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Microencapsulation of Fish Oil-milk Based Emulsion by Spray Drying: Impact on Oxidative Stability

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Abstract

Omega-3 poly unsaturated fatty acids (PUFA) have numerous human health benefits. Fish oil has been known as a source of PUFA, but their addition to foods is limited by oxidative rancidity. Hence, fish oil has to be protected against oxidation preferably by microencapsulation. In the present study, an attempt was made to prepare fish oil encapsulates. Fish oil-milk based emulsion was prepared and encapsulated by spray drying using either fish gelatin or maltodextrin as wall materials. Fish oil and wall material was used at the ratio of 1:2. In order to study the effect of natural antioxidants on the fish oil encapsulates, ginger essential oil was added at 0.25% concentration. Morphological characterization of fish oil encapsulates by scanning electron microscopy (SEM) revealed spherical shape of particles without any cracks. Encapsulation efficiency was improved significantly ($p<0.05$) from 34.48-35.52% to 44.42-49.34% by the addition of fish gelatin or maltodextrin as wall material. Fish oil encapsulates were packed in two different ways which include normal and vacuum packing and stored at room temperature (28±2°C). Oxidative stability of the fish oil encapsulates showed better protective effect against oxidation (1.99 mg malonaldehyde kg^{-1}) for fish oil encapsulates prepared with fish gelatin and ginger essential oil and packed in vacuum condition than the control (8.22 mg malonaldehyde kg^{-1}). Results from the study indicated that fish gelatin was able to encapsulate fish oil and it was comparable with that of maltodextrin. Addition of essential oil as natural antioxidant improved the oxidative stability of fish oil encapsulates.

Keywords: Microencapsulation, spray drying, fish oil, oxidative stability, essential oil

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Introduction

Fish oil represents a functional food ingredient, which contains important components for maintenance of good health and prevention of a range of human diseases via its beneficial effects on the heart, brain and nervous system (Wu et al., 2009). Autoxidation of polyunsaturated fatty acids (PUFA) in fish oil leads to the development of volatile secondary oxidation products and limit the shelf-life of the foods (Lee et al., 2006). Due to reasons like contribution of unsaturated lipids to health protection and economics, many investigations have been undertaken with the aim to enhance the stability of lipids and lipids containing products. Application of antioxidants is one of the technically simplest ways of reducing fat oxidation (Karpinska et al., 2001). Emulsion systems are being utilised for delivery of lipophilic health active compounds, such as PUFA, particularly eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) where they provide convenient and practical means for delivering these nutrients in human diets (Augustin & Sanguansri, 2003). Generally, fish oil in its natural state has a taste and smell that makes it less attractive to consumers. Processing technology to mask the smell and taste in food systems is facing a great challenge. Interest in the encapsulation of long-chain polyunsaturated omega-3 oils is rapidly growing due to their beneficial health effect. Encapsulation is a rapidly expanding technology with a lot of potential in different areas including pharmaceutical and food industries. Among the different techniques available, spray drying is the most important technique for the encapsulation of bioactive food ingredients (Desai & Park, 2005). Spray drying is a well-known technology in the food industry and is the most commonly used microencapsulation technique. It is also useful for the processing of heat-sensitive materials due to very short exposure time of product to heat. Before spray drying, the formed

emulsion must be stable over a certain period of time (Liu et al., 2001). Typical wall materials for microencapsulation by spray-drying are low molecular weight carbohydrates like maltodextrins or saccharose, milk or soy proteins, gelatin and hydrocolloids like gum arabic or mesquite gum.

Information on the effect of food processing procedures on the antioxidant activity or chemical composition of spice essential oil employed in the food industry is scarce. Hence, in the present study an attempt was made to prepare fish oil encapsulates with essential oil and evaluate its stability to oxidation at room temperature.

Materials and Methods

Fish oil (liver oil of sea cod) was used for the preparation of emulsion and encapsulates. Ginger (*Zingiber officinale*) was used as a source of natural antioxidant. Fish gelatin was extracted from the skin of ghol fish (*Protonibea diacanthus*) and was used as a source of emulsifier and wall material for encapsulation. Commercially available pasteurized and double toned milk (Mother Dairy) was used for the preparation of emulsion for encapsulation. Essential oil (EO) of ginger (*Zingiber officinale*) was obtained by hydro-distillation according to the method of AOAC (1980). Fish gelatin was extracted by the procedure described by Gudmundsson & Hafsteinsson (1997).

