THERMOSTABILITY STUDY OF NATURAL POLYMER MICROCAPSULES

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Microcapsules represent a stand-alone system that has applicability in a multitude of fields. The raw materials for microcapsules are very varied and with different properties. In this paper, biodegradable raw materials from natural sources were used to create/develop microcapsules. The chemical-structural stability of microcapsules under working conditions is a factor that must be considered. The aims were to obtain microcapsules from the previously specified raw materials, to perform a microscopic characterization, to establish their dimensional profile as well as their thermal stability over a range of 25-100°C, in aqueous solution. The study of the thermal stability of microcapsules can provide information regarding the temperature of the environment in which they can be used, specifically, whether they can withstand in medical products, which are subjected to high thermal treatments (up to 100°C), at the same time being susceptible to degradation by chemical action, gradually releasing the active components they may contain.

Keywords: microcapsules, thermal stability, thermal treatments

INTRODUCTION

Microencapsulation is the technique by which a solid, liquid, or gaseous component is retained by a second compound to protect the active component from environmental actions (Gharsallaoui *et al*., 2007). The materials used to make the microcapsules are called coatings/membranes/walls. These materials can be part of a wide range of compounds such as polymers, sugars, proteins. Components contained in microcapsules are called "fillers" or "core". Encapsulation can be performed for pure compounds, mixtures or living organisms (Gharsallaoui *et al*., 2007; Dubey *et al*., 2009; Rowe *et al*., 2009). The microcapsules can have dimensions between 1 µm and 1000 µm, dimensions that depend on the obtaining method (Ghosh, 2006). Microcapsules obtained from natural polymers are in high demand because, due to the very nature of the raw materials, which are biodegradable, their decomposition does not produce toxic products. The structure of a microcapsule depends on the physico-chemical properties of the core, the composition of the wall and the technique used for microencapsulation. In this sense, the obtained particles can have a shape as close as possible to a sphere or with an irregular shape, with a single or multi-layer coating. At the same time, they can have multiple cores, which can be found either in the center of the microcapsule or in the shell. At the same time, a matrix structure of the microcapsule can be obtained, in which case the active substance is uniformly distributed in the structure of the microcapsule. The microcapsule aspect can be seen in Figure 1 (Bakry *et al*., 2016).

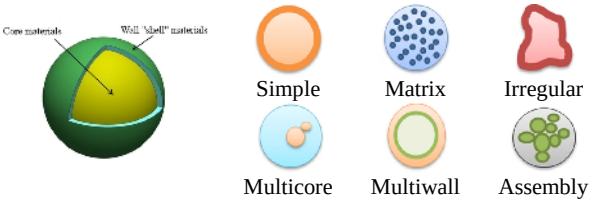

Figure 1. Microcapsule types

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EXPERIMENTAL

Materials

Collagen hydrolysate (powder) – obtained by atomizing the collagen hydrolysate solution, obtained from bovine skin, within the Collagen department of The National Research & Development for Textiles and Leather – Leather and Footwear Research Institute Division.

Chitosan – purchased from Sigma-Aldrich, Germany. Chitosan is obtained from chitin by applying chemical or enzymatic treatments to the exoskeleton of crustaceans.

Sodium alginate – purchased from Sigma-Aldrich, Germany.

Acetic acid – purchased from Merck-Millipore, Germany.

Glutaraldehyde (25% aqueous solution) – purchased from Merk-Millipore, Germany, and was used as a crosslinking agent.

Equipment

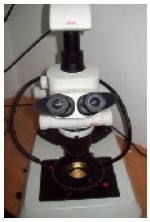
Magnetic Stirrers with Hot Plates – with 50-300°C temperature interval.

Stereomicroscope – S8AP0 (Leica). Magnification is from 10x to 160x, it has incident and transmitted light and possibility to observe the samples with polarized light.

Micro-hot table (Caloris) – device that has the possibility to heat with a preset speed, allowing to visualize the sample behavior, from the upper part of the equipment, with the help of a stereomicroscope.

Zetasizer Micro ZS (Malvern) – particle size determination.

Hot plate



Optical stereomicroscope

Micro-hot table

Zetasizer Micro ZS

Figure 2. Equipment

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RESULTS AND DISCUSSIONS

Because the raw materials used are part of the group of natural polymers, although they are soluble in water, for this study, 2% solutions were made for each individual polymer. The recipe for microcapsule is displayed in the Table 1.

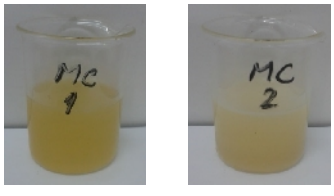
Table 1. Microcapsule recipe

No.	Sample code	Collagen hydrolysate	Sodium alginate	Chitosan
1	MC-1	Yes	Yes	-
2	MC-2	Yes	-	Yes

In order to obtain the microcapsules, the following operations were performed:

- collagen hydrolysate solution was heated to temperature interval of 40-60°C and mixed at 1000 rpm;
- addition of the secondary polymer, while maintaining the mixing speed and temperature;
- decrease medium temperature below 10°C, followed by the pH correction, in the sense of establishing an acid environment;
- gradual addition of the crosslinking agent, with permanent monitoring of the reaction temperature;
- completing the crosslinking by keeping the mixing speed at a lower speed then initial, for 3 hours.
- increasing medium temperature up to 40-60°C interval with permanent mixing for 2 hours;
- washing the obtained microcapsules with water, to remove unreacted materials.

