Effect of environmental humidity humidity on oxidative stability of spray-dried whey isolate-flaxseed oil emulsions

R. Partanen[1], J. Raula[2], J. Buchert[1], E. Kauppinen[2] and P. Forssell[1*]
[1] VTT Technical Research Centre of Finland, Espoo, Finland
[2] Helsinki University of Technology, Espoo, Finland
[*] Pirkko.Forssell@vtt.fi

Introduction

There is a considerable challenge in incorporation of polyunsaturated fatty acids into food matrixes, as their rapid oxidation causes both off-flavour formation and potential toxicity (McClements et al., 2000). Oxidation reactions are fairly well characterised for bulk oils, but rate determining factors for this multi-step reaction still remain unsolved for oil dispersed in biopolymer matrices. In dry, solid, glassy matrix, oxygen transport may be limited by solubility and diffusion of oxygen in the matrix, both of which are influenced by the amount water present (Whitcomb et al. 2005). The aim of our work was to study the potential of whey protein isolate matrix in increasing oxidative stability of flaxseed oil at varying environmental humidities. Flaxseed oil is rich in linolenic acid (60-70 % of the total fatty acids), and thus sensitive to oxidation. The results are discussed in relation to water and oxygen dynamics.

Material and methods

Flaxseed oil was a product of Elixi oil Oy (Finland). Whey protein (Lacprodan) was an isolate purified from lactose (Arla, Sweden).

Emulsification of oil. 10 % whey protein isolate solution was pre-homogenized with flaxseed oil (40 % oil of the dry weight of the emulsion) with a Heidolph Diax 900 (Germany) homogenizer at maximal speed for 2*2 minutes. Pre-emulsion was fed to M-110Y pressure homogenizer (Microfluidics, USA) and circulated for 10 minutes at 40 psig. Droplet size distribution was determined in fresh emulsion.

Droplet size distribution. Oil droplet size distribution in emulsions was analysed by laser diffraction by a Coulter LS 230 (USA) equipped with polarization intensity differential scattering (PIDS) assembly for particles smaller than 0.4 μm. Duplicate measurements were performed.

Spray drying of emulsions. Emulsions were spray dried by a Niro Mobile Minor (Denmark) laboratory spray-drier with a co-current two-fluid nozzle. The inlet air temperature was adjusted to 180 ^{o}C, and the outlet temperature was kept at 90 ± 3 ^{o}C by controlling the flow rate. Atomization pressure was 1 bar. A control sample for SEM was prepared by drying whey protein isolate solution with the same parameters.

Extraction of encapsulated oil for peroxide value. A powder sample of 0.5 g was weighted into a test tube and suspended in 5 ml of water. The tube was shaken for 30 minutes to dissolve the matrix. Once dissolved, a 300 μl portion was taken and vortexed 3 times 10 s with 1.5 ml of iso-octane:isopropanol (2:1) mixture to extract the oil. The phases were separated by centrifugation (1000 g for 4 minutes). Longer times were applied if necessary. Duplicate extractions were performed.

Peroxide value determination. Peroxide value was determined spectrophotometrically according to IDF standard 74A:1991. 0.3 g of oil was weighted or in case of powder samples 200 µl of extraction media was taken for analysis and added to 9.6 ml of chloroform:methanol (7:3) mixture. For colour formation, 50 µl of both iron(II)chloride and ammonium thiocyanate solutions were added. The sample was briefly vortexed, reacted in dark for exactly 5 minutes, and measured at 500 nm. Duplicate measurements were performed.

SEM micrographs. Dry powder samples were mounted on gold-coated SEM stubs. SEM (Leo DSM982 Gemini, LEO Electron Microscopy, Inc., Germany) was operated at 0.7 kV. For cross-section images, samples were mounted on the stubs and torn with tape.

Storage stability test. Samples were spread on petri dishes and stored in closed chambers with supersaturated salt solutions at 37°C (RH 11, 49, 75, 90 %) and P_2O_5 (RH 0 %).

Results and Discussion

The median droplet size of fresh emulsion was below 200 nm, the largest droplets being less than 800 nm in diameter. The structure of spray-dried powder particles depends on both wall material and drying kinetics. The porosity of the matrix and distribution of oil in it could have an effect on availability of oxygen for hydroperoxide formation. Microstructure of the dried emulsion powder particles was characterised by SEM (figure 1a), using spray-dried whey protein isolate as a reference (figure 1b). Both sample particles for cross-section images had remarkably thin walls surrounding a hollow centre. A distinct difference was found between the inner structures of the dried emulsion (a) and the dried protein (b): the dried emulsion seemed to consist of the primary particles of the original emulsion, where the protein is surrounding the oil droplets. Porosity caused by drying is clearly seen in the reference sample (b), but can not be discriminated from the oil droplets in the emulsion powder sample (a).

