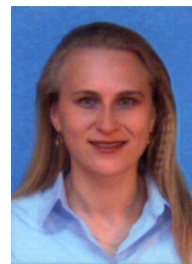


Aroma retention and flavour release of model flavours spray-dried in modified starches

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Introduction

The encapsulation of active components in powder has become a very attractive process in last decades, and the encapsulation of flavour ingredients is among the most important applications in food industry. The main purposes of microencapsulation is entrap sensitive ingredients, such as volatile and labile flavours, into solid carriers to increase their protection, reduce evaporation, promote easier handling and control their release during storage and application. Spray-drying emulsions are particularly simple and economically effective means of microencapsulating chemically reactive volatile oils and aroma compounds (Pegg et al., 1999; Gouin, 2004; Reineccius, 2006).

The main goal of this study was to investigate the effect of different commercial modified food starch carrier materials on the model flavours system retention during spray-drying encapsulation. The following objectives were considered as an important task in achieving this goal: (i) to determine the emulsification efficiency, retention of model aroma compounds and evaluate the efficiency of microencapsulation; (ii) to assess the changes in the composition of model flavours taking place during processing; and (iii) to assess the release of volatiles from different modified starch matrices by dynamic headspace gas chromatography analysis.

Material and methods

Materials. Five aroma components, benzaldehyde, limonene, 1,8-cineole, linalool, and geranyl acetate, were combined into one model mixture at equal parts by weight (20% w/w) and used as core material. The following modified food starches matrices were used as encapsulating agents: chemically *n*-octenyl succinic anhydride (OSAN)-modified starches HI-CAP 100 (refined from waxy maize), N-LOK (starch with corn syrup added), CAPSUL (derived from waxy maize), and the acid and/or enzyme hydrolysed starches (dextrins) ENCAPSUL 855 (refined from tapioca and maize starch) and CRYSTAL TEX 627 (refined from tapioca starch) were obtained as a gift from National Starch Group; OSAN starches CIEmCap 12633 (stabilized and acid-thinned instant waxy maize starch), CIEmCap 12634 (spray-dried waxy maize starch ester) and CIEmCap 12635 (stabilized and acid-thinned instant waxy maize starch) – were kindly supplied by Cerestar.

Preparation of microencapsulated flavours. The solutions of coating matrices (30% w/w) were prepared by dispersing dried powders in 40°C deionized water; after cooling were mixed overnight to enhance hydration. Model flavours (15% w/w of matrix solids) was emulsified into the hydrated coating material. Homogenization was accomplished by Ultra Turrax Ika 25 homogenizer (Janke & Kunkel GmbH&Co, Germany) operating at 13500 rpm for 7 min. Emulsions were spray-dried in a Büchi 190 Mini Spray Dryer (Donau, Switzerland) under the following parameters: spray nozzle (inlet) temperature 200±10°C, outlet air temperature 120±10°C, pressure – 400 mm/H₂O.

Total and surface oil determination. Total oil content of the liquid emulsions and spray-dried microencapsulated products were determined in duplicate by distilling 10 g of liquid emulsion or encapsulated powder for 3 h in a Clevenger-type apparatus (AOAC). The volume of model flavour system collected in the trap was multiplied by a density factor 0.91 g/mL to calculate the weight of oil recovered from the sample. Surface oil was being washed from 10 g of spray-dried encapsulated powder for 4 h in a Soxhlet extraction apparatus by using pentane. One mL of pentane containing IS, decane 0.3% (v/v) was added prior extraction; each extract was concentrated to ~2 mL at room temperature under a stream of nitrogen. The compositions of pure, total, isolated from emulsions, processed products and surface (non entrapped into matrices) oils were analysed by GC, GC-MS.

Release of volatiles by dynamic headspace gas chromatography (DHS-GC-FID). 5 g of each spray-dried encapsulated model flavours powder, with surface oil removed was placed into a 125 mL sample flask. The flask was placed in water bath of 25°C temperature; the glass tops were connected to nitrogen. 1 min preflush was used to remove the volatiles

accumulated in the gas phase. Then sample was purged with the nitrogen at a flow of 400 mL min⁻¹ to recover the volatiles accumulated in the headspace during the timed interval. The volatiles trapped on 0.5 g Tenax, TA 35/60 mesh were desorbed by 15 mL of diethyl ether. Tubings were changed every 10 min. The total purge time was 100 min. After adding 1 mL IS (decane in diethyl ether 0.3 % v/v) to the desorbed volatiles, they were evaporated to a final volume of 1 mL under a stream of nitrogen and analysed by GC and GC-MS. Two replicates were carried out for each sample.

