Spray drying behaviour and functionality of beta-lactoglobulin-/pectin-stabilized oil-in-water emulsions

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Abstract

Aim of the present study was to investigate the impact of atomization and drying on the functionality of emulsions with an oil/water-interface (o/w-interface) consisting of beta-lactoglobulin (single layer emulsion) and sequentially adsorbed pectins with varying degree of methylation at pH<pI (bilayer emulsions). Thus, the emulsion systems were characterized with respect to their behavior during atomization, their drying behavior in single droplet experiments and the oxidative stability of the dispersed phase (fish oil) during storage of liquid and spray-dried single and bilayer emulsions.

The o/w-interface of the emulsions was predominantly elastic, although the elasticity was higher in single layer emulsions compared to bilayer emulsions. The drying behavior of the different emulsions during levitation of single droplets was similar. Regarding the atomization process, the emulsion spray droplet size generally decreased with increasing energy input irrespective of the type of atomizer. With rotary atomization, the spray droplet size distribution of the different emulsions was similar. The oxidative stability of the oil was influenced by both the physical state of the emulsions and the different constituents at the o/w-interface. In the liquid state, the oxidative stability was higher in the original emulsions when compared to the reconstituted emulsions. The differences in oxidative stability in the spray-dried emulsions can partly be attributed to the microencapsulation efficiency, but also the physical characteristics of the o/w-interface, which needs to be investigated in more detail.

Introduction

During microencapsulation of sensitive (food) ingredients by spray drying, one important step is the spray drying process itself, which affects the emulsion droplet size distribution, the emulsion stability with regard to the oil droplet size as well as the structural integrity of the interface. The latter has a strong impact on the encapsulation efficiency and the physical stability of reconstituted emulsions. By interfacial engineering the barrier properties and the packing density at the oil/water (o/w) interface can be modified. The interface can be engineered by e.g. layer-by-layer electrostatic deposition technique that involves sequential layering of polymers at the o/w-interface of an emulsion. By that means so-called bilayer or multilayer emulsions can be obtained. However, studies on the characterization of layer-by-layer emulsions in relation to the spray drying process, especially with respect to the type of atomization and the drying behavior are lacking and literature on the oxidative stability of spray-dried multilayer emulsions is scarce.

Aim of the present study was to investigate the impact of atomization and drying on the functionality of emulsions with an o/w interface consisting of beta-lactoglobulin and sequentially adsorbed pectins with varying degree of methylation at pH<pI. The approach described by Serfert et al. [1] for the bilayer system lecithin-chitosan was used to characterize the emulsion systems of the present study in terms of atomization, single droplet drying and oxidative stability during storage of liquid, reconstituted and spray-dried single and bilayer emulsions.

Experimental Approach

Beta-lactoglobulin (bLG; 89.6% purity, Davisco Foods International, Inc., USA), low (38%) methylated pectin (LMP) and high (71%) methylated pectin (HMP; Herbstreith & Fox KG, Germany) were used for the preparation of single and bilayer-emulsions containing 5wt% fish oil (Cognis Deutschland GmbH, Germany) at pH 4.0 with 0.1 m acetic acid buffer. bLG and pectin content were set at 0.25 and 0.2wt%, respectively. Electrostatic interactions between the oppositely charged protein and polyelectrolytes were analyzed via zeta potential measurements by applying the Smoluchowski model (Zetasizer Nano-ZS, Malvern Instruments GmbH, Germany). Interfacial elasticity of the a/w-interface was analyzed at an amplitude of 0.1mm and 10^{-2} to 10^{0} Hz by a

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contact angle meter (OCA-20, Dataphysics Instruments GmbH, Germany). The single droplet drying behavior was characterized by acoustic levitation at 80°C in a custom made acoustic levitator as described elsewhere [1]. Spray droplet and oil droplet size distribution were measured by laser diffraction (Spraytec, Malvern Instruments GmbH) after two-fluid-nozzle (Niro A/S, Denmark) and rotary atomization (SL24-50/M) at different energy inputs. Spray drying was carried out at 180/70 °C inlet/outlet temperature (Mobile Minor 2000, Niro A/S). The particle size was determined after dispersing an aliquot of the powder in an inert oil (MCT oil, Gustav Hees Oleochemische Erzeugnisse GmbH, Stuttgart, Germany) by laser diffraction. The morphology of the particles was analyzed by scanning electron microscopy (CamScan 44 REM/EDX; CamScan USA Inc, USA). The oxidative stability of the fish oil was monitored via hydroperoxide and propanal content [2].