Six different emulsion formulations for encapsulation were made, namely 1% fish oil, 1% fish oil + 0.25% ginger essential oil, 1% fish oil + 2% fish gelatin, 1% fish oil + 2% fish gelatin + 0.25% ginger essential oil, 1% fish oil + 2% maltodextrin and 1% fish oil + 2% maltodextrin + 0.25% ginger essential oil. Fish oil and wall material [fish gelatin/ maltodextrin (16 Dextrose Equivalent)] was used at the ratio of 1:2. Milk was used as the base material for all formulation for making emulsion. In order to utilize milk proteins as an encapsulating material, fish oil was added to milk to make an emulsion. After the dissolution of wall material, fish oil and essential oil were added and further it was homogenized with a tissue homogenizer (Poly system PT 2100, Kinematica, AG) at 25000 rpm for 5 min. Samples were allowed to stabilize at room temperature for 1 h and then spray dried using a table top spray dryer (S. M. Scientech, Kolkata, India) under the following experimental conditions viz., inlet temperature 160°C; outlet temperature 80°C; spray flow feed rate 5 ml min^{-1}; nozzle diameter 3 mm; drying air flow 0.5 l h^{-1}, air pressure 4 bar. Fish oil encapsulates were packed into two types viz., normal and vacuum packing and stored at room temperature (28±2°C) for further analysis.

Moisture content of fish oil encapsulates was determined by using moisture analyzer (Denver Moisture Analyzer, model IR 120, Germany). Encapsulation efficiency (EE) was derived from the relationship between total oil and surface oil or free oil. Total oil extraction was based on the Rose-Gottlieb method (Richardson, 1985) and free oil fraction was extracted according to Sankarikutty et al. (1988).

$$EE\ (\%) = \frac{\text{Total oil (\%)} - \text{Surface oil (\%)}}{\text{Total oil (\%)}} \times 100$$

Morphology of the fish oil encapsulates was analysed by scanning electron microscopy (FEI Quanta 200 ESEM and EDAX system, Netherlands). Fish oil encapsulates was mounted on a bronze stub covered with carbon tap and was imaged at an acceleration voltage of 20 kV, magnification at 2000x and pressure at 60 Pa by using Large Field Detector (LFD). Lipid peroxide value (PV) of fish oil encapsulates was determined according to the method described by Shantha & Decker (1994). Changes in secondary oxidation products of the fish oil encapsulate were determined by measuring thiobarbituric acid reactive substances (TBARS) according to the method of McDonald & Hultin (1987).

The data obtained were analyzed by one way analysis of variance (ANOVA) using statistical package for social science (SPSS) software version 16.0 (SPSS Inc, Chicago, Illinois, USA). A one way ANOVA was used to evaluate difference in the mean value (PV and TBARS) of samples and control. All mean separations were carried out by Duncan multiple range test using the significance level of 95% ($p<0.05$).

Results and Discussion

Moisture content of the fish oil encapsulates ranged between 2.18±0.07 and 2.95±0.35%. Incorporation of wall material showed significant ($p<0.05$) decrease in the moisture content. Similar results were reported by Klaypradit & Huang (2008) in tuna oil powders (2.89-3.02%). The moisture levels were below the maximum limit specified for dried

powder in the food industry which is between 3-4 g 100 g^{-1} (Klinkesorn et al., 2006). It indicates the suitability of fish gelatin and maltodextrin as wall materials for microencapsulation.

