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Comparative study on fish oil encapsulation using cassava- and corn-based OSA starch as encapsulating carriers

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Abstract

Encapsulation technology has been approached as a solution by protecting fish oil from oxidation and masking fishy flavour and taste, thus enabling it to be delivered to food products without affecting sensory properties. Octenyl succinic anhydride (OSA) treated starches contain hydrophobic octenyl side chains which impart an emulsifying capability to the starches; it has been used as a potential inexpensive alternative encapsulation material of fish oil for many years. The objective of this study was to evaluate the suitability of two different types of commercially available OSA-starch, cassava- and corn-based octenyl succinylated starches, and process conditions on encapsulation efficiency and physical characteristic of encapsulated fish oil. Morphological characteristics of encapsulated fish oil powders were characterized by scanning electron microscope (SEM) and dynamic light scattering analyzer. The encapsulation efficiency of fish oil as a core material was evaluated. The attention was given to the surface oil content which are very significant parameters in the encapsulation process. The results obtained from this study suggest that the encapsulation efficiency of fish oil was no effect by the type of encapsulant materials. Microcapsules obtained from spray drying were found to be nearly spherical but had many dents on the surface. However, no visible holes and fractures were observed in the outer surfaces of the capsules.

Keywords: Encapsulation process, OSA-starch, fish oil powders, cassava starch, corn starch

1. Introduction

Currently, more and more studies suggest that omega-3 fatty acids lower the risk of cardiovascular disease, some forms of cancer, and play a key role in brain development [1-3]. However, due to their highly unsaturated nature they are very sensitive to lipid oxidation. This leads to an entire scale of off-smells and off-tastes, varying from grass- and bean-like, to cardboard- and fish-like flavors. The oxidation of lipid proceeds by a free radical mechanism, which can be described in terms of initiation, propagation, and termination processes [4-6]. To prevent or slow-down the lipid oxidation, the following can be done; prevent the initiation reaction from occurring, reduce the oxygen concentration, add anti-oxidants to scavenge radicals and thus terminate the oxidation reaction, lower the storage temperature etc. [7-8]. Speed of the earlier mentioned reactions also depends on the initial quality and subsequent handling of the raw materials, and on the food structure and composition. Alternatively, encapsulation can reduce oxidation (prevent off-flavor) [9]. The encapsulated product can preventing contact between oxygen and fish oil, preventing direct exposure to light and trapping off-flavor [9]. These conditions can be achieved by the entrapment of the fish oil in a glassy state. Below the glassy state, the molecules in amorphous materials have little relative mobility. In addition, advantage of encapsulation might be the conversion of a lipid into a

powder, which may ease the handling during supply chain or incorporation into food powder products.

Starch has been used in a variety of encapsulation processes, which have been reviewed in detail elsewhere [10]. Indeed the use of starch in many encapsulation processes has provided solutions to problems such as process induced controlled release, thermal stabilization, and extended shelf-life of sensitive compounds. There are two major starch polymers: amylopectin and amylose. Amylose and amylopectin have different properties. For example, amylose has a high tendency to retrograde and produce tough gels and strong films, whereas amylopectin, in an aqueous dispersion, is more stable and produces soft gels and weak films [11]. These facts lead us to think that, different native based starches OSA modified could have different encapsulation efficiency and characteristics of encapsulated powders. Since, corn and cassava starches have been extensively used as a raw material in modification with octenyl succinic anhydride (OSA) and commercially available. The purpose of the present study is therefore to ascertain the effectiveness of using cassava- and corn-based OSA starches as encapsulating agent for fish oil by conventional spray dry method.

2. Materials and Methods

2.1 Materials

Pure fish oil was purchased from Sigma-Aldrich (St. Louis, MO, USA) owing to its relatively high content of ω-3-fatty acid. This fish oil was used as the main core component in the preparation of capsules. Cassava- and corn-based octenyl succinate starches (equal degree of substitution) were purchased from retail market in Thailand. All other chemicals were of analytical grade and were used from the indicated sources without further purification procedures.

