

Microcapsules PCL with essential oil citronella

Abstract

The technology associated with the modification of the release of active ingredients is wide in various industrial sectors. Among these technologies, natural and synthetic polymers matrix systems are widely applied as the advantage of nanoparticles with controlled release and/or prolonged substance incorporated therein. In this study, preparation and characterization of Microcapsules of biodegradable polymer with high stability has been performed. The poly-ε-caprolactone (PCL) containing the essential oil of Citronella (*Cymbopogon winterianus* Jowwitt), as its bioactive compound, through an emulsion technique followed evaporation of the solvent, which consists in the precipitation of a preformed polymer, evidencing significant influence on drying methods. Using the chosen technique, it was possible to produce particles with an average size of 4 micrometers with spherical morphology and smooth surface when dehydrated under reduced pressure, do not retain these characteristics when subjected to the lyophilization process.

Keywords: microcapsules, citronella, poly-ε-caprolactone, lyophilization

Volume 2 Issue 2 - 2017

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Received: December 14, 2016 | **Published:** April 05, 2017

Abbreviations: PCL, poly-ε-caprolactone; TGA, thermo gravimetric analysis; SEM, scanning electron microscopy; IR, infrared

Introduction

Since the PCL appears and became commercially available, many scientific groups start to choose this synthetic polymer following its characteristics that could be degraded by microorganisms. There are various mechanisms which affect the polymerization of PCL and these are anionic, cationic, co-ordination and radical. Each method affects the resulting molecular weight, molecular weight distribution, end group composition and chemical structure of the copolymers. PCL is a semi-crystalline polymer having a glass transition temperature (T_g) of -60°C and melting point ranging between 59 and 64°C, dictated by the crystalline nature of PCL which enables easy formability at relatively low temperatures. The number average molecular weight of PCL samples may generally vary from 3000 to 80,000 g/mol and can be graded according to the molecular weight.

PCL is suitable for controlled drug delivery due to a high permeability to many drugs excellent biocompatibility and its ability to be fully excreted from the body once bio resorbed. Biodegradation of PCL is slow in comparison to other polymers, so it is most suitable for long-term delivery extending over a period of more than 1 year. PCL also has the ability to form compatible blends with other polymers, which can affect the degradation kinetics, facilitating tailoring to fulfill desired release profiles.

Nanotechnology is a multidisciplinary field that has advanced rapidly in recent years attracted the interest of numerous research groups in the world. Due to its application in various industries, nanotechnology has the potential to revolutionize widely various technological and scientific fields as Duran et al.¹

Technology associated with modification of the release of active ingredients in the industrial sectors such as drugs, pesticides, dyes, flavorings, water treatment, food industry and so on. Among these technologies, polymer matrix systems are widely applied as the advantage of nanoparticles with controlled release and/or prolonged substance incorporated therein according.²

The nanoparticles produced from biodegradable polymers have been the subject of studies due to its greater stability and therapeutic potential in its biological fluids, and during storage, according to Guterres et al.³

Nanoparticles is a term used generally to Nanospheres, and Microcapsules, but they differ in structural aspects like the crystallinity and amorphous part, reactivity and by the absence or presence of an oily core. The nanospheres do not have oil in their composition and are formed of a polymeric matrix and the Microcapsules are comprised of a polymeric film disposed around its oily core according to Souza et al.⁴

Poly-ε-caprolactone polymer (PCL) is a biodegradable polymer capable of incorporating various substances in their chemical structure. This polymer is insoluble in water, but it can permeate their polymer chains, and their degradation is slow in an aqueous medium without causing risks to the environment as Grilo et al.⁵

The problems of instability of the suspensions can be minimized by suitable drying methods. The lyophilization process (water extraction in the form of ice) by sublimation has been widely used for drying nanospheres, however, few studies have been conducted with this procedure, according to.²

This work presents the preparation and characterization of Microcapsules of poly-ε-caprolactone (PCL) containing essential oil of citronella (*Cymbopogon winterianus* Jowwitt) as their bioactive compound, according to Bizzo et al.,⁶ through an emulsion technique followed by solvent evaporation, consisting in the precipitation of a preformed polymer under Grilo et al.⁵

Materials and methods

Different methods have been reported in the literature for the preparation of drug entrapped nanoparticles including, emulsion polymerization in a continuous aqueous phase, emulsion polymerization in a continuous organic phase, interfacial polymerization, interfacial disposition, solvent evaporation, desolvation of macromolecules, and dialysis. Select methods for preparing PCL nanospheres are discussed below.