Results and Discussion

Characterization of liquid emulsions

The zeta potential of the single layer emulsion was +35.5 mV. The addition of pectin induced a charge reversal as the pectin concentration was increased from 0 to 0.35wt%. Above a pectin concentration of 0.2wt% the zeta potential was almost constant at -17.3 and -30.0 mV for the bLG-HMP and the bLG-LMP bilayer emulsion, respectively, which can be attributed to saturation of the interface with pectin. The single layer emulsion had a viscosity of 39 mPa·s, whereas the viscosities of the bilayer emulsions increased to 66 and 59 mPa·s after addition of HMP and LMP pectin, respectively.

In general, the surface dilational modulus E^* of the air-water-interface increased with increasing frequency in all emulsions. At all frequencies, E^* was lower in the bLG-pectin bilayer emulsions compared to the bLG-single layer emulsion. Distinct differences occurred according to the type of pectin. For instance, at $f = 10^{-1}$ Hz, E^* of the HMP and LMP bilayer emulsion was 32.4 and 10.1 mN m^{-1}, respectively, whereas in the single layer emulsion E^* amounted to 45.7 mN m^{-1} (Table 1). In all emulsions, the real part E' of the modulus was several times higher than the imaginary part E'' which indicates the predominantly elastic character of the interface. At 0.1 Hz, the phase angels were the same for the bLG-single layer and bLG-LMP bilayer emulsion (10.6°), in the bLG-HMP bilayer emulsion, the phase angle was slightly higher (14.6°).

Table 1 Mean value of the viscoelastic properties at the air-water interface of the single and bilayer emulsions at an amplitude of 0.1 mm and different frequency f

Frequency f [Hz]	interfacial dilational modulus E^* [mN m^{-1}]			real part E' [mN m^{-1}]			imaginary part E'' [mN m^{-1}]		
	bLG	bLG/HMP	bLG/LMP	bLG	bLG/HMP	bLG/LMP	bLG	bLG/HMP	bLG/LMP
10^{-2}	37.0	27.1	8.1	36.2	26.3	7.9	8.4	6.5	1.6
10^{-1}	45.7	32.4	10.1	44.9	31.3	9.9	8.3	8.2	1.8
10^{0}	52.4	38.4	10.6	51.8	37.5	10.4	7.3	8.4	1.6

With regard to the atomization process, the emulsion spray droplet size generally decreased with increasing energy input irrespective of the type of atomizer (Figure 1). In two-fluid nozzle atomization but not in rotary atomization, the spray droplet size distribution was markedly influenced by differences in emulsion viscosity. Furthermore, the spray droplet size distribution was narrower with rotary atomization compared with two-fluid nozzle atomization. As a narrow particle size distribution induces a better overall drying performance [3], the emulsions used for microencapsulation of fish oil were spray-dried by rotary atomization.

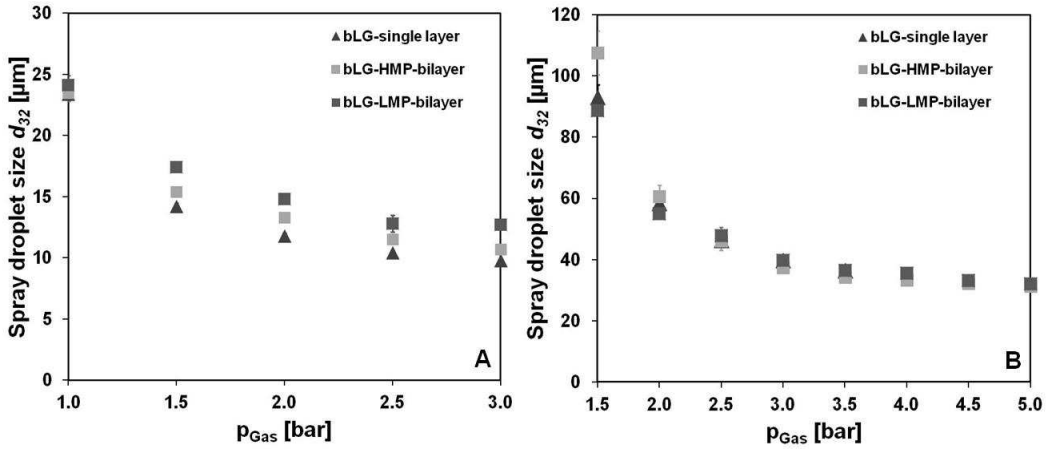

Figure 1 Spray droplet size of the single and bilayer emulsions during atomization at different energy inputs by two-fluid nozzle (A) and rotary atomizer (B)

During atomization, the oil droplet size of the emulsions was only slightly affected by the different energy inputs. However, in the reconstituted state, the oil droplet sizes were slightly higher than in the original emulsions (data not shown), which can be attributed to coalescence during droplet shrinkage in the drying process. The drying behavior of the differently stabilized emulsions measured as volume transfer density during levitation of a single droplet was similar (Figure 2).