Encapsulation efficiency is the most important parameter to ascertain the capacity of different wall materials for encapsulating core material. Encapsulation efficiency of fish oil encapsulates ranged from 34.48±0.21% to 49.34±0.14% (Table 1). There is significant ($p<0.05$) difference in the encapsulation efficiency of fish oil encapsulates made without addition of wall material which showed less encapsulation efficiency (34.48±0.21). Klaypradit & Huang (2008) observed encapsulation efficiency of 79.3 - 83.5% for the spray dried tuna oil powder using chitosan, maltodextrin and whey protein isolate as wall materials. In the present study, milk was selected as a source of protein for encapsulation instead of protein isolates. The differences in encapsulation efficiency can be attributed to different core and wall materials used. It may be due to the different conditions of the emulsion formation, considering that the oil droplet size in the emulsions influence directly the amount of surface oil (Soottitantawat et al., 2003). This was most likely due to the presence of insufficient wall material to effectively encapsulate all the oil present (Faldt et al., 1995).

SEM analysis of fish oil encapsulates prepared by using fish oil + fish gelatin and fish oil+ maltodextrin showed spherical shape with some wrinkles on the surface irrespective of the drying conditions (Fig 1 & 2). It was observed that encapsulates made by spray drying showed higher variation in sizes, which indicates that during this process a very different family of drops was formed. Encapsulates prepared by using fish oil in milk emulsion contained fish gelatin, maltodextrin had maximum size range of 15 μm, 13 μm respectively, while the smallest size was 1 μm. Kolanowski et al. (2007) observed spherical structure of microencapsulates with different sizes by spray drying of fish oil. Kagami et al. (2003) reported different degrees of formation of surface indentations for fish oil containing microcapsules produced from protein and dextrin wall materials.

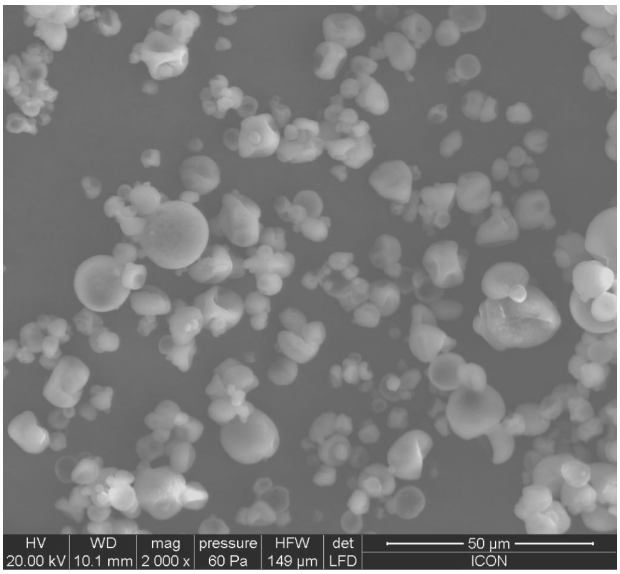

Fig. 1. Scanning electron micrograph of fish oil encapsulates prepared by using fish gelatin

Table 1. Moisture content and encapsulation efficiency of the fish oil encapsulates

Sample	Moisture (%)	Total oil (%)	Surface oil (%)	Encapsulation efficiency (%)
1% Fish oil (FO)	2.92±0.1^{d}	10.56±0.27^{a}	6.81±0.23^{c}	35.52±0.25^{b}
1% FO + 0.25% Ginger essential oil (EO)	2.95±0.3^{d}	11.35±0.28^{b}	6.9±0.025^{c}	34.48±0.21^{a}
1% FO + 2% Fish gelatin	2.35±0.3^{b}	11.34±0.16^{b}	6.03±0.12^{ab}	46.83±0.18^{d}
1% FO + 2% Fish gelatin+ 0.25% Ginger EO	2.47±0.45^{c}	11.22±0.12^{b}	6.23±0.15^{b}	44.42±0.25^{c}
1% FO + 2% Maltodextrin	2.18±0.0^{a}	11.45±0.09^{b}	5.80±0.16^{a}	49.34±0.14^{e}
1% FO + 2% Maltodextrin+ 0.25% Ginger EO	2.29±0.1^{b}	11.33±0.15^{b}	6.01±0.17^{ab}	46.97±0.32^{d}

Results are mean ± SD, n=3; Values within a column with different superscript letters are significantly ($p<0.05$) different

