Oligochitosan as potential antioxidant agent during the spray-drying of fish oil

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Introduction

Fish oil is a source of long-chain polyunsaturated fatty acid of omega-3 (EPA - eicosapentaenoic and DHA - docosahexaenoic acids). Both EPA and DHA strongly contribute to beneficial health effects, where their regular intake may prevent cardiovascular diseases, certain types of cancer, inflammations and allergies as well as improve proper development and function of central nervous system. Therefore, a number of functional foods enriched with omega-3 PUFA via fish oil addition have been recently developed. Specifically dried microencapsulated fish oil in the powder form is of special interest of food industry, because it can be long-term stored and applied both to instant powder or liquid products. Already fish oil powder has been incorporated into many food products, e.g. bread, biscuits, fruit bars, low-fat cakes, diet powder, fruit juice, milk powder, instant soups, infant formula.
Spray drying is a low-cost microencapsulation technology and the most commonly used in the food industry. This technique has been widely used for drying heat-sensitive foods and other substances, because of the rapid evaporation of the applied solvent from the droplets. It may also be useful for microencapsulation of omega-3 PUFA. It has been concluded in many scientific papers, that the production of fish oil microcapsules by spray drying technique is possible, however its oxidative stability has to be improved (Kolanowski 2006). Recently we have shown that addition of chitosanoligosaccharide (water-soluble chitosan) has some positive influence on stability of fish oil (peroxide value) immobilized in hydrogel microcapsules during storage in aqueous medium (Tarnowiecka 2006).
The aim of this study was to investigate the influence of spray draying on formation and oxidative stability of dry microencapsulated fish oil coated with modified starch, typically used in food industry for immobilization of hydrophobic compounds. This sample was obtained by spray drying of emulsion which consisted of water solution of modified starch and fish oil either in pure form or their mixtures with two types of oligochitosans.

Materials and methods

Fish oil (LYSI Ltd.. Iceland) as immobilized material and modified starch Capsul (National Starch Food Innovation) as polymer matrix were used as main components during the spray-drying process. Capsul as lipophilic starch were derived form wax maize base and modified with n-octenyl succinic anhydride and is typically applied in the flavor encapsulation industrial technologies. Oligochitosan-C (salt of ascorbic acid) and oligochitosan-H (KunPoong Bio Co., Ltd., South Korea) were used as potential protection agents against oxidation processes during emulsification and spray-drying process.
Spray drying : The wall material (modified starch - Capsul) 30% w/w was dispersed in distilled water and allowed to hydrate with stirring for 24 hours. Fish oil was gentle mixed with oligochitosan (1% and 0,1%) either in H or C form. For each oil either in pure form or as with oligochtosans was added to solution in a ratio wall material solid 1:1. The mixture was homogenized (Heidolph, SilentCrusher M) at a rotation speed of 15.000 rpm for 5 min.. This emulsion fed to the spray dryer (Mini Spray Dryer B-290, Switzerland). The optimal operational

condition of the spray drying were as follow: air inlet temperature 120 ^{o}C, air outlet temperature 70 ^{o}C, feed rate of 10 ml/min., and air flow 35 m^{3}/h. All powders were collected in glasses vessels (both in column and in cyclone comtainer).

Characterization of spray–dried fish oil : The oxidation stability of fish oil in emulsions and powders were characterized by determination of peroxide value (PV) according standard procedure (BN 74/ 8020-07) described by Kolakowska at al (Kołakowska et al., 2002). Additionally there were analysed in 2:1 chloroform:methanol solution using the UV-VIS spectrometer (Helios γ, Spectro-Lab, USA) recording spectra in range of 200-400 nm. The oil was extracted from powders and emulsion directly after preparation. Furthermore, both ATR-FTIR (Spectrum 100, Perkin Elmer, USA) equipped with GoldenGate ATR (Specac, UK) and Raman Spectroscopy (RamanStation 400), Perkin Elmer, USA) were applied to observe typical change in chemical composition of fish oil during various stages of immobilization process in powder and emulsion forms, respectively.