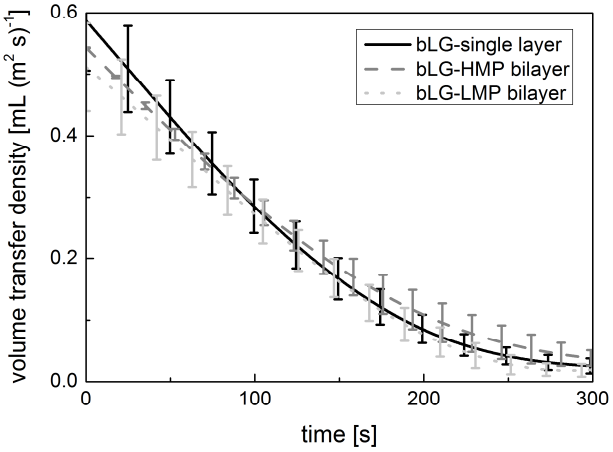

Figure 2 Mass flow transfer of a levitating single droplet of the single and bilayer emulsions at 80 °C

Characterization of spray-dried emulsions

The particle sizes (d_{32}) of the spray-dried emulsions varied between 9.46 µm for the bLG-HMP bilayer emulsion and 10.14 µm for the bLG-LMP bilayer emulsion. Regarding the surface morphology, no differences could be observed between the single and bilayer emulsions (Figure 3). The extractable oil content of the bLG-single layer emulsion amounted to 5.6%. In the bilayer emulsions, the amount of extractable oil was 4.1 and 1.5% when stabilized by bLG-HMP and bLG-LMP, respectively.

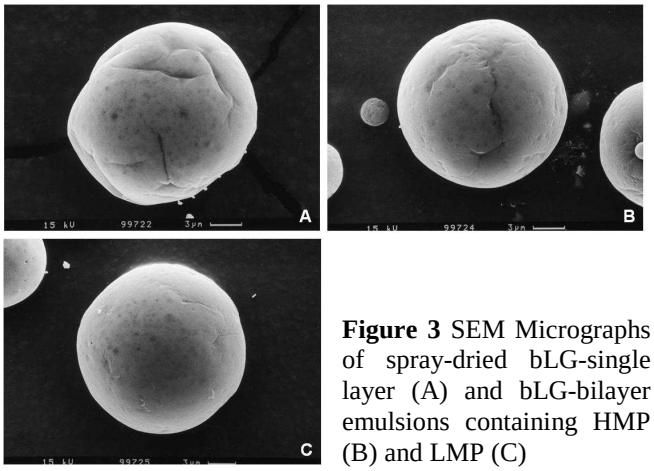

Figure 3 SEM Micrographs of spray-dried bLG-single layer (A) and bLG-bilayer emulsions containing HMP (B) and LMP (C)

Oxidative stability of liquid and spray-dried emulsions

With respect to lipid oxidation, the oxidative stability of the oil was influenced by both the physical state of the emulsions and the different constituents at the o/w-interface. In the liquid state, the oxidative stability was higher in the emulsions when compared to the reconstituted emulsions, i.e. the spray-dried emulsions after dissolution in water (Figure 4). Moreover, the hydroperoxide content was higher in the single layer emulsion containing positively charged oil droplets than in the bilayer emulsions with negatively charged oil droplets dependent of the type of pectin involved.

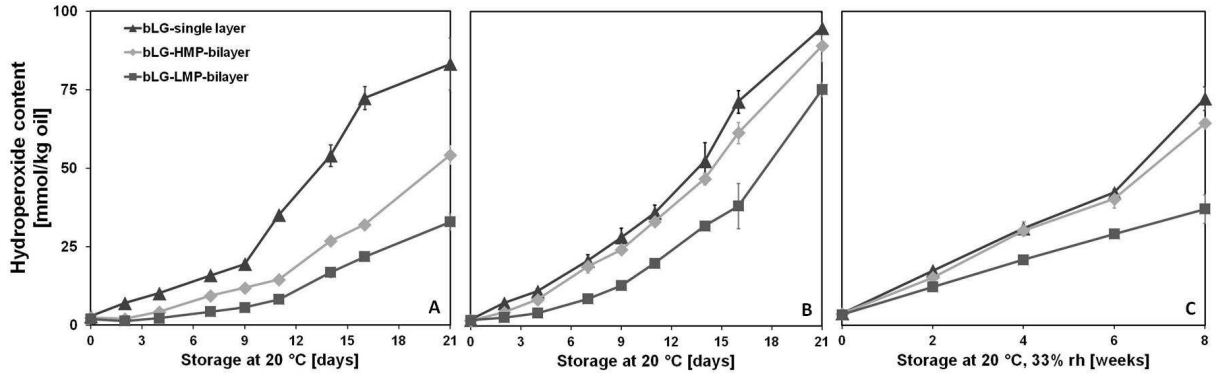

Figure 4 Development of the hydroperoxide content during storage of liquid (left), reconstituted liquid (center) and spray-dried (right) single and bilayer emulsions during storage