The Microcapsules were prepared by the nanoprecipitation method of poly- ϵ -caprolactone polymer (molecular weight 70,000g/mol, from sigma Aldrich) consisting in forming an emulsion oil/water, followed by evaporation of the solvent. Initially were used 0.4g PCL dissolved in 30mL of dichloromethane (organic solvent from vetec), with the aid of a magnetic stirrer, and then added 0.8g of citronella (essential oil from WNF-Germany) and 0.1g of Span 80 (surfactant from sigma Aldrich). The solution was placed in a Ultraturrax® emulsifier (IKA® T10) for one minute, at 8,000rpm, thus was formed the primary emulsion. The aqueous phase was composed of 0.1g Tween® 80 - sigma Aldrich (surfactant) and 60mL of distilled water.

Subsequently, the oil phase was slowly added into the aqueous phase and the solution was again placed under stirring emulsifier at 20,500 rpm for seven minutes, forming the second emulsification. At the end, the formed emulsion was placed on a magnetic stirrer, where the solvent was evaporated for 24hours under normal temperature and pressure conditions.

The Microcapsules were isolated by centrifugation (3500rpm) for fifteen minutes. The sample was divided into two portions for drying thereof, was used two different drying procedures: one portion was dried under reduced pressure (MC-1 sample) using a vacuum pump until constant weight, the other portion (MC-2 sample) was frozen in liquid nitrogen and lyophilized for 24hours (FAQUI/PUCRS). Finally, the Microcapsules were stored in a desiccator.

Scanning electron microscopy (SEM)

The analysis of morphology and surface of the samples was performed using the Scanning Electron Microscope (SEM), PHILIPS XL30 model (LabCEMM/PUCRS) with a resolution of 3.5nm (secondary electron) and increases the range of 1000-4000times, 20kV acceleration voltage using gold plating the samples. As well as the equipment JEOL JSM-6510LV Model Laboratory of Advanced Studies in Materials/FEEVALE). The particle size study was measured using the software image J. 1.48V, Wayne Rasband - National Institutes of Health, USA. ([http://imagej.nih.gov/ij-Java 1.6.0_20 \(32-bit\)-2369k of 1536MB](http://imagej.nih.gov/ij-Java 1.6.0_20 (32-bit)-2369k of 1536MB)).

Vibrational spectroscopy, infrared (IR)

The infrared analyses were performed in a Perkin Elmer Instruments FT-IR Spectrometer, in the range 4000-650 cm^{-1} . The samples were analysed by UATR accessory.

Thermal gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) were performed in a TA Instruments Q600 equipment, using a heating ramp of 20°C/min from room temperature to 800°C.

Results

Scanning electron microscopy (SEM)

According to Souza et al.⁴ the scanning electron microscope (SEM) is the best way to study the morphology of the Microcapsules, with a core which contains some material. The Figure 1A & Figure 1B, shows the Microcapsules obtained by the used method in this research.

The formed Microcapsules showed distinct morphological characteristics in two drying methods used. As Figure 2, it can be observed that the freeze-drying method broke the material, forming an oily film on the sample which came from the core, thus freeing

its encapsulated active agent and the drying method under reduced pressure, retained the morphological characteristics, i.e., keeping its encapsulated material. Confirming that the freeze-drying technique is not suitable for drying Microcapsules suspensions, as already depicted in the literature by Schaffazick & Guterres.³ The particle size was obtained using the Image J software, which was performed to measure the diameter of the sample. It was observed the average size of particulates was 4 μm , with a standard deviation around 1 μm .

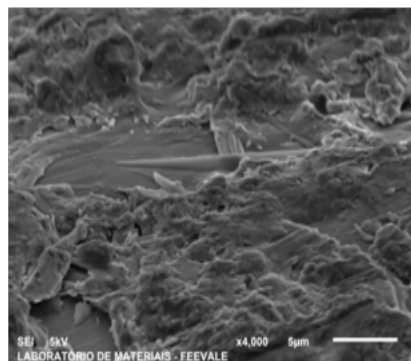


Figure 1A Pure PCL micrograph an increase of 4000x

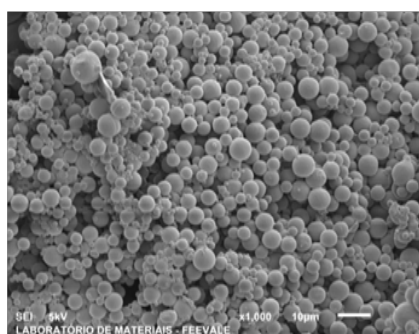


Figure 1B PCL Microcapsules with citronella oil, (MC-1) at 1000x magnification.

