

### Microencapsulation of flavours in Caranauba wax

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### INTRODUCTION

Flavours are considered as valuable ingredients in any food formula. They are usually expensive, delicate and volatile. Therefore, food manufacturers are usually concerned about the preservation of aromatic additives.

Encapsulation can be employed to retain aroma in food product during processing or storage and/or allow a controlled release. Controlled release may be defined as method by which one or more active agents or ingredients are made available at a desired site and time and at a specific rate (Pothakamury & Barbosa-Canovas, 1995). An enormous range of different materials have been used to achieve the above application. These include proteins (e.g. milk, gelatine), carbohydrates (e.g. sucrose, maltodextrins, starches, cyclodextrins, and cellulose), lipids, fats, gums (e.g. acacia) (Madene et al. 2006). Among all edible waxes, Carnauba wax is the hardest, highest-melting, natural commercial wax. It is a plant exudate from the Brazilian 'tree of life' (*Copernicia cerifera*), composed almost entirely of esters of C<sub>24</sub> and C<sub>28</sub> carboxylic acids and C<sub>32</sub> and C<sub>34</sub> straight-chained primary alcohols. Compared to other waxes (such as beeswax), carnauba wax is significantly less viscous (thus easier to manipulate with during capsule processing), more elastic, and more resistant to deformations (Shellhammer et al., 1997). Various ways of preparing the wax capsules have been tested. In a recent report, solid and liquid preparation techniques were described, both based on emulsifying the water phase into molten wax phase (Mellema et al. 2006).

The idea is to create a microenvironment for the flavouring that reduces the volatility and/or mobility of the flavour constituents, and provides better retention during baking. This idea has prompted us to investigate a feasibility of improving the retention by absorbing the flavouring in wax particles. Since natural waxes are solid at room temperatures, stable, inert, and considered as safe, they are suitable for encapsulation of flavours.

### MATERIALS AND METHODS

Feed grade *Carnauba* wax was purchased from Carl Roth GmbH (Germany), emulsifiers (Tween 20, Span 40, Span 60) were supplied from Sigma Aldrich (Germany), ethyl vanillin and other aromatic compounds were obtained as a kind gift from Ireks aroma (Croatia) and Aroma (Serbia). Preparation of the encapsulated micro particles. Carnauba wax (8 % w/w) was melted in purified water containing an emulsifier (mixture Tween 20/Span 40) at 95 °C in thermostated water bath. The content of the emulsifier varied in range 0-1 % w/w. Ethyl vanilline was added to the dispersion of molten wax in water in weight ratio to wax 1:10 while stirring rigorously (1200 r/min for 4 min) by mechanical stirrer with two blade impeller. The solidification of the micro droplets were performed by adding cold water (2-5°C) to the resulting dispersion in order to cool it down. Finally, the microparticles were collected by filtration under reduced pressure, washed with water and dried at elevated temperature (50°C).

The thermal behavior of the particles was investigated employing the simultaneous DSC-TGA technique using a TA Instruments model SDT Q-600 (New Castle, Delaware, US). The samples

(mass approx. 10 mg) were heated in a standard alumina sample pan. All experiments were performed out under dynamic air of a flow rate of 0.1 dm<sup>3</sup>/min using a heating rate of 10 °C/min run.

The surface morphology of the microcapsules was imaged using a scanning electron microscopy (SEM). Samples were coated with a Au film of a 1.5 nm thickness using a Sputer coater device Baltec SCD 005 and micrographs were taken with a SEM-Jeol JSM 6460LV instrument at a voltage of 15 kV with a probe current of 30mA.

### RESULTS AND DISCUSSION

The TG curves of wax microparticles entrapping vanilline and vanilline-wax physical mixture are shown in Figure 1. From 20 to 200 °C, microcapsules of wax encapsulating vanilline exhibited nearly no weight loss (less than 1 %). In comparison, about 7 % weight loss was observed for physical mixture wax-vanilline (9:1 w/w) in the same temperature range.

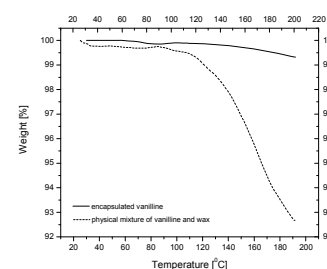


Figure 1: TG curves of wax microparticles entrapping approx. 10 % w/w ethyl vanilline and physical mixture of ethyl vanilline and wax in weight ratio 1:9

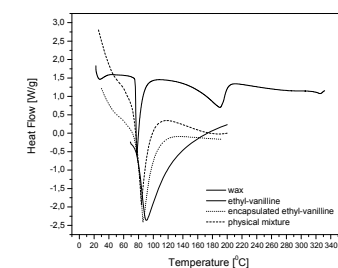


Figure 2: DSC scans of Carnauba wax, ethyl-vanilline, wax microcapsules containing ~10 % w/w vanilline and wax-vanilline physical mixture containing 10 % w/w vanilline.