GC. Diluted in pentane pure model flavours, samples of retained after spray-drying total and surface oils (10 µL in 1 mL) were analysed on a *Fisons 8000* series GC equipped with a flame ionization detector (FID) and a DB-5 fused silica capillary column (polydimethylsiloxane, 5% phenyl, 50 m length, 0.32 mm i.d., 0.25 µm film thickness). The carrier gas was helium at a linear flow velocity of 43 cm s⁻¹ at 50 °C; the detector's temperature was 320 °C, the oven temperature was programmed from 50 °C (2 min) to 280 °C (10 min) at the ratio of 5 °C min⁻¹. A split/splitless injector was used at 260 °C in split mode at a ratio of 1:5, the injection volume was 1 µL. The content of eluted compounds was expressed as GC peak area percent; mean values were calculated from quadruplicate injections. The coefficient of variation is defined as the ratio of corresponding standard deviation (%RSD) to the average value from 4 replicate injections.

The model flavours trapped on Tenax tubes and then desorbed by thermal desorption device were directed through a heated transfer line to injection port of a Shimadzu GC-2010 series gas chromatograph equipped with a flame ionization detector (FID) and FS-SE-54-CB-0.5 fused silica capillary column (50 m length, 0.25 mm i.d., 0.5 µm film thickness). The carrier gas was nitrogen at a linear flow velocity of 29 cm s⁻¹ at 50°C; the detectors temperature was 300°C, the oven temperature was programmed from 50°C (2 min) to 230°C at the ratio of 10°C min⁻¹. A split/splitless injector was used at 280°C in split mode at ratio of 1:5, the injection volume was 1µL.

GC-MS. GC-MS analyses were performed using a *Perkin Elmer Clarus 500* GC coupled to a *Perkin Elmer Clarus 500* series mass selective detector in the electron impact ionization mode at 70eV, the mass range was *m/z* 29-550. Volatile compounds were separated using an Elite – 5 MS capillary column (dimethylpolysiloxane, 5% diphenyl, 30 m length, 0.25 mm i.d., 0.25 µm film thickness). The oven temperature was programmed from 50 °C (for 2 min) to 280 °C (hold 10 min) at the ratio of 5 °C min⁻¹. Carrier gas, helium, adjusted to a linear velocity of 36.2 cm s⁻¹ at 50 °C. Split mode was used at ratio of 1:20 and an injector temperature of 250 °C.

The components were identified by comparison their Kovats retention indexes (KI) related to C₅-C₁₈ *n*-alkanes obtained on nonpolar column with those provided in the literature (Adams, 2001) and by comparison of their mass spectra with the data provided by the NIST mass spectral library.

Statistical analysis. Data were statistically handled by one-way analysis of variance (ANOVA, vers. 2.2., 1999). Duncan's multiple-range test was applied for the calculation of the significant differences among the microencapsulated into different wall materials model flavour system products, at the probability level *P*=0.05.

Results and discussion

Properties of liquid emulsion and spray-dried microencapsulated products. Total oil content in liquid homogenized model flavour system emulsion ranged from 13.46 g 100g⁻¹ for ENCAPSUL 855-emulsified product to 14.73 g 100g⁻¹ for N-LOK, CIEmCap 12634 and 12635-emulsified products (Table 1). Emulsification efficiency of model flavours in the liquid emulsions varied from 89.71% (ENCAPSUL 855) to 98.71% (CIEmCap 12635). There were no statistical differences in emulsification efficiency of oil in liquid emulsions at *P*=0.05 almost for all modified starches. It mostly depends to the emulsification properties of matrix and its tendency to form films at the interfaces between the emulsion phases; this is in agreement that maltodextrins usually lack the emulsification efficiency (Pegg et al., 1999). The high volatility and solubility of flavours might also lead a higher loss of flavours during spray-drying (Soottitantawat et al., 2003).