Regarding the surface charge of an emulsion and its oxidative stability, a similar observation was reported by [4] for fish oil in bLG and bLG-pectin stabilized single and bilayer emulsions. They presumed that the interfacial membrane in the bilayer emulsion consisting of b-lactoglobulin and pectin was thicker than the interface of the single layer emulsion consisting solely of b-lactoglobulin. By that means metal-lipid interactions would be inhibited. They also assumed the iron binding capacity of pectin to be responsible for their observation. Recently, Chen et al. [5] showed that the iron-binding capacity of low methylated pectin (degree of esterification: 37%) was higher than in the high methylated pectin (degree of esterification: 70%) presumably due to a higher level of acid groups in LMP, whereas no differences in radical-scavenging ability between the pectins could be measured. The authors also investigated the role of continuous phase pectins (0.02 to 0.1wt%) in Brij 35-stabilized fish oil emulsions. The non-ionic emulsifier was chosen to avoid electrostatic interactions between the pectins and the emulsifier. As observed in the present study, the oxidative stability was lower in emulsions with HMP than with LMP in the concentration range studied [5].

In the spray-dried emulsions, the hydroperoxide content was similar in the spray-dried bLG-single layer and the spray-dried bLG-HMP bilayer emulsion (Figure 4). At the end of the storage period, the hydroperoxide content amounted to 72.3 and 64.4 mmol/kg oil in the single layer and the bLG-HMP bilayer emulsion, respectively. In contrast, the highest oxidative stability was observed in the bLG-LMP bilayer emulsion with 37.1 mmol/kg oil after 8 weeks of storage. Data from headspace-gas chromatography measurements were not viable probably due to protein-aldehyde interactions, which impair the analysis of secondary lipid oxidation products.

It is generally accepted that microencapsulation efficiency is a crucial point in terms of stability of the spray-dried emulsion and is partly responsible for the differences in oxidative stability in the present study. However, Drusch and Berg [6] have shown that in case of a high microencapsulation efficiency other parameters like the oil droplet distribution need to be taken into consideration. In the present study the microencapsulation efficiency is above 95 % in all samples. A shift in oil droplet size after drying of the emulsion occurred, which is related to oil droplet coalescence during processing and which affects the encapsulation efficiency. This conclusion is supported by the data on the interfacial elasticity, where distinct differences between the samples with relevance for the physical stability occurred. However, the thickness of the interfacial layer, its contribution to steric stabilisation of the oil droplets during shrinkage of the emulsion droplet during spray-drying and the effect on the barrier properties of the interfacial layer need to be investigated to further elucidate the differences observed for pectins with varying degree of esterification.

Summary and Conclusions

The present study provides new insights in the characterization of beta-lactoglobulin based single and bilayer emulsions with regard to the spray drying process and the functionality of spray-dried emulsion particles. Droplet size after atomization was affected by atomization conditions, but only to a limited extent by emulsion composition. Volume transfer densities were similar for all samples indicating a similar drying behavior of single layer emulsions and bilayer emulsions. Microencapsulation efficiency in all samples was high and ranged from 95 to 99%. However, a shift in oil droplet size as well as corresponding data from interfacial elasticity measurement indicate that oil droplet coalescence occurred within the process. The oxidative stability differed between the single layer emulsion and the bilayer emulsions, which can partly be attributed to the microencapsulation efficiency, but also the physical characteristics of the o/w-interface, which needs to be investigated in more detail.

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References

[1] Serfert, Y. et al., *Journal of Microencapsulation*, in revision process (2012).
[2] Serfert, Y., Drusch, S., Schwarz, K., *Food Chemistry* 113: 1106-1112 (2009).
[3] Huang, L.X., Kumar, K., Mujumdar, A.S., *Chemical Engineering and Processing* 45: 461-470 (2006).
[4] Katsuda, M.S. et al., *Journal of Agricultural and Food Chemistry* 56: 5926-5931 (2008).
[5] Chen, B., McClements, D.J., Decker, E.A., *Journal of Agricultural and Food Chemistry* 58: 3779-3784 (2010).
[6] Drusch, S., Berg, S., *Food Chemistry* 109: 17-24 (2008).