The encapsulation of fish oil by using cassava- and corn-based OSA starches

For encapsulation, an emulsion with 55% total solids was prepared. Oil content was set at 25% of the total solids. The emulsion was prepared using cassava- and corn-based octenylsuccinate derivatized starches as encapsulating agent at a concentration 30% (OSA starch can act as encapsulating agent and emulsifying properties itself). Pre-emulsions were prepared by a hi-speed homogenizer (Ultra-Turrax® T25, IKA Labotechnik, Staufen, Germany). The fish oil which used as a core material was added into OSA starch solution during pre-emulsion preparation and homogenized at 12,000 rpm for 5 min. A coarse emulsion was prepared by microfluidizer (Microfluidic®, MA USA) at various pressures (500-800 bar with three passed). Spray drying of the emulsion was performed on a laboratory scale spray dryer equipped with a rotating disk for atomisation. The operation conditions of spray drying were as followed, air inlet temperature of 170ºC, air outlet temperature of 70ºC and flow rate of feeding sample as 8 ml/min. The dried powder was collected and stored at room temperature before used in further experiment.

2.2 Methods

Characterization of encapsulated fish oil powders

Scanning electron microscopy using Hitachi S3400N (Tokyo, Japan) was applied to view and describe the characteristics of the microcapsules. A laser-diffraction sensor (PCS; Nano-ZS90 nanoseries, Malvern Instruments, Worcestershire, UK) equipped with cuvette was used for determination of the particle size and oil droplet size of the capsules. For the size measurements, all the formulations were diluted with 1 mL of distilled water. Particle size diameter and poly-dispersity index (PDI) values were obtained as a triplication at 25ºC. The refractive index of the fish oil nanoemulsions containing OSA starches in water obtained at 1.33 by using a refractometer (ATAGO, RX7000 alpha, Tokyo, Japan) to check how much

the light is scattered in the medium. In this study, there was assumed that all the initial oil was retained in the powder. The surface oil or free oil content was criteria for encapsulation efficiency. Petroleum ether (*bp* 40-60ºC) was selected to extract the free fish oil from the encapsulation powder, according to the method of Garcia et al. (2006). Briefly, a proper ratio of petroleum ether was mixed into the fish oil powder, and was shaken in incubating shaker (mini-shaker, IKA Labotechnik, Staufen, Germany) for 15 min. The sample was then filtered through filter paper (No. 41, Whatman, Maidstone, UK). The solvent supernatants were collected for evaporation under vacuum evaporator condition. The amount of free fish oil was determined gravimetrically. The data were analyzed by ANOVA using the SAS statistical program 9.1 (SAS Institute, Cary, NC, USA). Differences among the means were compared using Duncan's Multiple Range test, and the correlations between independent variables and measured values were calculated as Pearson's correlation coefficients. Each treatment had three replicate determinations.

3. Results and Discussion

Particle sizes of redispersed powder containing OSA starch were shown in Fig. 1. After powder preparation, the particle size of all formulations was in range of 140 to 240 nm (Figure 1). When the samples were stored at room temperature for 2 months, the particle size of redispersed fish oil powder prepared by corn-based OSA starch was insignificantly different from the control (day 0). Whereas, redispersed fish oil powder prepared by cassava-based starch, the particle size considerably increased according to increase the storage time. Moreover, the particle size distribution of redispersed fish oil powder containing corn-based OSA starch was homogenous with a narrow (data not shown) and the low poly-dispersity index (PDI) values (Fig.1) during storage time. On the other hand, the redispersed powder containing cassava-based OSA starch shows the increase of PDI value depended on increasing storage time.

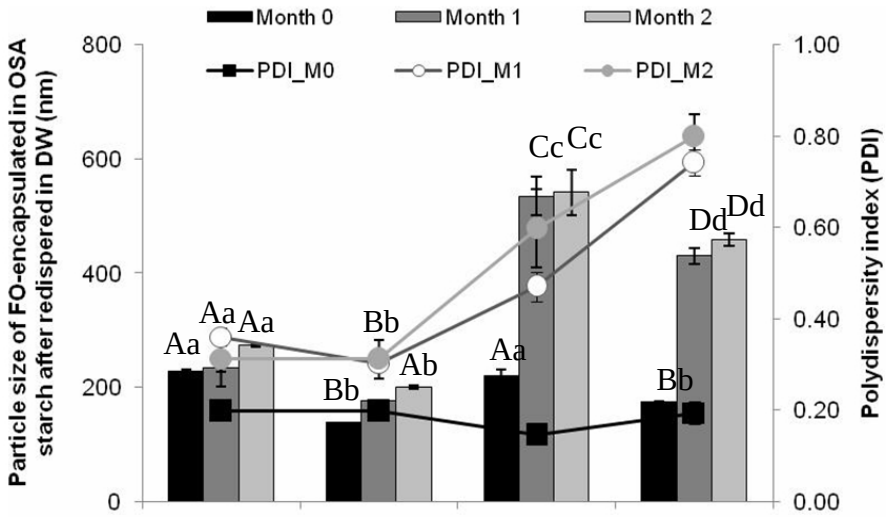

Figure 1 Size distribution of encapsulated fish oil (after redispersed in distilled water) ($p<$ 0.05).