Microscopic evaluation of dried samples has been performed using both FTIR and optical microscopes.

Results and discussion

The observation of appearance and size of formed dry particles measured by light microscopy (Fig. 1) confirms that despite the high content of immobilized oil (around 50% wt. – Tab. 1) one can obtained using the appropriate material and conditions during the spray drying process the free-flowing powders of microcapsules of size in the range 10-30 μm. Such dry products have some tendency to form agglomerates which can be easily dispersed in any aqueous system.

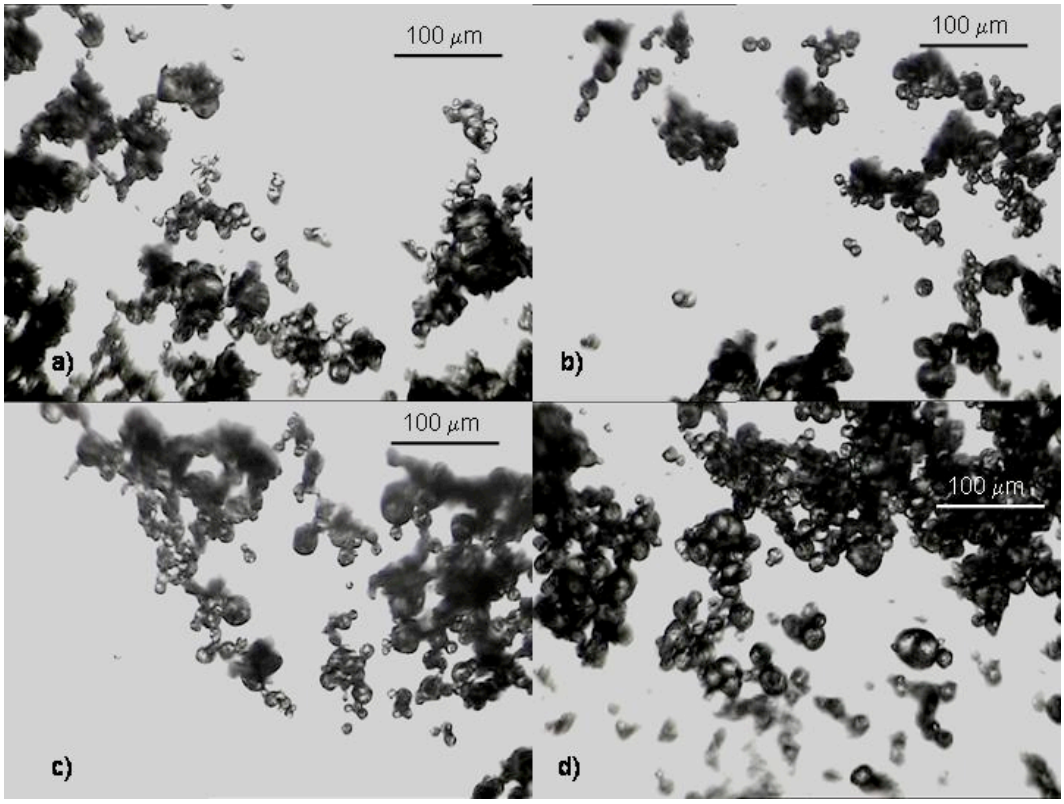

Figure 1: Microscopic pictures of fish oil/Capsul powders obtained after spray-drying: a) sample Capsul+oil, b) Capsul+oil/0,1% chit.H; c) Capsul+oil/1% chit.H; d) Capsul+oil/0,1% chit.C

Measurements of fish oil content in the obtained powders showed high microencapsulation efficiency (Tab. 1). In all cases it was above 82%, only form system with addition of 1% Oligochitosan-C there is only in total 65% of oil in final product.

Table 1: Yield of immobilization during the spray drying process

Sample No.	Oil concentration in dry powder [%] wt.	Yield of immobilization [%]
7	48,3	82,1
8	56,1	95,4
9	38,4	65,0
10	48,3	82,1
11	52,5	89,3

The oxidative stability of samples was evaluated by peroxide value measurements and determination of conjugated dienoic and trienoic cid concentration. It was observed that oxidation changes already during the emulsification process were much slower in systems with addition of both oligochitosans in comparison to non-modified system.

