

P-010 Evaluation of surfactants of thyme oil microcapsules prepared by coacervation

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INTRODUCTION AND OBJECTIVES

Encapsulation has grown over the years. **Microencapsulation** is used for several applications and there are a numerous techniques available for the encapsulation of many types of liquid cores. The encapsulation of **oils** in a core-shell material is very important to protect the volatilization of compounds from evaporation and those defend to oxidation from degradation by atmospheric oxygen during storage (Yow HN 2006, Job Ubbink 2007, Moretti MDL 2002, Lumsdon SO 2005).

The formation of microcapsules (size, shape and stability) is greatly affected by the conditions used in the o/w emulsion preparation, being particularly relevant the used **surfactant** (Guo HL 2005, Mohamed F 2006, Yuan Q 2009).

The objective of this work is to study the effect of using different surfactants with hydrophilic-lipophilic balance (**HLB**) values from 11 to 16.5 in the encapsulation process of **thyme oil** by **coacervation** using **polylactide** (PLA) with polymer wall. Different emulsions of thyme oil were prepared and the surfactants investigated were Tween[®] 20, Tween[®] 80, Tergitol[™] 15-S-9 and a combination of Tergitol[™] 15-S-9 with Span[®] 85. Microcapsules size, morphology and encapsulation efficiency were studied as a function of the used surfactant.

MATERIALS AND METHODS

Microcapsules of PLA with thyme oil were prepared according to the procedure described in Figure 1.

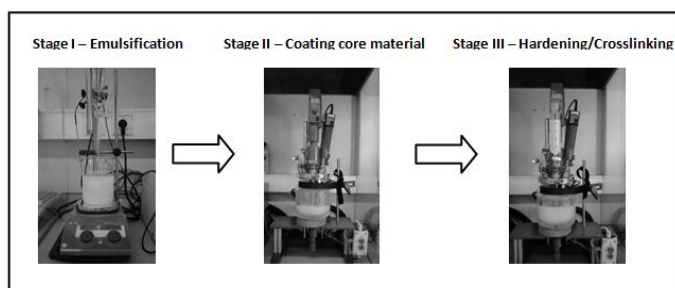


Figure 1. General process scheme of the preparation of thyme oil microcapsules.

Firstly, the o/w emulsion was obtained by dispersing a chosen amount of thyme oil in water using an ultraturrax at 11 000 rpm during 90 seconds (stage I – emulsification). Thereafter, the emulsion was transferred to a batch

reactor. Before microcapsules formation, the PLA solution in dimethylformamide (DMF) was added dropwise to the prepared thyme oil emulsion. Upon contact with water, the homogeneous solution of PLA in DMF, promote the precipitation of PLA around the thyme oil core (stage II - coating core material). The encapsulation process continued under stirring for one hour at room temperature. The microcapsules formed were hardened by adding OCMTS, and allowed to stand during one hour (stage III – hardening). After hardening, the microcapsules were decanted and sequentially washed with Pluronic[®] F68 solution, an ethanol solution and finally hexane. The procedure was repeated with different types of surfactants/surfactant mixtures as described in Table 1. Details of the used formulation can be found elsewhere Martins IM 2008.

Table 1. HLB values of surfactants and surfactant mixtures, mean particle size in volume of microcapsules and microcapsules wall thickness for each type of surfactants.

Surfactant System	%	HLB value	Particle size (µm) (mean + SD)	Wall thickness (µm)
Tween [®] 20	100	16,5	42,24 +17,94	3.06
Tween [®] 80	100	15,0	32,94 ± 16,96	2.30
Tergitol [™] 15-S-9	100	13,3	29,30 ± 18,37	2.01
Tergitol [™] 15-S-9 + Span [®] 85	80+20	11,0	32,52 + 17,24	2.34

RESULTS AND DISCUSSION

Figure 2 shows the experimentally measured particle size distributions, both in volume and in number, for PLA microcapsules prepared with different types of surfactants.

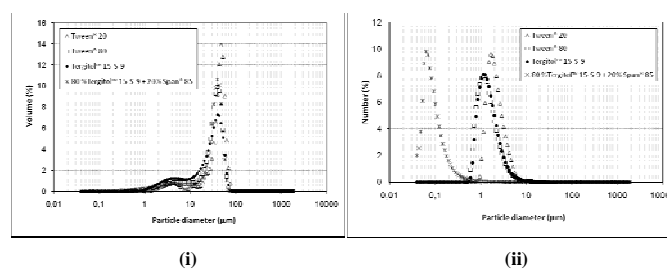


Figure 2. Particle size distribution in volume (i) and in number (ii) of polylactide microcapsules with thyme oil for different surfactant systems.

The distributions in volume for all the studied formulations have showed a similar distribution model, i.e., a

bimodal distribution and pointed out that the use of Tergitol™ 15-S-9 generates smaller particles. The corresponding distributions in number were quite narrow and unimodal in shape. For the mixture 80 %Tergitol™ 15-S-9 + 20% Span® 85 it can be observed that the curve shifts to the left showing an increase, in number, of smaller microcapsules.