Encapsulation efficiency analyses, based on the contents of oil un-entrapped in capsules, are showed in Table 1. It was found that the powder consisting both of OSA starches have lower amounts of surface oil during storage time. Interestingly, fish oil encapsulated powder containing corn-based OSA starch which was prepared by microfluidization under pressure 500 bar, the lowest amounts of surface oil was found in this formulation when compared with

others. While, the increase in pressure of microfluidization has no effect on the encapsulation efficiency of the powder containing cassava-based OSA starch. This result indicated that type of starches and processing were importance for fish oil encapsulated OSA starch preparation.

Table 1 The encapsulation efficiency (surface oil) of fish oil-encapsulated powder containing OSA starches after spray drying.

Formulation	Surface oil (mg/100 g powder)
OSA-cassava starch, Pressure 500 bar	$107.5^{a} \pm 2.12$
OSA-cassava starch, Pressure 800 bar	$348.0^{b} \pm 2.83$
OSA-corn starch, Pressure 500 bar	$334.0^{b} \pm 5.66$
OSA-corn starch, Pressure 800 bar	$314.5^{b} \pm 4.95$

Means within the same column followed by different letters (a, b, c) are significantly ($P < 0.05$) different.

Figure 2 shows the morphology of fish oil encapsulated powder containing corn-based OSA starch and cassava-based OSA starch. It was found that fish oil powder prepared by corn-based OSA has less surface shrinkage than the powder prepared by cassava-based OSA starch. In addition to all formulations, they show a fast crust formation that may relate with low levels of surface oil content obtained with solvent extraction as there is less opportunity for the core material droplets to come onto the surface particles [11]. However, there was no difference between the morphology of fish oil powder prepared by different pressure condition of microfluidizer. In conclusion, preliminary results from our laboratory demonstrated the potential of OSA starch as material for fish oil encapsulation. The fish oil encapsulated powder had high encapsulation efficiency (with low surface oil content). Interestingly, the pressure of microfluidization has influence on encapsulation efficiency of the encapsulated powder prepared by corn-based succinylated starch, whereas has no effect on the encapsulation efficiency of the sample containing cassava-based succinylated starch. SEM study shows fish oil encapsulated powder was spherical shapes with wrinkled surface, which was attributed to drying and cooling solidification involved during spray-drying. Further study on stability of fish oil related to glassy state of different starch used as encapsulating agent are required to examine these results.

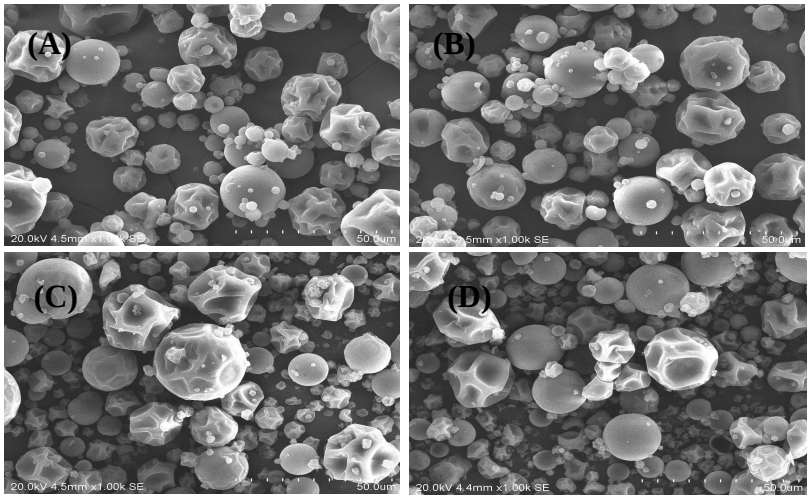

Figure 2 SEM micrographs of fish oil encapsulated powders containing corn-based starch, (A) and (B); and cassava-based starch, (C) and (D) prepared by microfluidization at pressure 500 and 800 bar, respectively.

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