Comparison of wall materials for the microencapsulation of thyme essential oil

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INTRODUCTION

The encapsulation of active components in powders has become a very useful process in the last decades, while the microencapsulation of flavour ingredients is among the most important applications for these techniques in food industry. The main purposes of microencapsulation are entrapping sensitive ingredients (e.g. hydrophobic flavours) in solid carriers to increase their protection against oxygen, water and/or light, promoting easier handling, reducing evaporation, and controlling their release. Controlled release can improve the effectiveness of food additives, to broaden the application range and to ensure optimal dosage (Gouin, 2004; Reineccius, 2006). The ability of carbohydrates to retain volatiles during drying processes makes them the most commonly used as coating materials (Jackson et al., 1991). Typical shell materials for flavour encapsulation include gum acacia, maltodextrins, hydrophobically modified starches, such as octyl-substituted starches, and mixtures thereof (Gouin, 2004).

This study was aimed to investigate the properties of several commercial food starch and milk protein based matrices for the coating of thyme essential oil by spray-drying.

MATERIAL AND METHODS

Materials. Thyme (*Thymus vulgaris*) essential oil (EO) was from Frey&Lau (Germany). Modified starches, namely 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 hydrolyzed starches (dextrins) ENCAPSUL 855 (refined from tapioca and maize starch) and CRYSTAL TEX 627 (refined from tapioca starch) were donated by National Starch Group. Skimmed milk powder (SMP) was from Belgamilk (Belgium).

Preparation of Microencapsulated Flavors. The solutions of coating matrixes (30 % w/w) were prepared by reconstituting and dispersing dried powders in 40°C deionised water; after cooling they were being mixed overnight to enhance hydration. EO (15% w/w of matrix solids) was emulsified into the hydrated coating material. Homogenization was accomplished by using Ultra Turrax basic homogenizer operating at 16000 rpm for 5 min. Emulsions were spray-dried in a Büchi 190 mini spray dryer under the following parameters: spray nozzle (inlet) temperature 180±5°C, outlet air temperature 90±5°C, pressure 750-800 mm H_2O.

Solid Phase–Microextraction (SPME) and Dynamic Headspace Analysis (DHS). SPME was performed with polydimethylsiloxane (PDMS, 100 μm), carbowax-divinylbenzene (CW-DVB, 65 μm) and polyacrylate (PA, 85 μm) (Supelco, Bellefonte, PA). For SHS-SPME sampling, 0.1 g of product were placed in a 4 mL vial, closed with an open hole cap faced with a PTFE/white silicone septum and equilibrated at 40°C for 30 min. The fibre was exposed to the HS of encapsulated flavours during 5 min at 40°C. Afterwards, the fibre was withdrawn into the housing, the SPME

device was removed from the sample vial and the fibre was desorbed into the GC-MS injector. 5 g of each encapsulated product sample with removed surface oil were placed into a 250-mL flask and purged for 10-90 min with nitrogen gas (>99.8%) at a flow rate of 100 mL/min to recover volatiles accumulated in the HS during 10 min timed intervals. The purged volatiles were adsorbed on a Tenax, TA 35/60 mesh chemical trap. Volatile compounds were desorbed at room temperature washing with 15 mL of diethyl ether; then 1 mL of I.S. (0.3% v/v decane in diethyl ether) were added and evaporated to a final volume of ~1 mL under a stream of nitrogen and analyzed by GC.

Gas Chromatography (GC). The oils diluted in pentane (1% v/v) were analyzed on a Fisons 8000 series gas chromatograph with a flame ionization detector (FID) and a BPX-5 capillary column (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 (5 min hold) to 270°C (5 min hold) at a rate of 4°C min^{-1}. A split/splitless injector was used at 250°C in split mode at a ratio of 1:5; the injection volume was 1 μL. The content of compounds was expressed in GC peak area percent (three replicate injections).