Optical microscopy images of the microcapsules are shown in Figure 3. All figures shows that the droplets of thyme oil have been individually encapsulated as spherical particles with size distribution consistent with a bimodal distribution, and one can notice also the absence of agglomerates.

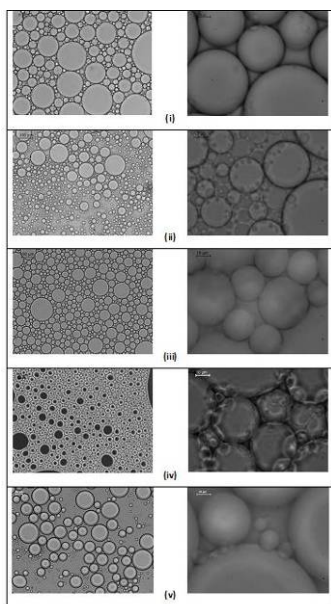


Figure 3. Optical microscopy of microcapsules solution after the production and without washing using: (i) Tween® 20 (ii) Tween® 80 (iii) Tergitol™ 15-S-9 (iv) Tergitol™ 15-S-9 (in dark field option) (v) 80 %Tergitol™ 15-S-9 + 20% Span® 85 as surfactants. Magnification of images: 100x and 1000x.

Figure 4 shows the effect of using different surfactant systems on the encapsulation efficiency of thyme oil and we can notice that the apolar compounds of thyme oil were preferentially encapsulated in detriment of the polar ones for all surfactant systems studied. It was observed that with Tergitol™ 15-S-9 obtains 80% of encapsulation for the apolar compounds while for the polar compounds only 54% was achieved. The larger is the hydrophobic chain of surfactant the lower is the surface tension at the o/w interface and consequently it becomes easier to form the emulsion. The encapsulation efficiency (percentage of thyme oil present in microcapsules) using Tergitol™ 15-S-9 as surfactant accounts for 65% of the loaded oil used in the encapsulation process and the percentage encapsulated of thyme oil apolar compounds around 80%.

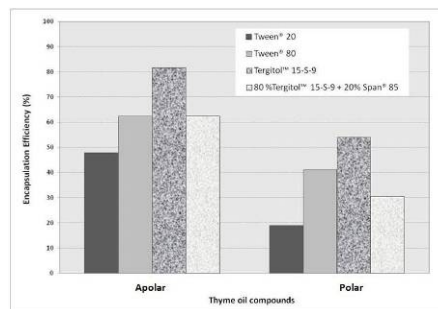


Figure 4. Values of encapsulation efficiency of apolar and polar compounds of thyme oil using different systems of surfactants.

CONCLUSIONS

With this work it was investigated the effect of using different surfactants systems in the particle size distribution, morphology and yield of encapsulation of PLA thyme oil microcapsules. Microcapsules particle size showed a bimodal distribution in volume with mean particle size of 40 µm for Tween® 20 and 30 µm for Tergitol™ 15-S-9 and for the mixture of 80 %Tergitol™ 15-S-9 + 20% Span® 85. In number the distribution was quite narrow and. Analysis by optical microscopy confirmed the spherical shape morphology for all microcapsules produced. Quantification of the encapsulated oil was studied and it was observed that the apolar compounds of thyme oil were preferentially encapsulated in detriment of the polar ones and the encapsulation efficiency of thyme oil was higher using Tergitol™ 15-S-9 (nonionic surfactant with HLB value of 13.3) and around 65%.

REFERENCES

- Yow HN et al. (2006) *Formation of liquid core-polymer shell microcapsules*. *Soft Matter*. 2 940-49.
- Job Ubbink et al. (2007) *Flavor delivery systems*. in book *Kirk-Othmer Encyclopedia of Chemical Technology*. Copyright John Wiley & Sons, Inc. 5th Edition. New York. Vol. 11. 527-563.
- Moretti MDL et al. (2002) *Essential oil formulations useful as a new tool for insect pest control*. *AAAPS Pharm-scitech*. 3 (2) 64-74.
- Lumsdon SO et al. (2005) *Encapsulation of oils by coacervation*. WO 2005/105290 A1.
- Guo HL et al. (2005) *The relation between narrow-dispersed microcapsules and surfactants*. *J. Microencapsul*. 22(8) 853-62.
- Mohamed F et al. (2006) *PLGA microcapsules with novel dimpled surfaces for pulmonary delivery of DNA*. *International Journal of Pharmaceutics*. 311 97-107.
- Yuan Q, et al. (2009) *Surfactant selection for accurate size control of microcapsules using membrane emulsification*. *Colloids and Surface A: Physicochem. Eng. Aspects*. 347 97-103.
- Martins IM et al (2008). *Microencapsulation of thyme oil by coacervation*. *J. Microencapsul*. 26(8) 667-75.