The total oil content of the spray-dried model flavours products were statistically different at *P*=0.05 and ranged from 8.85 g 100g⁻¹ (ENCAPSUL 855) to 14.24 g 100g⁻¹ (CAPSUL) (Table 1). The lowest ability to retain model flavours was obtained for both dextrans matrices in our study. The literature show that maltodextrins do not perform excellent in volatiles retention. It was reported that maltodextrins retain aroma compounds well that are water soluble or soluble at their use level; the poor retention of insoluble aroma compounds by maltodextrins relates to their lack of emulsification properties (Reineccius et al., 2003).

The content of oil remained on the surface of the spray-dried powder is important factor for storage stability, because surface oil can be easily oxidized and form unacceptable off-flavour compounds.

The content of surface oil on the spray-dried microencapsulated model flavours products powder particles varied from 0.12 g 100 g⁻¹ for N-LOK to 0.30 g 100 g⁻¹ for ENCAPSUL 855 encapsulated products. The moisture content of spray-dried microencapsulated model flavours products ranged from 1.20 mL 100 g⁻¹ (CIEmCap 12634) to 3.13 mL 100 g⁻¹ (CAPSUL) (Table 1).

Table 1. Properties of liquid emulsion and spray-dried microencapsulated model flavours products

	HI-CAP 100	N-LOK	CAPSUL	ENC 855	CR TEX 627	CIEmCa p 12633	CIEmCa p 12634	CIEmCa p 12635
	liquid microencapsulated product							
total oil content, g 100 g ⁻¹	13.86 ^{abc}	14.73 ^{cd}	14.49 ^{abc}	13.46 ^a	14.17 ^{abc}	14.57 ^{abc}	14.73 ^{bc}	14.81 ^c
emulsification efficiency, %	92.38 ^{ab}	98.18 ^{cde}	96.60 ^{cde}	89.74 ^a	94.49 ^{bc}	97.13 ^{cde}	98.18 ^{cde}	98.71 ^c
	spray-dried microencapsulated product							
total oil content, g 100 g ⁻¹	12.88 ^b	12.40 ^f	14.24 ^{cd}	8.85 ^a	10.41 ^c	13.97 ^{cd}	12.87 ^b	13.71 ^d
surface oil content, g 100 g ⁻¹	0.15 ^{bc}	0.12 ^a	0.14 ^{ab}	0.30 ^f	0.19 ^d	0.14 ^{ab}	0.17 ^{cd}	0.22 ^e
encapsulation efficiency, %	84.84 ^{bc}	81.89 ^b	94.0 ^e	56.98 ^a	70.68 ^f	92.26 ^{cde}	84.73 ^{bc}	89.91 ^{cde}
moisture, mL 100 g ⁻¹	1.28 ^a	2.75 ^{bcd}	3.13 ^d	2.21 ^{bcd}	2.09 ^{ab}	2.68 ^{bcd}	1.20 ^a	2.54 ^{bcd}

* Computed on the basis of a theoretical oil content of 15 % of the solids. ^{a-c} Values within rows followed by the same letter do not differ statistically at $P=0.05$.

Effectiveness of microencapsulation of model flavours via spray-drying into different carbohydrate-based matrices varied from 56.98% (ENCAPSUL 855) to 94.0% (CAPSUL), and there were statistical differences at $P=0.05$ between different encapsulated flavour products. Maltodextrins do not perform well in volatile retention, mostly to the lack of their emulsification properties (Pegg et al., 1999; Reineccius et al., 2003). Encapsulating modified starches involve the addition of lipophilic groups. It was reported that both of CAPSUL and HI-CAP 100, which were derived from waxy maize base, were modified with n-octenyl succinic anhydride (OSA) for using in the flavour encapsulation process; HI-CAP 100 is blended with high DE corn syrup solids with the final of 32-37 DE and designed for the high load encapsulation agent (Soottitawat et al., 2005).

The compositions of pure, emulsified and encapsulated in different starches based matrices model flavours system were quite similar, however some changes in the percentages of some individual compounds were observed. More remarkable differences in the compositions of surface oils from various encapsulation products were determined. This phenomenon could be explained by the losses of more volatile hydrophobic compounds not entrapped in the capsules and consequently not protected from evaporation. In general, the highest molecular weight aroma compound geranyl acetate showed the lowest losses after spray-drying; while, the lower molecular weight flavour compound benzaldehyde showed significant losses after processing. It could be explained that low molecular weight compounds has the greater ability to diffuse through the matrice during drying (Goubet et al., 1998).

