stearic acid flake, DSC results confirmed that stearic acid melting endotherms of coated particles were similar to the melting endotherms of the physical mixtures. Stearic acid only coated without interaction or incompatibility with corn starch and the process did not induce new morphology of the solid substances.

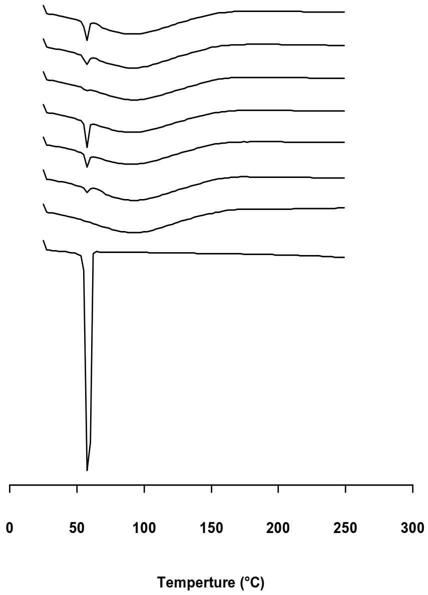


Figure 8 DSC thermograms of coated corn starch obtained by RESS process with $ScCO_2$ temperature of 60 ºC and 3000 psi and using the varied weight ratios of corn starch to stearic acid at 2.80 : 0.20, (a); 2.90 : 0.10, (b); 2.95 : 0.05 (c); physical mixtures of corn starch to stearic acid ratio at 2.80 : 0.20, (d); 2.90 : 0.10, (e); 2.95 : 0.05, (f); uncoated corn starch and stearic acid.

FT-IR spectra of coated corn starch and the physical mixtures of corn starch and stearic acid were relatively similar (Figure 9). In comparison with the spectrum of the uncoated corn starch, the major changes in the spectra of coated corn starch and the physical mixtures were the presence of a carbonyl (C=O) absorption frequency at 1705 cm^{-1} of stearic acid and the occurrence of sharp bands at 2918 and 2850 cm^{-1} which are the characteristics of the C-H stretching vibration for stearic acid.[11] The strong O-H stretching band at 3434 cm^{-1} in the uncoated corn starch spectrum was also found in the coated corn starch spectra[12]. The existence of the carbonyl band at 1705 cm^{-1} suggested the presence of stearic acid on corn starch particles, which supports the results discussed earlier.

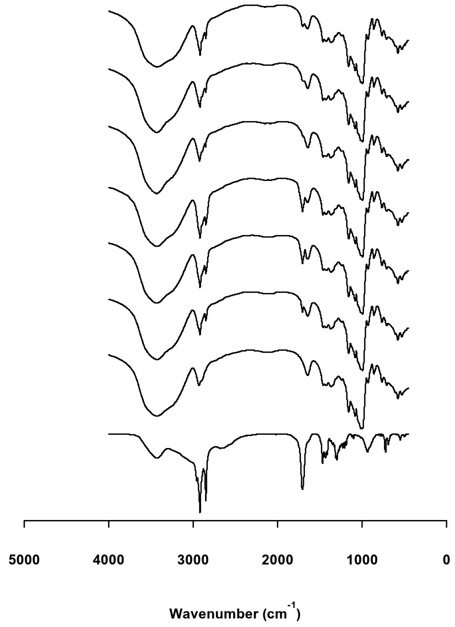


Figure 9 FT-IR spectra of coated corn starch obtained by RESS process with $ScCO_2$ temperature of 60 ºC and pressure of 3000 psi using the varied weight ratios of corn starch to stearic acid at 2.80 : 0.20, (a); 2.90 : 0.10, (b); 2.95 : 0.05 (c); and physical mixtures of corn starch to stearic acid ratio at 2.80 : 0.20, (d); 2.90 : 0.10, (e); 2.95 : 0.05, (f); and uncoated corn starch and stearic acid.

Conclusions

The findings showed that film formation of stearic acid on corn starch particles could be accomplished via rapid expansion of supercritical solution (RESS) process. The process of particle coating using RESS is a promising alternative method for coating fine particles with no organic solvent involved. This process could be useful for coating pharmaceutical particles for surface modification, taste masking or stability improvement.

Acknowledgements

This work was financially supported in part by the Graduate School, Chulalongkorn University. The authors wish to thank Dr. Narueporn Sutanthavibul for helpful comments on this work.

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Editorial note
Manuscript received in original form on July 1, 2011 ;
accepted in final form on March 19, 2012