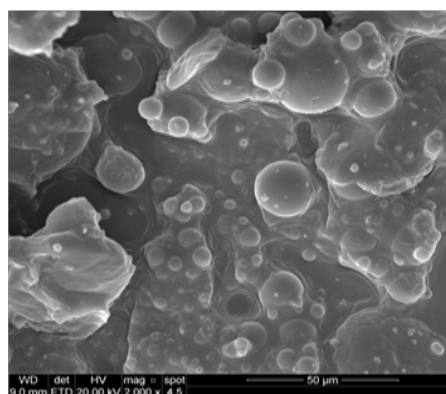


Figure 2 Micrograph of PCL with citronella oil Microcapsules (MC-2) with increase of 2000x.

Vibrational spectroscopy, infrared (IR)

The infrared spectroscopy (IR) was used to check the encapsulation of the citronella oil and no formation of secondary phase. The essential oil of citronella infrared spectrum Figure 3 showed characteristics absorptions, like the axial deformation of the OH (3363 cm^{-1}) also related with water absorption, as Silverstein et al.⁷ The CH stretch

(2976 cm^{-1} and 2899 cm^{-1}) and the C=C (1647 cm^{-1}). It can be, also, observed the vibration of methylene, i.e., the folding CH in 1451 cm^{-1} and 1381 cm^{-1} and the folding OH in 1044 cm^{-1} , according with literature, Paiva et al.⁸

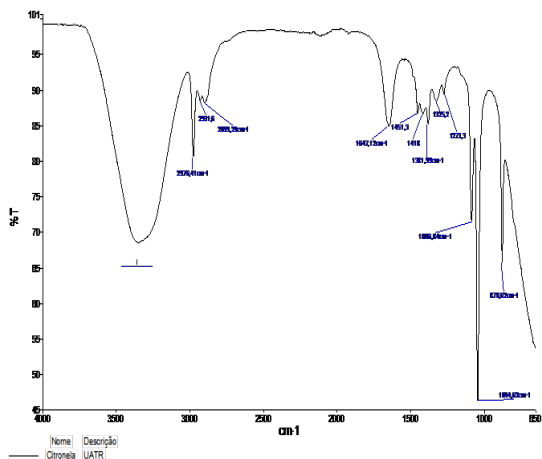


Figure 3 Infrared spectrum of essential oil of citronella

The vibrational spectrum of the pure PCL Figure 4 shows where was observed the vibration of methylene (CH_2) in 2942 cm^{-1} and 2869 cm^{-1} . This spectrum, also, showed the stretch C=O (1721 cm^{-1}) and the folding CH (methylene group) in 1477 cm^{-1} and 1420 cm^{-1} . Finally, still, was exhibit the functional group of ether CO due to its stretch in 1160 cm^{-1} and an asymmetric angular. Deformation in methylene plane 730 cm^{-1} as Silverstein et al.⁷

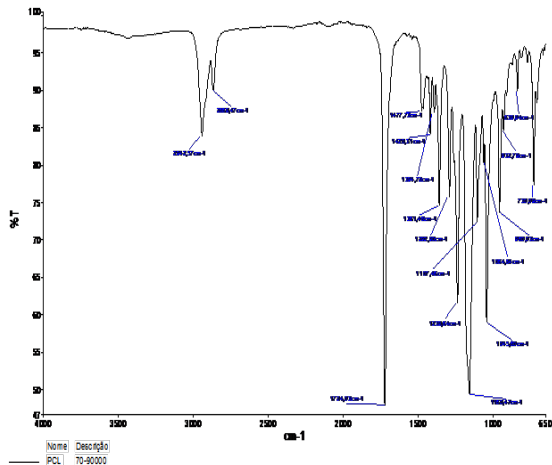


Figure 4 Infrared spectrum of pure PCL

The infrared of the MC-1 sample Figure 5 showed the characteristic groups of both materials, the PCL and citronella oil the axial deformation of the CH (2936 cm^{-1} and 2865 cm^{-1}) along with the vibration of the carbonyl group (C=O)1721 cm^{-1} . Also shown is the functionality of the ether group (C-O) in 1163 cm^{-1} and the methylene group (CH_2) with an angular deformation in the plane 731 cm^{-1} , according to Silverstein et al.⁷ However, through this spectrum had not been characterized in the presence of the citronella oil and no changes of the functional groups of the raw material.