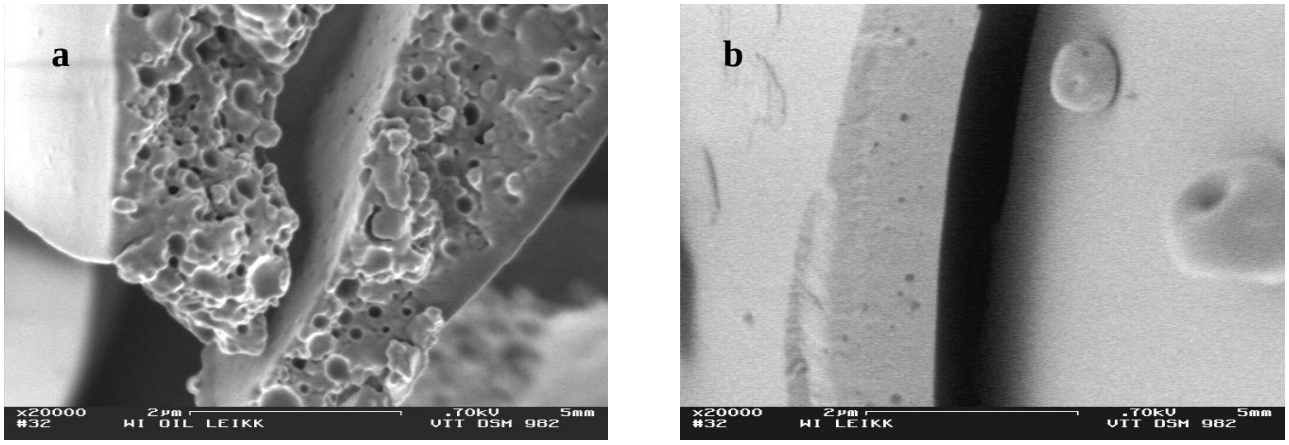

Figure 1. Cross-section of spray-dried whey protein isolate-flaxseed oil emulsion (a) and spray-dried whey protein isolate particles. The bar in the bottom is 2 µm.

The effect of relative humidity on the rate of oxidation of flaxseed oil was studied. The amounts of hydroperoxides in oil samples are presented in figure 2. Oxidation rate depended on storage humidity. Flaxseed oil was most stable at intermediate humidity (RH 49%). Oxidation was fastest at the high humidity end. At the low end, no systematic difference was found between dry and RH 11 % conditions.

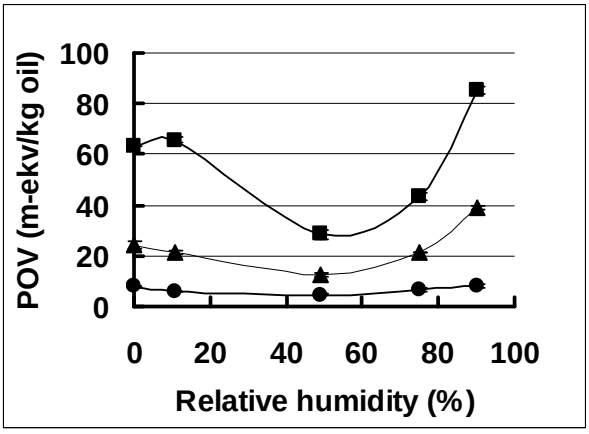

Figure 2. Peroxide value of flaxseed oil (error bars showing standard deviation) as a function of relative humidity in storage at 37 °C (●2 weeks; ▲4 weeks; ■ 6 weeks).

The potential of whey protein isolate matrix in increasing oxidative stability of flaxseed oil was studied as a function of relative humidity. Peroxide values of encapsulated oils (figure 3) were systematically lower than those of bulk oil (figure 2). Similar trend in respect to the effect of relative humidity was found. The rate of oxidation was highest at low (RH 0%) and high (RH 90%) humidity ends, whereas the samples, which were stored at intermediate humidities (RH 49% and RH 75%) were relatively stable for the time period of the study. Earlier, the effect of RH on oxidation of sensitive oils has been mostly studied in carbohydrate matrices. In our earlier studies with carbohydrate matrices (Partanen et al . 2005) suggested, that oil would be most stable, when the matrix is in glassy state. Water acts as a plasticiser for hydrophilic macromolecules, and has also been suggested to increase the solubility of oxygen in carbohydrate matrices (Whitcomb et al. 2005). Oxidative stability of oil in protein matrix seems to differ significantly from that in carbohydrate matrix. Rapid oxidation in the system, where little water was present (RH 0%) suggest, that solubility of oxygen may not be similarly rate limiting in protein as in carbohydrate matrix.

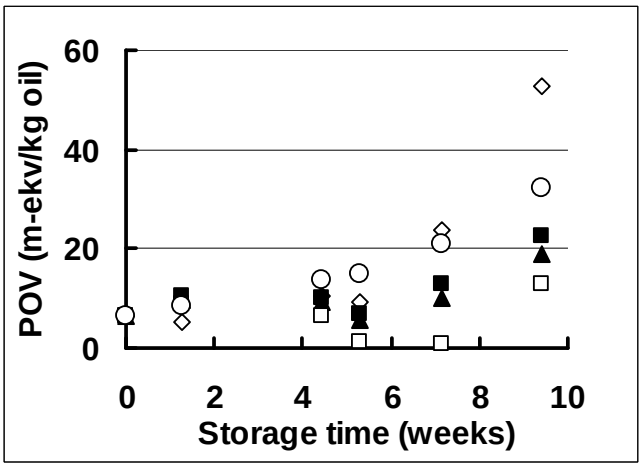

Figure 3. Peroxide values flaxseed oil in whey protein isolate matrix in 37°C storage at different RHs: ◊ RH 0%; ■RH 11%; ▲RH 49%; □ RH 75%; ○ RH 90%.

Conclusions

After spray-drying of whey protein isolate-flaxseed oil emulsion particles, protein-coated oil droplets were still identified. Oxidation in protein matrix followed the same dependence of humidity that was found for bulk oil. This result is especially interesting, since it differs from the results found earlier for carbohydrate matrices. They are typically good oxygen barriers at low humidity but lose the barrier properties with water plasticisation close to glass transition. The enhanced stability of flaxseed oil in protein matrix at intermediate humidity remains to be confirmed by fatty acid analysis in the future.

References

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