O1-3	**Novel encapsulation technology for the preparation of core-shell microparticles**

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INTRODUCTION

Encapsulation and release systems, also known as delivery systems, are used in a broad range of applications, ranging from the slow release of fragrances in cosmetic formulations, or the protection of oxygen sensitive nutritional ingredients, to the triggered release of active ingredients from pharmaceutical formulations. A wide range of microencapsulation procedures is known and many are successfully applied in a various fields, including the pharmaceutical market. However, many of these methods have inherent limitations, including low encapsulation efficiency, limited loading capacity or processing conditions incompatible with sensitive ingredients.
Within TNO a new process principle has been developed that enables production of well-defined core-shell microcapsules in an efficient and continuous manner. Using a high viscosity ink jet printing technique (Houben 2004), uniformly sized droplets with precise velocity and direction of motion are prepared from the core material of interest. The droplets are subsequently impacted onto a liquid encapsulation film of controlled thickness, speed, and relative orientation, resulting in the formation of core-shell microcapsules (Figure 1). Composition and morphology of the encapsulates may be optimized by tuning the impact parameters, i.e. speed, direction, rotation, and the material characteristics, such as surface tension, viscosity, and density.

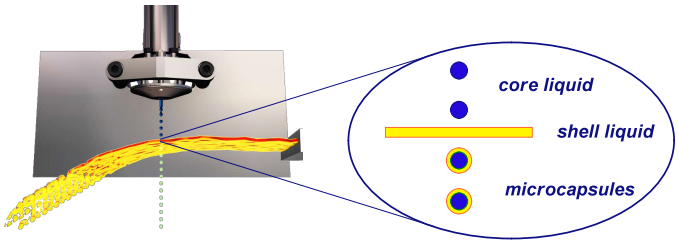


Figure 1 : Schematic representation of the encapsulation printer

In this paper, we present some examples of microcapsules that have been prepared using the encapsulation printer.

MATERIALS AND METHODS

An inkjet printing set-up with printing nozzles of 80 or 120 µm was used. For the printing of encapsulated oil particles, linseed oil was used as the ink, and carrageenan (3 wt%) was dissolved in demineralised water for the shell material. The shell material solution was heated to 75°C for the encapsulation process. For the printing of alginate particles, solutions of sodium alginate (3 wt%) and $CaCl_2$ (5 wt%) in demineralised water were used. For the preparation of heat-sensitive capsules, a solution of blue dye (JO-LA blue) in demineralised water was used as core fluid, and a mixture of stearic acid (75 wt%) and carnauba wax (25 wt%) heated to 95°C was used as shell material. Release of the aqueous core was quantified by UV-VIS spectroscopy.

RESULTS AND DISCUSSION

A broad variety of micro particles were produced, using different material combinations, resulting in water-in-lipid, water-in-water and lipid-in-water based microcapsules with a core-shell morphology. As an example, linseed oil was printed through a film of aqueous carrageenan solution at elevated temperature. Immediately after encapsulation, the droplets were cooled, resulting in solidification of the carrageenan shell. Monodisperse microcapsules with a core of liquid oil and a soft polymer shell with a thickness of less than 10 µm were obtained (Figure 2). The size of the particles could be tuned between 200 and 450 µm by adjusting printing frequency and flow rate of the liquid screen. Core-to-shell volume ratios were around 85:15. The thin polymer shell showed good mechanical stability when handling the microcapsules. By specifically puncturing the capsules with a pipette, the oil could be released (Figure 2, bottom left).

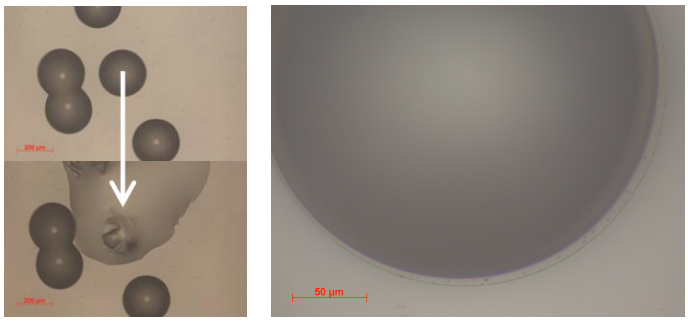


Figure 2 : Monodisperse oil microcapsules with a diameter of 280 µm and a shell of 7 µm; bottom left: release of encapsulated oil by mechanical disruption of the polymer shell.

The encapsulation printer can also be used for systems in which core and shell liquids react together. As an example, complexation of core and shell material was demonstrated by the preparation of alginate gel particles. Aqueous alginate solution droplets were printed through a liquid screen composed of aqueous calcium chloride solution, resulting in the formation of monodisperse alginate beads of 200 µm diameter (Figure 3) in a continuous

manner. Because the printing process is mild in terms of temperature and mechanical stress that is induced on the constituents, various ingredients might be incorporated inside the alginate particles by mixing them in the sodium alginate solution.

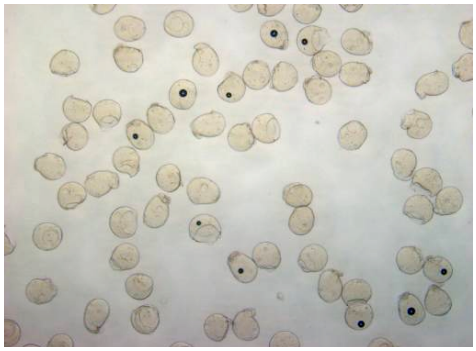
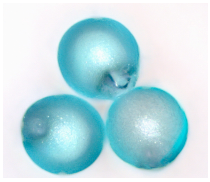


Figure 3. Monodisperse alginate particles with a diameter of 200 µm

Hydrophobic shell materials such as fats or fatty acids are very interesting materials because of their water barrier properties. In addition, encapsulation of aqueous core materials with a fat shell allows heat-triggered release. To test this approach, core-shell capsules were prepared by printing aqueous dye solutions through a liquid film of molten fat. Monodisperse microcapsules of 150 – 200 µm were obtained (Figure 4, left). To test the intact nature of the fat shell, a release test was performed in water. No release of dye was observed in water at room temperature, demonstrating effective encapsulation of the core material. In hot water, a rapid release of dye was observed, as a result of the melting of the fat shell (Figure 4, right).



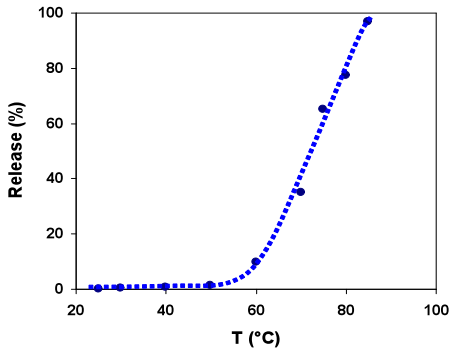


Figure 5 : (left) Monodisperse microcapsules (160 µm) consisting of an aqueous core encapsulated by a fat shell; (right) heat-triggered release of the core fluid.

Future research will be focused on the preparation of smaller microcapsules (50 – 100 µm) and on further tuning of core-shell ratios as well as barrier and release properties of the microcapsules.

CONCLUSIONS

The encapsulation printing process enables the continuous production of well-defined monodisperse microcapsules of varying compositions. Due to the efficiency of the process, high loading capacities may be achieved. The separated input streams for core and shell material allow the use of different input temperatures or the use of reactive components that should only react at the interface between core and shell.

REFERENCES

- Houben R.J. (2004), *Apparatus and method for printing a fluid material by means of a continuous jet printing technique*, Patent application WO2004018212