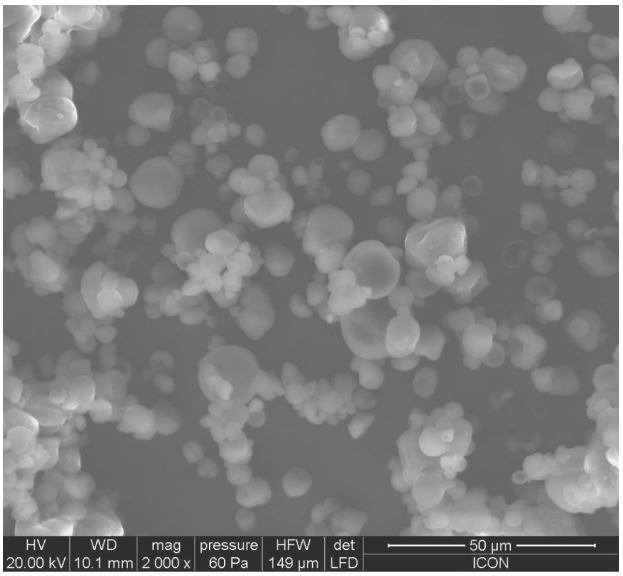

Fig. 2. Scanning electron micrograph of fish oil encapsulates prepared by using maltodextrin

Stability of fish oil encapsulates to oxidation was evaluated up to 25 days at known interval. In normal packed fish oil encapsulates prepared with fish gelatin and 0.25% ginger essential oil showed lowest peroxide value of 1.26 mmolO_2 kg^{-1} on 21st day compared to the control (11.42 mmolO_2 kg^{-1} on 21st day) (Fig. 3). Serfert et al. (2009) observed lowest content of hydroperoxides in samples with rosemary extract antioxidant system. Similarly, in vacuum packed fish oil encapsulates prepared with fish gelatin and 0.25% ginger essential oil showed the lowest peroxide value (1.17 mmolO_2 kg^{-1} on 21st day) than the control (6.31 mmolO_2 kg^{-1} on 21st day) (Fig.4). The results show that peroxide value increased up to 3 weeks and thereafter decreased in the control. There is significant ($p<0.05$) difference in formation of lipid hydroperoxides of fish oil encapsulates packed in normal and vacuum condition. Results of oxidation studies for vacuum-stored microencapsulated fish oil are in agreement with other studies (Kolanowski et al., 2007) which suggest that shelf-life of encapsulated fish oil may be improved when stored under vacuum. However, the peroxidation value of fish oil microencapsulates was comparable with standard specification value of 10 meqO_2 kg^{-1} value accepted in oils and fats (Romeu-Nadal et al., 2006).

During storage, TBARS value of fish oil encapsulates steadily increased at room temperature in normal and vacuum packed condition. The increase in thiobarbituric acid value was significantly ($p<0.05$) higher in the control (11.47 mg malonaldehyde kg^{-1}) compared to all other samples. In normal packed fish oil encapsulates prepared with fish gelatin and 0.25% ginger essential oil showed the lowest TBARS value (2.34 mg malonaldehyde kg^{-1} on 25th day) than the control (11.47 mg malonaldehyde kg^{-1} on 25th day) (Fig. 5). Similarly, in vacuum packed fish oil encapsulates prepared with fish gelatin and 0.25% ginger essential oil showed lowest TBARS value (1.99 mg malonaldehyde kg^{-1} on 25th day) than the control (8.22 mg malonaldehyde kg^{-1} on 25th day) (Fig. 6). Results