In the case of conjugated dienoic acid numbers there is only after spray drying a significant reduction for all samples, where smaller changes are observed for samples with both oligochitosans, but in case C-one only for lower 0,1% concentration.

Table 2: Oxidation change of immobilized fish oil either as emulsions or powders after after spray-drying

No.	Sample description	Peroxide value [mqO/kg]	Conjugated dienoic acid [233 nm] [1g/1%]	Conjugated trienoic acid [268 nm] [1g/1%]
1	Fish oil	**2,3**±0,27	1,809	4,444
Emulsion 30%				
2	Capsul +oil	**4,6**±0,52	2,452	4,312
3	Capsul+oil/0,1% chit.C	**2,5**±0,06	2,531	4,778
4	Capsul+oil/1% chit.C	**3,1**±1,03	2,141	4,488
5	Capsul+oil/0,1% chit.H	**0,9**±0,29	2,258	4,726
6	Capsul+oil/1% chit.H	**2,5**±0,54	2,042	4,500
Dry powder – after spray drying				
7	Capsul +oil	**22,1**±2,64	0,890	4,493
8	Capsul+oil/0,1% chit.C	**19,3**±1,88	1,749	4,726
9	Capsul+oil/1% chit.C	**6,2**±0,18	0,773	4,892
10	Capsul+oil/0,1% chit.H	**3,4**±0,26	1,492	4,753
11	Capsul+oil/1% chit.H	**1,5**±0,02	1,204	4,635

Additionally, oxidation deterioration and quality parameters of fish oil were monitored by ATR-FTIR and Raman spectroscopy by indirect comparison of recorded spectra, which leads to information of the type and relatively change of concentration of specific functional groups. The intense heating of oils causes an oxidizing thermal degradation with the formation of decomposition products and a change in physical properties. Both techniques have been used to monitor oxidation of immobilized fish oil either in emulsion form before and as dry powders after spray drying process. The major differences among the spectra of the fish oil immobilized in different matrixes are located at the bands 1267, 1655 and 3007 cm^{-1}, which correspond to vibrations in cis double bonds. The intensities of these bands reflect the total unsaturation. Thermal oxidation of unsaturated

oils is accompanied by considerable isomerisation of double bonds leading to products containing trans double bonds and conjugated double bond systems.

The following two major regions of most prominent changes in Raman and FTIR spectra have been monitored (Muik et al., 2005) (Tab. 3):

- 1600-1775 cm^{-1} – increase in 1655 cm^{-1} region - C=C stretching; bands in this region comprise the formation of conjugated double bond systems, of trans double bonds and the loss of cis double bonds;
- 2800-3050 cm^{-1} – decrease of cis-double bonds intensity of band 3007-3012 cm^{-1}.

Table 3: Characteristic Raman and FTIR spectral values (intensity I and peak area A) of products either in emulsion or powder form.

Sample	Emulsion Raman		Dry powder – after spray-drying ATR-FTIR	
	I_{3010}/I_{1745}	$A_{(1620-1680)}/I_{1625}$	I_{3010}/I_{1745}	$A_{(1620-1680)}/I_{1625}$
Capsul +oil	7,99	25,3	0,396	121
Capsul+oil/0,1% chit.C	8,70	24,8	0,393	112
Capsul+oil/1% chit.C	8,50	25,2	0,699	104
Capsul+oil/0,1% chit.H	7,59	24,9	0,631	87
Capsul+oil/1% chit.H	10,99	24,5	0,721	84

One can observe that there is a clear correlation between both characteristic spectroscopic numbers (Tab. 3) and peroxide values (Tab. 2) either for emulsion or spray-dried products.

Conclusions

It can be concluded, that already relatively small addition of oligochitosan in pure form led to significant improvement of fish oil oxidation stability during the spray drying process. However, further investigations including monitoring of oxidative stability of such powders during storage in different conditions are necessary.

Acknowledgments

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