MW profile of the matrix affects the stability of microencapsulated fish oil.

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Introduction

Encapsulation of sensitive food ingredients in an amorphous carrier matrix of carbohydrates is the basic principle of microencapsulation technologies like spray-drying, freeze-drying or extrusion. These techniques are predominant in applications for encapsulation of aroma compounds, essential oils and nutritional oils like oils rich in long chain polyunsaturated fatty acids. The amorphous carrier matrix is described as a rigid solid with an extremely high viscosity (Roos et al., 1991) and thus, molecular mobility within the matrix is significantly reduced. In contrast, diffusion of small molecules might occur through amorphous carbohydrate matrices. Orlien et al. (2000) summarised that in the 1990s a theory of diffusants travelling in cavities in the amorphous matrix has been developed and increased diffusion coefficients for small molecules have been observed with an increase in molecular weight of the carbohydrates forming the glassy matrix.
With respect to autoxidation of microencapsulated lipophilic food ingredients, oxygen diffusion through the glassy matrix must be considered to be one of the key factors of the reaction rate. In the present paper experimental evidence for the impact of molecular packaging of the shell material and thus gas permeability on the oxidative stability of microencapsulated fish oil is presented.

Materials and methods

Fish oil with 18 % eicosapentaenoic acid and 12 % docosahexaenoic acid was microencapsulated by spray-drying. The oil load of the microcapsules was 40 %. In a first step the oil was dispersed in an aqueous solution of the carrier matrix and subsequently homogenized at 250/50bar using a high pressure homogenizer (Panda 2k, Gea Soavi, Italy). Emulsions were spray-dried at 180/70 °C on a Niro Mobile Minor (Niro A/S, Denmark). The composition of the samples presented in this contribution comprise fish oil encapsulated into matrices containing n-octenyl-succinate-derivatized starch and different carbohydrates as well as caseinate glycated with different carbohydrates.
The microencapsulated oil was stored for eight weeks under controlled relative humidity of 33 % and 20 °C. Lipid oxidation was monitored through analysis of the hydroperoxide content according to a reference method published by the IDF with slight modifications (International Dairy Federation, 1991). Secondary lipid oxidation products were detected by static headspace gas chromatography. For the analysis 1 g of sample was re-dissolved in 2 ml which EDTA solution (0.5%). Samples were equilibrated at 70 °C for 15 min. An aliquot of the headspace (1 mL) was injected into a Agilent 6890 gas chromatograph equipped with a HP-Innowax column (60m x 0.32 mm x 0.5 µm) and a Agilent 5975 inert mass selective detector. Injector and detector temperature were set at 270 and 250 °C, respectively. Initially, the oven temperature was set at 50 °C and was held for 1.5 min. Temperature was increased to 240 °C at a rate of 20 °C min^{-1}, where it was held for 3 min. The mass spectrometer was operated in electron ionisation mode (70 eV), and data were acquired in the full-scan mode for the range m/z 20-200.
Depending on the experiment presented, physicochemical characterization of the microcapsules included the determination of the extractable oil content, the oil droplet size of the feed-emulsion as well as the microcapsules, determination of the particle size, the particle surface area with nitrogen adsorption, determination of the true density using helium as well as positron annihilation lifetime spectroscopy for detecting nano-structural differences in the matrices.

Results and discussion

First evidence on the impact of molecular weight profile on the rate of autoxidation in microencapsulated fish oil resulted from experiments on the influence of protein glycation on stability of the encapsulated oil. Aim of the study was to investigate the possible impact of the antioxidative activity and the altered technological properties of glycated caseinate on the oxidative stability of microencapsulated nutritional oils. The results lead to the conclusion that neither an antioxidative effect of the Maillard reaction products nor an improved emulsifying activity is responsible for the increase in oxidative stability of oils encapsulated in heated protein-carbohydrate mixtures. Data rather indicate that the molecular weight profile of the carrier matrix is one of the key determinants for the oxidative stability. The hydroperoxide and propanal content of the oils encapsulated in the caseinate-glucose blend were significantly lower compared to these parameters in oils encapsulated in the caseinate-glucose syrup blend (Figure 1).

