P-010

Production by coacervation of thyme oil microcapsules with PLA: evaluation of surfactants

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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.

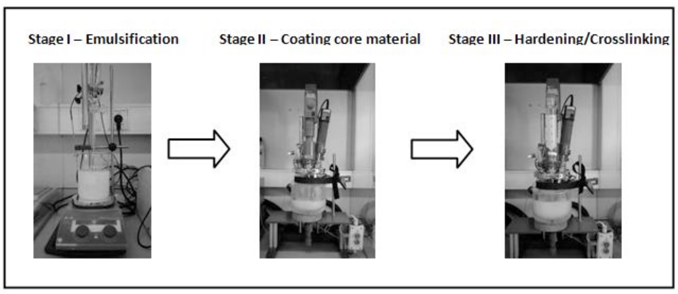

Figure 1. General process scheme of the preparation of thyme oil microcapsules with biodegradable polymer.

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 a hardening agent, 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
ergitol™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 four different kinds of surfactants.

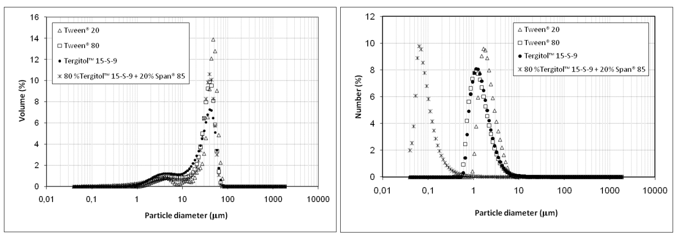

Figure 2. Particle size distribution of polylactide microcapsules with thyme oil for different surfactant systems and after washing the microcapsules. Distribution in volume (i) and in number (ii).

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.

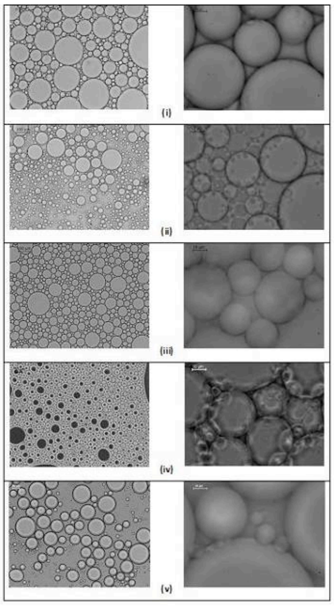

Figure 3. Optical microscopy of microcapsules solution after the production and without washing using: (i) Tween® 20 (ii) Tween® 80 (iii) Tergitol™ 15-S-9 (iv) Tergitol™ 15-S-9 (in dark field option) (v) 80 %Tergitol™ 15-S-9 + 20% Span® 85 as surfactants. Magnification of images: 100x and 1000x.

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%.

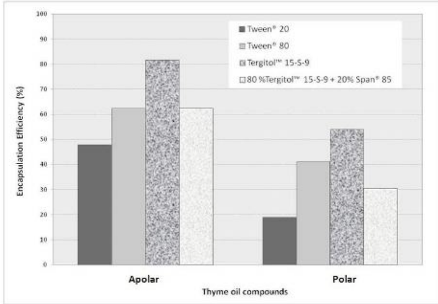

Figure 4. Values of encapsulation efficiency of apolar and polar compounds of thyme oil for all surfactant system.

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%.

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