The weight loss in this heating range can be reasonably attributed solely to the ethyl-vanilline, since carnauba wax starts to evaporate at a far higher temperature (about 250 °C), as shown in Figure 3. In the same figure the two peaks in DTG curves indicate that weight losses occur at around 363 °C and 447 °C. The result strongly supports the conclusion that vanilline is mostly encapsulated inside the wax matrix (not only physically adsorbed at the surface of the wax bead) and that the encapsulation enables complete retention of the flavour agent up to 200 °C, which is usually final temperature of backing process. For a comparison, free ethyl-vanilline starts to evaporate at 109 °C (weight loss of 5%) and up to 200 °C 93 % of mass is lost (Figure 4).

DSC scans of Carnauba wax, ethyl-vanilline, wax microcapsules containing ~10 % w/w vanilline and wax-vanilline physical mixture containing 10 % w/w vanilline are shown in Figure 2. Thermogram of ethyl-vanilline showed a sharp endothermic peak at 78 °C in agreement with the melting point of vanilline and a weak one at 190 °C which is attributed to vaporization. However, it was observed that neither the microcapsule formulation nor the physical mixture showed any endotherms corresponding to the melting point of vanilline. This suggests that vanilline dissolved in the wax matrix as the temperature was raised up to its melting point during the DSC run. From the scans it was also observed that untreated wax and wax in the physical mixture showed

endothermic melting peaks at 90°C and 84 °C, respectively, and wax in the microcapsule formulations showed an endothermic melting peak at 86 °C. According to the DSC scans, carnauba wax has a wide melting temperature range and thermal transition onset is 73 °C. This means that vanilline and wax melt simultaneously in certain temperature range. Slight variations in the enthalpy values and position of the melting point between samples may be explained by polymorphic transitions in the melt-cooled waxes, which are well documented in the literature (Eldem et al. 1991). However, DSC studies cannot be used to conclusively determine the physical state of vanilline in wax matrices.

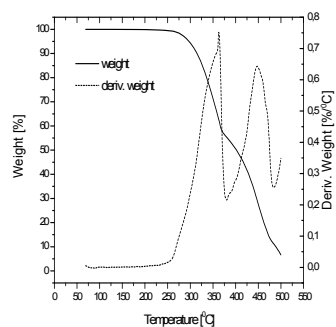


Figure 3: TG and DTG curves of Carnauba wax.

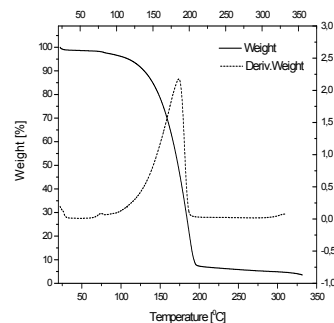


Figure 4: TG and DTG curves of ethyl-vanilline.

Figure 5 and 6 shows the SEM photos of the wax microcapsules encapsulating 10 %w/w ethyl-vanilline. SEM with low magnification showed that non-aggregated microparticles with a regular spherical shape were obtained (Figure 1). The fine core/shell microstructure of microcapsules can also be confirmed by the SEM image of a broken microcapsule as shown in Figure 6. The fracture of surface opened the empty interior of beads and showed the wall thickness of the order of several tenths of micrometers.

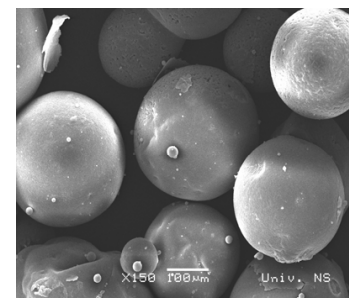


Figure 5: SEM images of wax microcapsules encapsulating 10 %w/w ethyl-vanilline (with low magnification)

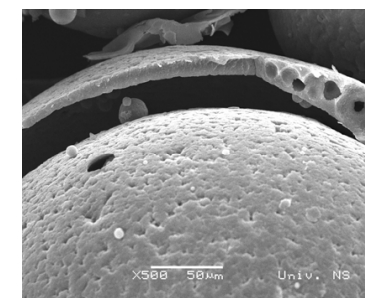


Figure 6: SEM images of wax microcapsules encapsulating 10 %w/w ethyl-vanilline (the cracked microcapsule)

## CONCLUSIONS

Thermal analysis showed differences in position of some characteristic peaks of encapsulated and pure substances. Also, the scanning electron microscopy confirmed good characteristics of emulsification. Microparticles with a regular spherical shape can be produced, without aggregation of particles.

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