Gas Chromatography–Mass Spectrometry (GC-MS). GC-MS were performed on a HP 5890 (II) gas chromatograph coupled to a HP 5971 series mass selective detector in the electron impact ionization mode at 70eV, the mass range was *m/z* 30-550. Volatile compounds were separated using an HP5-MS capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness). The temperature was programmed from 40°C (2 min hold) to 180°C at 4°C min^{-1} and finally increased to 270°C at 10°C min^{-1}. Helium was used as a carrier gas at a linear flow velocity of 36.2 cm/s at 40°C.

RESULTS AND DISCUSSION

Total oil content in liquid homogenized thyme EO emulsions was from 13.3 g 100 g^{-1} for ENCAPSUL 855 to 14.9 g 100 g^{-1} for HI-CAP 100 emulsified product; consequently emulsification efficiency of thyme EO in liquid emulsions varied from 88.6 % to 99.5 %, respectively. It was observed that the lowest emulsification efficiency was obtained for maltodextrin based liquid emulsions. It depends mostly on the emulsification properties of a matrix and its tendency to form films at the interfaces between the emulsion phases. It was reported that maltodextrins usually lack emulsification efficiency (Pegg, et al., 1999). The total oil contents of the spray-dried microencapsulated thyme EO products were statistically different (*P=0.05*) and ranged from 7.3 g 100 g^{-1} for ENCAPSUL 855 microencapsulated thyme EO product to 14.1 g 100 g^{-1} for HI-CAP 100 product. It is interesting to note that milk protein based matrix SMP was almost of the same ability to retain thyme essential oil and not statistical different (*P=0.05*) to that of food starch modified matrix N-LOK. It is obvious that the type of applied solids influences the retention of volatiles. The lowest ability to retain thyme EO was obtained for both dextrin matrices. It is in agreement with published data showing that the performance of maltodextrins in volatiles retention is not very good. It was also reported that maltodextrins retain aroma compounds well that are water soluble or soluble at their level of use; poor retention of insoluble aroma compounds by maltodextrins is related to the lack of emulsification properties (Reineccius et al., 2003).

The efficiency of microencapsulation of thyme EO via spray-drying into SMP and different carbohydrate-based matrices varied from 47.1% (ENCAPSUL 855) to 92.37% (HI-CAP 100). As it was already mentioned inefficient performance of maltodextrins in the retention of volatiles mostly depends on the lack of emulsification properties. Encapsulating modified starches involve the addition of lipophylic groups. It was reported that 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 dextrose equivalent (DE) corn syrup solids with the final DE of 32-37 and designed for the high load encapsulation agent (Soottitantawat et al., 2005). It seems that fine emulsion is stable during the atomization and spray-drying, and for the proper matrix the emulsion droplet size is a significant factor for the retention of flavours. It was reported that finer emulsion possesses the advantages for the insoluble flavour when preparing a solution for spray-drying, because it shows higher retention and lower surface oil content after the encapsulation, i.e., the change in the size of the larger emulsion droplet during atomization shows the major loss of flavours (Soottitantawat et al., 2003). It must be mentioned that fine homogenization at the elevated pressures has not been applied to the preparation of emulsions in our study and it could be also a reason for the loss of flavours during spray-drying process.

The recovery of the released into headspace thyme volatiles determined as a function of nitrogen purge time up to 90 min. The release kinetics of thymol from spray-dried powder products are presented in Figure 1. Total amount of thyme EO volatiles was released during 10 min of purge treatment at concentrations ranging from 19.7 ng g^{-1} by HI-CAP 100 encapsulated thyme oil product to 265.0 ng g^{-1} for ENCAPSUL 855 wall material. The major compound thymol (> 27%), was released during 10 min of purge treatment at concentrations ranging from 17.8 ng g^{-1} by HI-CAP 100 microencapsulated product to 139.3 ng g^{-1} for ENCAPSUL 855. The range of concentrations of oil volatiles during 90 min purge time was from 88.8 ng g^{-1} for HI-CAP 100 to 651.3 ng g^{-1} for SMP; of which the amount of released thymol constituted from 73.9 ng g^{-1} to 309.2 ng g^{-1}, for HI-CAP 100 and ENCAPSUL 855 encapsulated products, respectively.