Based on the Table 1 recipe, a number of two liquid suspensions were obtained, based on the raw materials used – Figure 3.



a) MC-1 b) MC-2

Figure 3. Obtained microcapsules

Optical microscopy test reveals the microcapsule spherical aspect for MC-1 (a) and MC-2 (b) – Figure 4.

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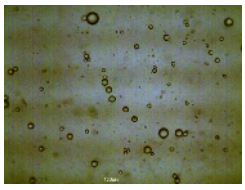

a) MC-1 (100x)

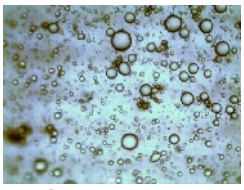
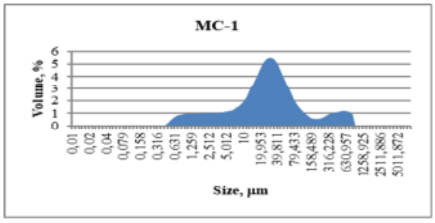
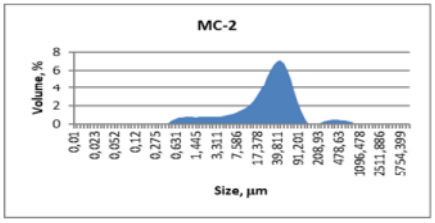

b) MC-2 (100x)

Figure 4. Optical microscopy for obtained microcapsules

Microcapsule size determination for MC-1 shows that the microcapsules have sizes between 0.6 and 63 µm diameter, the majority been of them having 20 µm diameter. Microcapsule size determination for MC-2 shows that the microcapsules have sizes between 0.6 and 1000 µm diameter, the majority been of them having 40 µm diameter. The microcapsules size shift can be explained due to variable mixing speed throughout the synthesis, a larger microcapsule size being the result of lower stirring speed. The microcapsule size profile can be seen in Figure 5.



a) MC-1 Microcapsule



b) MC-2 Microcapsule

Figure 5. Microcapsule size profile

Thermostability of the microcapsules was performed with an equipment combination of micro-hot table and stereomicroscope. The set temperature range was 25°C-95°C with 2°C/min heating rate and 20x magnification.

The behavior of MC-1 and MC-2 microcapsules was observed in aqueous environment, at regular temperature intervals. Sequential images of MC-1 microcapsules during the analysis demonstrate that microcapsules do not undergo structural changes for the entire temperature interval – Figure 6, which indicates good stability at high temperatures. The sequential images for MC-2 microcapsules taken during the analysis demonstrate the fact that they undergo structural changes at a temperature of 40°C, which indicates that their stability is maintained only up to this temperature.

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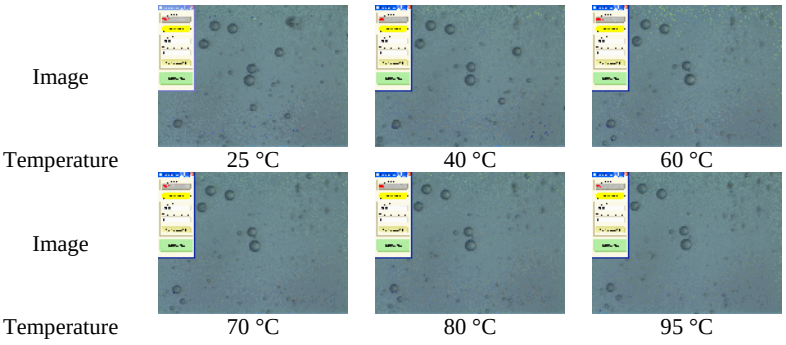

Figure 6. MC-1 microcapsules under thermal treatment, in aqueous medium

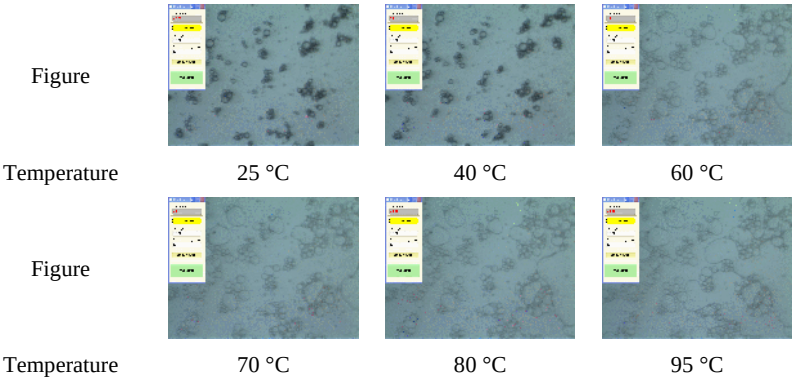

Figure 7. MC-2 microcapsules under thermal treatment, in aqueous medium

CONCLUSION

The optical microscopy for the obtained emulsions identified the presence of microcapsules. The size of the microcapsules is quite varied, also confirmed by the dimensional analysis graphs. Based on the profiles of the dimensional distribution of the microcapsules, it can be said that the obtained microcapsules are divided into two major areas, namely microcapsules with dimensions of 20 μm and 40 μm, respectively. At the same time, it is possible to identify the existence of microcapsules with dimensions between 0.5 and 10 μm as well as in the interval 40-90 μm and a small group around 200-1000 μm, due to the fluctuating stirring speed.

The thermal stability of the microcapsules up to 100°C (MC-1) indicates the possibility of using them in a wearable materials matrix that can be subjected to washing.

The thermal stability of the microcapsules up to 40°C (MC-2) can imply the use for controlled release of substances that they may contain.

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