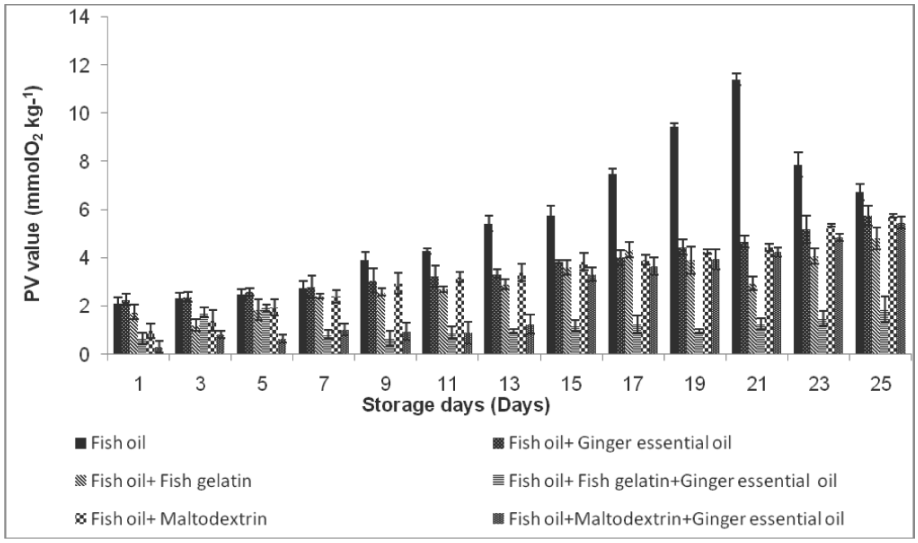

Fig. 3. Changes in peroxide value of normal packed fish oil encapsulates during storage at room temperature

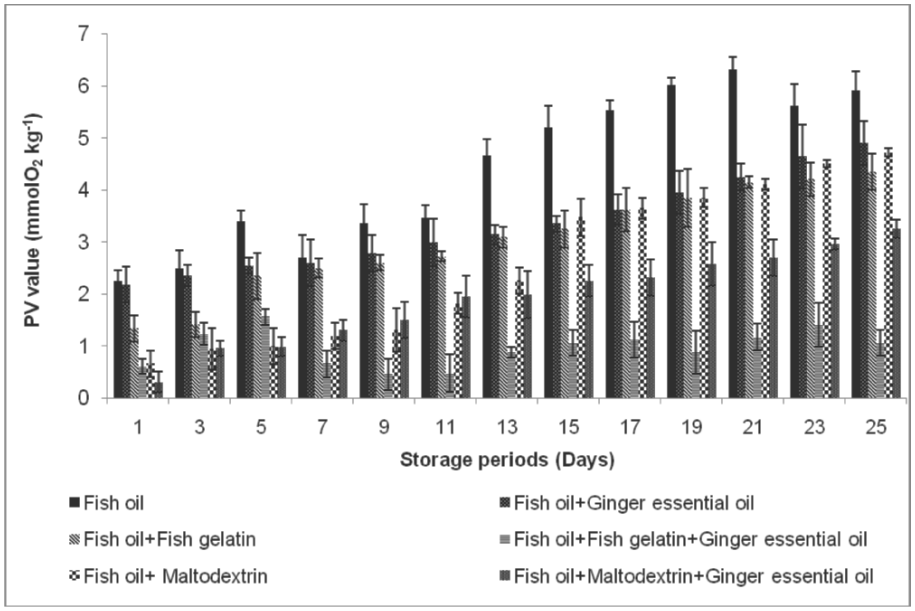

Fig. 4. Changes in peroxide value of vacuum packed fish oil encapsulates during storage at room temperature