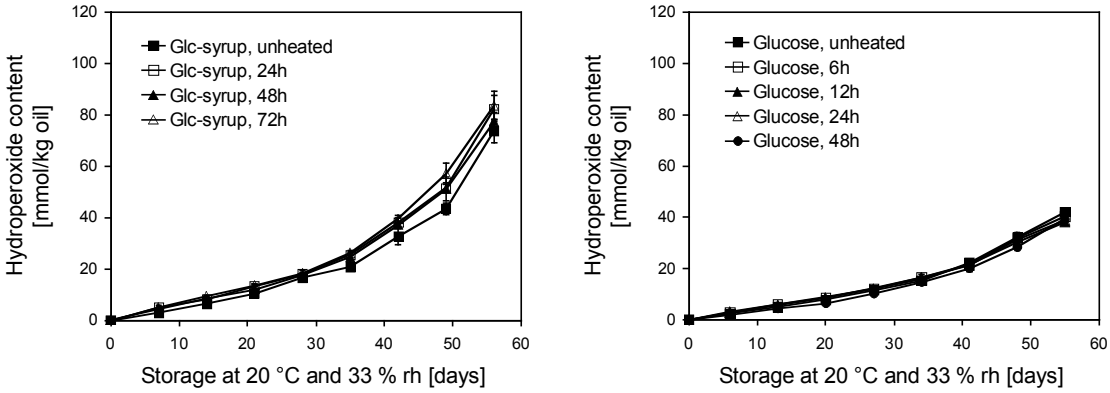

Figure 1: Development of the hydroperoxide content of fish oil encapsulated into matrices of caseinate glycated with glucose sirup or glucose during storage at 20 °C and 33 % relative humidity (Drusch et al., 2008)

Indications for the impact of the molecular weight profile on the oxidative stability of encapsulated nutritional oils also became evident in experiments on the contribution of physicochemical characteristics of microcapsules prepared from different shell materials on their oxidative stability. In this study principal parameters determining the oxidative stability of microencapsulated lipophilic core materials were identified (Drusch et al., 2007). When using n-octenylsuccinate-derivatised starch with varying degree of hydrolysis, thus molecular weight profile, differences in the oxidative stability were observed (Figure 2). The difference could not be attributed to differences in the drying behaviour of the in-feed emulsions and could not be explained by micro-structural characteristics of the microcapsules.

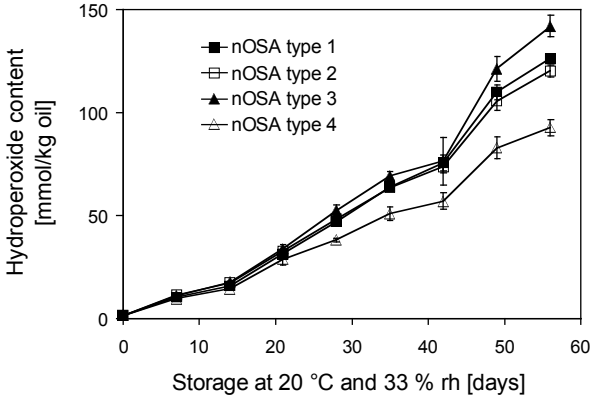

Figure 2: Development of the hydroperoxide content of fish oil encapsulated into blends of n-octenylsuccinate-derivatised starch and glucose syrup during storage at 20 °C and 33 % relative humidity.

Based on these results, a final study focussing on techniques to characterize porosity and gas permeability of the microcapsule was performed. Different carbohydrates and blends of these carbohydrates were used to prepare microcapsules with a different molecular weight profile of the bulk carrier matrix. The individual shell materials were maltodextrin with a dextrose equivalent (DE) of 18 (MD18), a commercially available glucose syrup (DE38; GLCS38), a blend of maltodextrin DE 18 and glucose with a final DE of 38 (GLCS-G38), a blend of maltodextrin DE 18 and maltose with a final DE of 38 (GLCS-M38) and maltose (DE50; M50). Drusch and co-workers (Drusch et al., 2006, Drusch et al., 2007) have shown that the molecular weight profile of the carrier matrix and the viscosity of the in-feed emulsion can significantly influence the drying behaviour and the resulting physicochemical characteristics of the microcapsules.