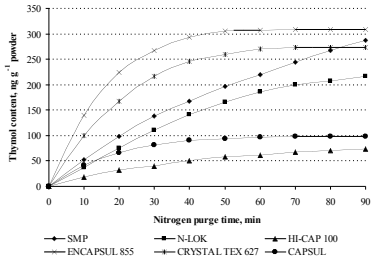

Figure 1: Release kinetics of thymol from spray-dried thyme EO products by DHS

p-Cymene, as the second major component of thyme oil (26.3%), during timed purge treatment was released from 0.9 ng g^{-1} for HI-CAP 100 to 180.6 ng g^{-1} for N-LOK microencapsulated products. The DHS-GC method was suitable for the comparison of microencapsulating properties of different wall materials. The obtained results revealed that the main thyme components were released at different rates by each of spray-dried microencapsulated thyme EO products. Figure 2 illustrates the concentration of the main compounds extracted from encapsulated thyme EO headspace by different fibres used.

HI-CAP 100 was the most effective to retain thyme volatile oil (90.1%) and it was considered as the least leaking matrix. Total volatiles absorbed with PDMS-coating fibre from encapsulated into HI-CAP 100 thyme EO headspace was $(25.3\pm1.9)\times10^6$ au. The highest enrichment to extract thyme volatile compounds was obtained with PA-coated fibre [$(669.4\pm71.8)\times10^6$ au] and it is mostly related to phenolic compounds in thyme EO; the combined CW-DVB coating extracted approximately 1.9 times lower amounts of aroma constituents [$(356.9\pm29.8)\times10^6$ au]. The most leaking matrix was ENCAPSUL 855, with the biggest content of released thyme volatiles, $(13249.1\pm1754.6)\times10^6$, $(1322.8\pm148.2)\times10^6$ and $(2805.1\pm453.2)\times10^6$ au on PDMS, CW-DVB and PA fibres, respectively. A very high amount of *p*-cymene [$(6731.1\pm976.7)\times10^6$ au] was detected in headspace of ENCAPSUL 855 with PDMS; while above HI-CAP 100 it constituted only

$(0.5\pm0.03)\times10^6$ au (Figure 2). The same component extracted with PDMS in headspace of Capsul and N-LOK constituted $(606.9\pm68.4)\times10^6$ and $(370.1\pm49.0)\times10^6$ au, respectively.

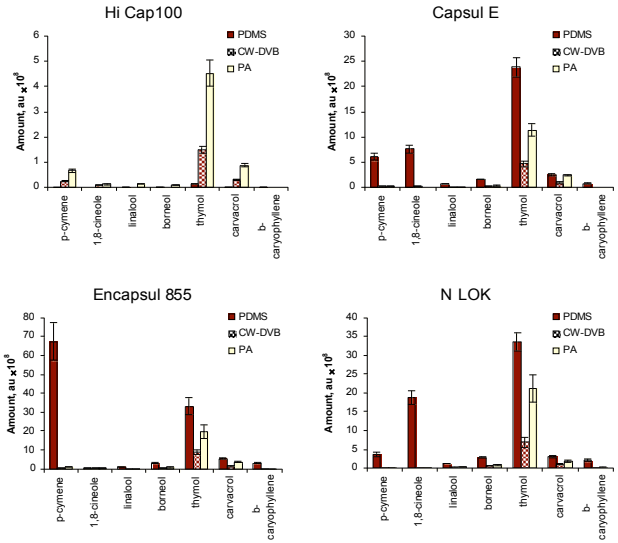

Figure 2: Flavour profiles of microencapsulated thyme EO constituents in the headspace

ACKNOWLEDGEMENTS. The study was performed in the framework of COST Action 865 and supported by the Agency for International Science and Technology Development Programs in Lithuania.

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