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New insights into the microencapsulation properties of milk proteins

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INTRODUCTION AND OBJECTIVES

Milk proteins are commonly used for microencapsulation of food ingredients, e.g. fish oil, olive oil, high linoleic sunflower oil, polyphenols or flavor compounds. Despite their allergenic potential they have unique properties, which cannot be easily replaced by other capsule matrix constitutents. Sodium caseinate is therefore an integral part in innovative encapsulation formulations like water-in-oil-in-water double emulsions (O'Regan, et al., 2010) formulations with retarded release of the encapsulated material containing glycated caseinate (Chung, et al., 2008) or transglutaminase-crosslinked caseinate-based hydrogel particles for the encapsulation of microalgal oil (Bao, et al., 2010).

Surprisingly little information on the impact of milk proteins on the physical structure of microcapsules and stability of encapsulated functional ingredients ara available. Aim of the present study therefore was to analyse relevant physical characteristics of emulsions, spray dried carrier matrices based on sodium caseinate and casein hydrolysate and microcapsules as well as the impact on the stability of a microencapsulated functional ingredient.

MATERIALS AND METHODS

Spray-drying of carrier matrix particles and preparation of microcapsules was performed on a Niro Mobile Minor (Niro A/S, Denmark) equipped with a rotating disk operated at 180/70 °C inlet and outlet temperature, respectively. For the preparation of spray-dried carrier matrix particles a solution of protein (sodium caseinate, hydrolysed casein) and glucose syrup was spray-dried. For microencapsulation of fish oil an emulsion was prepared. A coarse emulsion was prepared at 50 bar in a high-pressure homogenizer (Panda 2K, Niro Soavi Deutschland, Lübeck, Germany), which was subsequently homogenized at 200/50 bar with two passes.

Physical characterisation of spray-dried carrier matrix particles and microcapsules

True density of the spray-dried carrier matrix particles was determined using a helium pycnometer. Analysis of the surface composition of spray-dried carrier matrix particles by X-ray photoelectron spectroscopy (XPS). Free volume elements were analysed using positron annihilation lifetime spectroscopy (PALS). Extractable fat was measured gravimetrically after extraction with petrol ether.

Determination of the surface/interfacial elasticity by oscillating drop tensiometry

The surface dilatational modulus was determined using a video-based contact angle meter. The method involved an automatically controlled sinusoidal dosing of a defined volume of the sample solution providing a sinusoidal interfacial compression and expansion. The amplitude was 0.2, the frequency 0.1 Hz. The phase angle, the surface dilatational modulus, the elastic modulus E' and the viscous modulus E'' were determined at the air water-interface, interfacial elasticity was analysed after immersion of the droplet in MCT oil to simulate the oil-water interface.

Determination of the hydroperoxide content of micro-encapsulated fish oil

To monitor the stability of microencapsulated fish oil samples were stored in desiccators over a saturated solution of magnesium chloride. Relative humidity amounted to 33 % and the storage temperature was 20 °C. The hydroperoxide content was analysed every week for a period of 56 days. Prior to analysis the oil was extracted from the microcapsules after reconstitution with water using a blend of 2-propanol/isooctane (50/50). Hydroperoxide concentration was determined using the IDF standard method 74A:1991 for the determination of the peroxide value in anhydrous milk fat with slight modifications (International Dairy Federation, 1991).

RESULTS AND DISCUSSION

True density of spray-dried carrier matrix particles decreased with increasing content of sodium caseinate. Structural differences were also observed in the ortho-positronium lifetime ($\tau_{o\text{-}Ps}$), which correlates with size of the free volume elements in a polymer matrix. Protein-free spray-dried glucose syrup had an average $\tau_{o\text{-}Ps}$ of 1.26 ns. With increasing sodium caseinate content $\tau_{o\text{-}Ps}$ increased to 1.33 and 1.47 ns for spray-dried carrier matrix particles containing 1.25 and 5 % protein, respectively. With 1.37 and 1.50 ns a similar increase was observed for spray dried carrier matrix particles containing hydrolysed casein at the same content. An increase of $\tau_{o\text{-}Ps}$ is associated with an increase in the size of free volume elements, which may facilitate autoxidation of the encapsulated core material.

XPS revealed that the surface coverage with protein of spray-dried carrier matrix particles increased with increasing protein content in the formulation. The surface coverage was always higher in particles containing hy-

drolysed casein compared with particles containing sodium caseinate.

Interfacial rheology provides information on the adsorption of surface-active compounds to the interface, interactions between the adsorbed molecules and film compactness at the interface (Girardet, et al., 2000) and is thus a suitable parameter to characterise the stability of the emulsion during the process of spray-drying. The surface dilatational modulus for sodium caseinate solutions at the air/water interface amounted to 10 mN/m, irrespectively from the protein content. The low surface dilatational modulus observed for sodium caseinate in the present study therefore indicates that integrity of the film is preserved upon interfacial strain, remains intact and no diffusion of sodium caseinate from the bulk phase occurs. Since no differences between samples with varying content of sodium caseinate were observed, it can be concluded that the surface was completely covered with protein. In contrast, the surface dilatational modulus for solutions of casein hydrolysate decreased with increasing protein content from 48 to 27 mN/m.

In the present study, for sodium caseinate and hydrolysed casein at low protein content an increase in surface dilatational modulus at the oil/water interface compared to the air/water interface was observed. Interfacial stress is increased, since the interface is increased against the tension resulting from the incompatibility of a polar droplet and the non-polar bulk phase with a high viscosity.

The microencapsulation efficiency was generally high, when sodium caseinate was used as emulsifying carrier matrix constituent. The microencapsulation efficiency ranged from 97.4 to 99.5% at a protein content of 0.25 and 5% of the oil-free total solids content, respectively. Although the surface accumulation of casein hydrolysate in spray-dried carrier matrix particles was higher compared to sodium caseinate, the microencapsulation efficiency in spray-dried emulsions was always lower when using casein hydrolysate as emulsifier compared to the corresponding samples containing sodium caseinate.

The oxidative stability of the microencapsulated fish oil decreased with an increasing content of sodium caseinate in the carrier matrix. Based on the physical characterization of spray-dried carrier matrix particles in the present study it can be concluded that excess high molecular weight constituents affect oxygen permeability through the bulk carrier matrix and thus facilitate lipid oxidation. Since proteins accumulate at the interfaces and multiple layers build up through hydrophobic interactions it can be assumed that the distribution of the free volume elements is not homogeneous throughout the particle.

Lipid oxidation was faster in microcapsules containing hydrolysed casein compared to sodium caseinate containing microcapsules. It is postulated that the stability is only affected, when rupture of the interfacial membrane surrounding the oil droplets and oil droplet coalescence occurs. In the present study the high viscoelastic modulus of the interface stabilized with hydrolysed caseins indicates that rupture upon interfacial strain is more likely compared to caseinate-stabilised film, and thus the solvent-extractable oil is not encapsulated and more prone to autoxidation.

CONCLUSIONS

In conclusion, in the present study the impact of physical phenomena on the stability of a lipophilic ingredient encapsulated in protein-containing matrices has been investigated. For the first time, data on the impact of excess protein on the physical structure on a sub-micron-scale of microcapsules obtained/prepared by spray-drying have been reported. Excess protein negatively affects free volume elements and, thus, oxygen diffusion. Surface accumulation of proteins at the air-water interface leads to a modified surface composition, which is beneficial for certain applications. In case of lipophilic ingredients, interfacial rheological characteristics need to be taken into consideration to maintain the emulsion structure throughout the drying process and to minimize non-encapsulated oil.

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