In the present study all solutions of the carrier matrices showed similar emulsification properties. The 50th percentile of the oil droplet size ranged from 1.16 to 1.30 µm and the viscosity of the in-feed emulsion ranged from 14 to 19 mPa s. Based on these data a similar drying behaviour for all in-feed emulsions and similar particle characteristics on the microscale can be assumed. Particle size of the microcapsules was not affected by the different bulk carbohydrate constituents. True density varied from 1.181 to 1.200 g/cm3 for MD18 and M50, respectively, and surface area according to Brunau, Emmet and Teller ranged from 0.18 to 0.22 m2/g for GLCS38 and GLCS-G38, respectively. These data lead to the conclusion that there was no difference in the helium- and nitrogen-permeability of the samples. Figure 3 shows the development of the hydroperoxide content of the encapsulated oil over a storage period of eight weeks at 20 °C and 33 % relative humidity. Significant differences in the course of hydroperoxide and propanal formation were observed. In the maltose containing system M50 hydroperoxide and propanal content amounted to 262 mmol/kg oil and 277 µmol/kg oil after 49 days of storage, respectively. No difference in the course of lipid oxidation was observed for the samples GLCS-G38 and GLCS-M38. Finally, the lowest stability against autoxidation was found in the sample MD18. The hydroperoxide and propanal content amounted to 41 mmol/kg oil and 10 µmmol/kg oil, respectively. Extractable oil content decreased with an increasing amount of low molecular weight compounds.

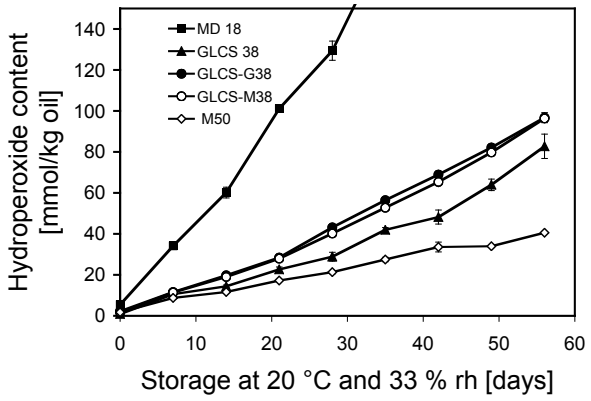

Figure 3: Development of the hydroperoxide content of fish oil encapsulated into carrier systems with different molecular weight profile

Drusch and Berg (2008) have recently shown, that extractable oil content is heterogeneously distributed in microencapsulated fish oil prepared by spray-drying. The authors postulated a similar distribution for the fraction of extractable oil as it was described for encapsulated milk fat (Buma, 1971) consisting of surface oil, surface-near encapsulated oil, oil covering pores within the particle and inner fractions, which are accessible to the solvent. It can be assumed that the solvent permeability of the carrier matrix differs in the samples of the present study and leads to differences in the amount of extractable oil. E.g. Hogan et al. (Hogan et al., 2001) reported an increase in microencapsulation efficiency when increasing the DE value of the carbohydrate used for encapsulation of fish oil in caseinate-carbohydrate systems. However, these differences can not explain the course of lipid oxidation, since the development of hydroperoxide and propanal content significantly differed between MD18 and GLCS38 s well as between GLCS-G38 and M50 although samples had almost the same content of extractable oil.

Conclusions

The results presented clearly show that the molecular weight profile of the carrier matrix, and thus the microcapsule structure on the nanoscale, significantly affects the stability of the encapsulated core material. Combination of low molecular weight sugars and high molecular weight carbohydrate derivatives led to a decrease in the development of lipid oxidation parameters. In product development, in a top-down approach changes of other physical properties of the shell material like glass transition temperature need to be taken into consideration. Strategies to actively modify these parameters are available in the literature and their impact on core material stability now need to be investigated.

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