Thermal gravimetric analysis (TGA)

TGA analyses carried out on purified PCL samples, deprived from

any residual catalyst or monomer, highlighted a two-step thermal degradation. Data analysis of TGA showed a one-step degradation mechanism of neat PCL versus multiple steps for the composites, indicating similar molecular structure and physical properties of neat PCL like the composite. Thermogravimetric analysis of the sample MC-1 Figure 6 showed initial degradation around 397°C.

Thermogravimetric analysis of pure PCL Figure 7 presented its initial degradation around 396°C. By thermal gravimetric analysis it was proved that the presence of citronella, at the core of the Microcapsules of PCL did not alter the thermal resistance of the material formed in relation to the pure polymer.

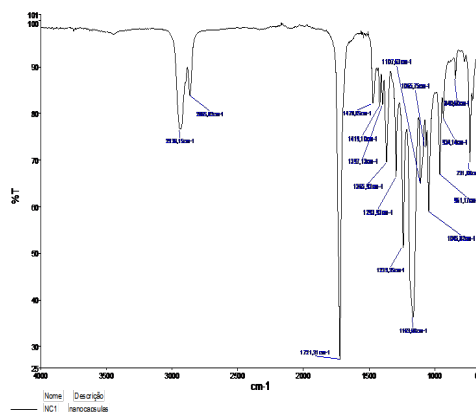


Figure 5 Infrared spectrum of the MC-1 microcapsules

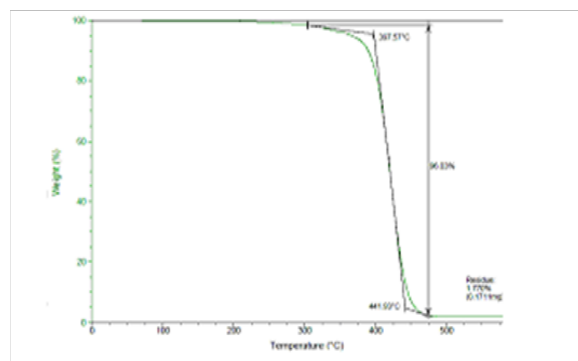


Figure 6 Thermogram of MC-1 microcapsules

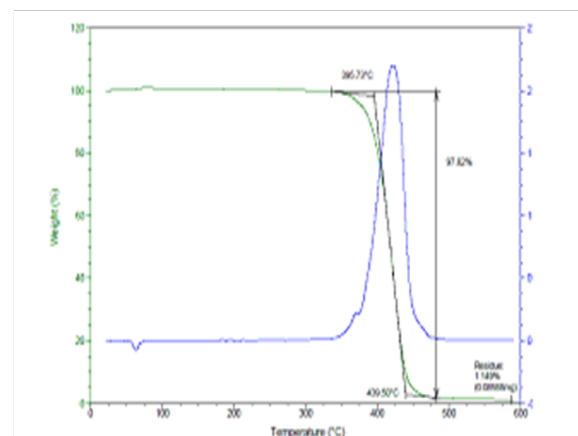


Figure 7 Thermogram of pure PCL

Conclusion

In the study it was possible to produce micro and Microcapsules by emulsion and solvent evaporation method through the preformed polymer (PCL) with an average size of 4 micrometres which was evidenced significant influence on the drying methods of the Microcapsules, as cited in literature, It was proved that the technique of lyophilization is not suited for the formation of Microcapsules. By thermal gravimetric analysis it was observed that the presence of citronella oil did not affected the thermal resistance of the PCL.^{9–13} But it would be still necessary to confirm the encapsulation of citronella oil by other characterization techniques, as well as to quantify the encapsulation compound.

Acknowledgements

The authors thank to FEEVALE, PUCRS and Lab. Biomatter at Lutheran University of Brazil.

Conflict of interest

The author declares no conflict of interest.

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