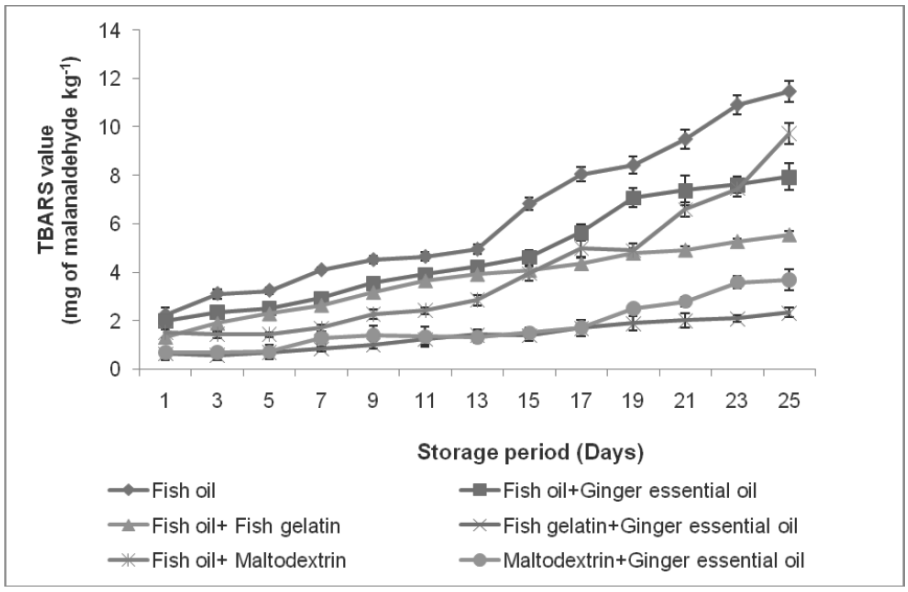

Fig. 5. Changes in TBARS value of normal packed fish oil encapsulates during storage at room temperature

showed that there is a significant ($p<0.05$) difference in secondary lipid oxidation of fish oil encapsulates packed in normal and vacuum condition. It is also noticed that rate of secondary lipid oxidation was lower in the fish oil encapsulates prepared by addition of wall material (fish gelatin/maltodextrin) when compared to the fish oil encapsulates prepared without addition of wall material. Drusch (2007) showed that micro-structural particle characteristics related to the type of emulsifier and particle characteristics related to the viscosity of the parent emulsion and its drying behavior are major determinants of the microcapsule stability. Keogh et al. (2001) observed that air inclusion influences the

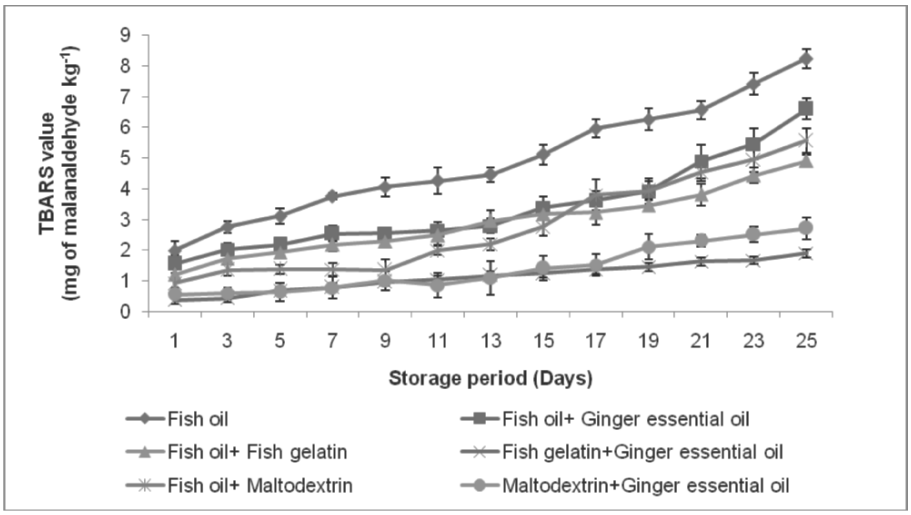

Fig. 6. Changes in TBARS value of vacuum packed fish oil encapsulates during storage at room temperature

shelf-life of microencapsulated fish oil. Though oils/fats were encapsulated, the oxidative deterioration may be due to the presence of free surface fat (Hardas et al., 2002). Results from the study suggested that comparison of the course of lipid oxidation with data reported in other encapsulation studies for oils rich in PUFA is generally difficult due to differences in the core material stabilization, the wall material used for encapsulation, the process and storage conditions and the parameters used to monitor lipid oxidation.

In conclusion, lipid oxidation of microencapsulated oils is affected by microcapsule characteristics. Fish gelatin was able to encapsulate fish oil and it was comparable with that of maltodextrin. Fish oil encapsulates prepared with fish gelatin and ginger essential oil improved the oxidative stability of PUFA at room temperature under vacuum condition than the control. Further, encapsulation of fish oil with ginger essential oil revealed the prospect of incorporating essential oils from diverse herbal sources into encapsulates for protecting highly susceptible omega-3 fatty acids from lipid oxidation.

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