Flavour Release of model flavour system volatiles by DHS--GC-FID. The recovery of model system volatiles that were released into the headspace of each of the spray-dried microencapsulated products (surface oil removed) was determined as a function of nitrogen purge time up to 100 min. The obtained results indicate that components were released at different rates by each of encapsulated products (Fig. 1). The most intensive permeability of volatiles from encapsulated products was observed during first 20 min of purge treatment and then appropriate slopes of volatiles were indicated in all matrices tested. The total amount of model system volatiles during 10 min of purge treatment was released at concentrations ranging from 9.3 ng g⁻¹ by CIEmCap 12634 to 50.5 ng g⁻¹ by HI-CAP 100 microencapsulated model system flavours products. The total amount of model flavours during 100 min of purge treatment ranged from 49.6 ng g⁻¹ (CIEmCap 12634) to 278.1 ng g⁻¹ (HI-CAP 100). The range of concentrations of benzaldehyde during 100 min purge time was obtained from 18.8 ng g⁻¹ (HI-CAP 100) to 28.5 ng g⁻¹ (CRYSTAL TEX 627). Limonene during purge treatment was released from 6.9 ng g⁻¹ (CAPSUL) to 24.0 ng g⁻¹ (HI-CAP 100). The

amount of released 1,8-cineole varied from 5.9 ng g⁻¹ (CIEmCap 12633, 12634) to 60.4 ng g⁻¹ (HI-CAP 100). The range of concentration of linalool during 100 min purge treatment was from 7.3 ng g⁻¹ (CIEmCap 12634) to 109.1 ng g⁻¹ ((HI CAP 100). Neryl acetate during purge time was released at concentrations ranging from 1.5 ng g⁻¹ (CIEmCap 12634) to 20.5 ng g⁻¹ (HI-CAP 100). The amounts of emitted geranyl acetate into the headspace above this spray-dried encapsulated product varied from 3.0 ng g⁻¹ (CIEmCap 12634) to 45.3 ng g⁻¹ (HI-CAP 100).

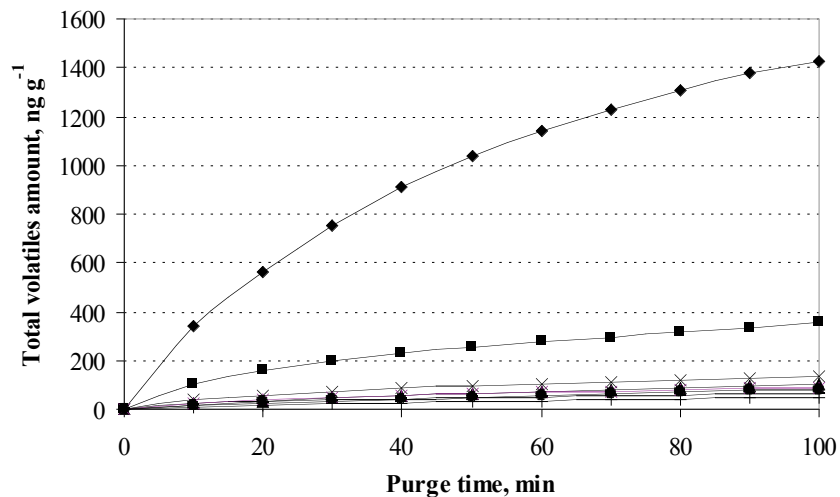


Fig.1. Amounts of total volatiles released from microencapsulated model flavour system products by DHS analysis; -◆- HI-CAP 100; -■- N-LOK; -▲- CAPSUL; -*-* CRYSTAL TEX 627; -x- ENCAPSUL 855; -●- CIEmCap 12633; -+- CIEmCap 12634; - - CIEmCap 12635

Conclusions

In general, obtained results show that the most effective to retain model flavours system volatiles was waxy maize starch ester CIEmCap 12634 and could be concluded as the least leaking matrix in our study. Quite similar results showed matrices CIEmCap 12633, CAPSUL and CIEmCap 12635 and were also very effective in flavour retention. While, the most leaking matrix was HI-CAP 100 with an exception in case of benzaldehyde.

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