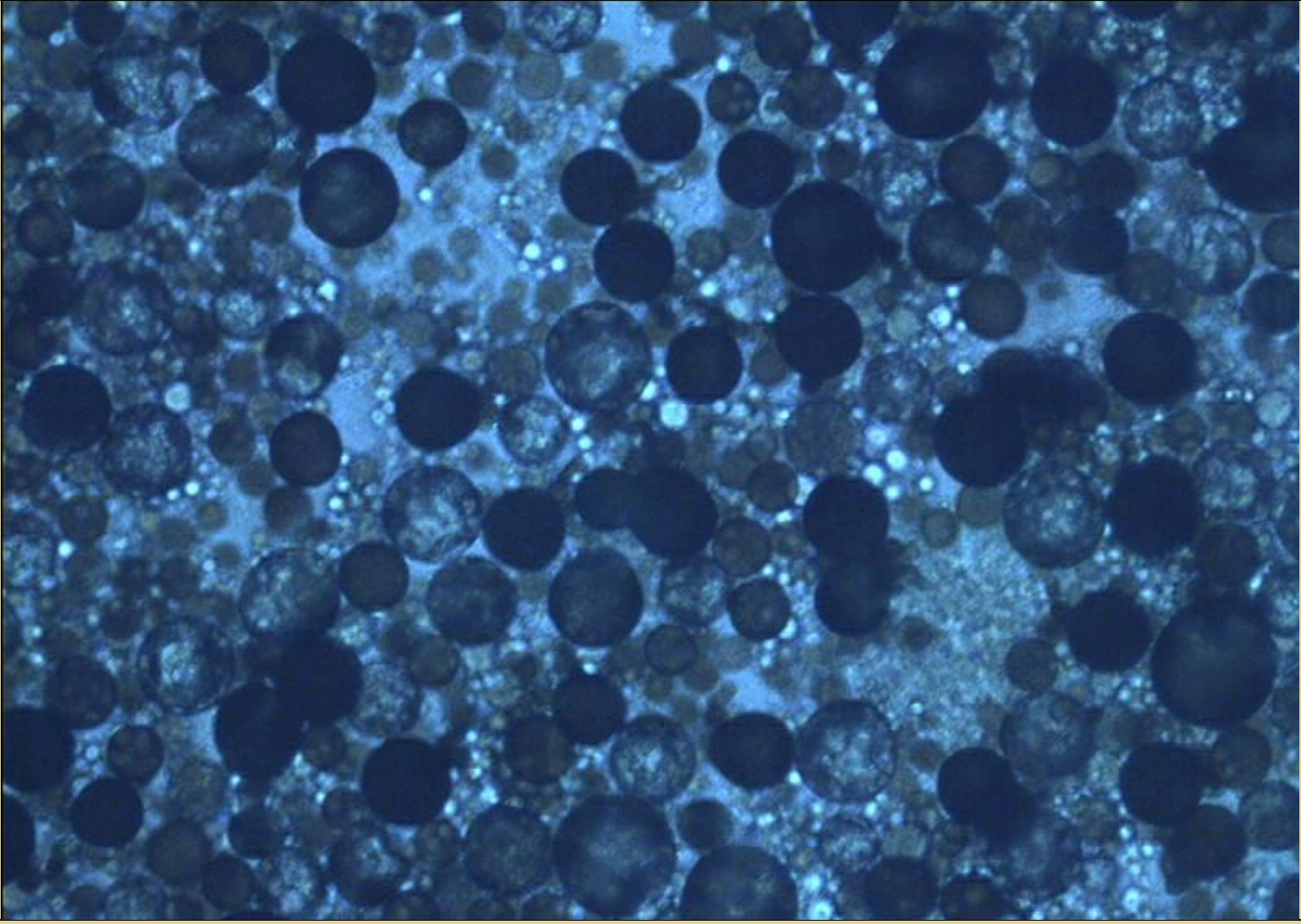

Natasha Rosemary Greg Pinto Pereira

Release of volatile compounds from polymeric microcapsules mediated by photocatatlytic nanoparticles

Biomedical Engineering Integrated Masters Dissertation in the field of Biomedical Instrumentation and Biomaterials presented in the Department of Physics of the Faculty of Sciences and Technology of the University of Coimbra

Sptember 2014

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FCTUC FACULDADE DE CIÊNCIAS
E TECNOLOGIA
UNIVERSIDADE DE COIMBRA

Natasha Rosemary Greig Pinto Pereira

Release of Volatile Compounds from Polymeric Microcapsules Mediated by Photocatalytic Nanoparticles

Dissertation presented to the University of Coimbra to complete the necessary requirements to obtain the degree of Master in Biomedical Engineering

Project Coordinator: Prof. Jorge Coelho

PhD. student Joana Góis

Coimbra, 2014

This work was developed in collaboration with:

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" Algunos persiguen la felicidad, outros la crean"

ABSTRACT

The synthesis of oily-core polyamide microcapsules, by interfacial polymerization from a diamine and a diacyl chloride, was reported. P-phenylenediamine (PPD) and sebacoyl chloride (SC) were used as monomers. The inner oily core of the microcapsules was composed by dodecane as proof of concept. The addition of oleic acid to the organic phase enhances the microcapsule membrane properties. The microcapsule membrane was characterized by Scanning Electron Microscopy (SEM). The surface of the polymeric microcapsules was coated with photocatalytic nanoparticles, for ultraviolet (UV)-light-induced oil release. The fixation of titanium dioxide nanoparticles (TDN) into the microcapsules surface was enhanced by using a cationic emulsifier, cetrimonium bromide (CB). Different methods and different CB concentrations were used in order to improve the TDN surface fixation. The degradation process of the TDN-coated polyamide microcapsules, under different UV irradiations and different time exposure were also evaluated using a simulated method based on polyamide pellets, but it was not possible to draw conclusions. Due to the lack of success of the tests performed, the TDN coated polyamide membrane degradation requires further studies. Due to its properties, the presented oily-core TDN-coated microcapsules could be used in various different applications, such as microencapsulation insecticide application.

Keywords: Oily core microcapsules, interfacial polymerization, titanium dioxide nanoparticles, ultraviolet light degradation

RESUMO

Foi realizada a síntese de microcápsulas de poliamida com óleo encapsulado, por polimerização interfacial a partir de uma diamina e de um cloreto diacílico. A *p*-phenilenodiamina (PPD) e o cloreto de sebacóilo (SC) foram utilizados como monómeros. Foi utilizado como modelo o interior oiléico das microcápsulas que é composto por dodecano. A adição de ácido oléico à fase orgânica melhora as propriedades da membrana das cápsulas. A membrana das microcápsulas foi caracterizada por Microscopia Electronica de Varrimento (SEM). A superfície das microcápsulas poliméricas foi revestida com nanopartículas fotocatalíticas, para a libertação de óleo induzida por radiação ultravioleta (UV). Foi melhorada a retenção de nanopartículas de dióxido de titânio (TDN) na superfície das microcápsulas usando o brometo de cetrimónio (CB) como um emulsificante catiónico. Foram usados diferentes métodos e diferentes concentrações de CB com o objectivo de melhorar a fixação do TDN na superfície. Foi também avaliado o processo de degradação das microcápsulas de poliamida revestidas com TDN, sob diferentes irradiações UV e diferentes intervalos de tempo de exposição, usando um método simulado baseado em pastilhas de poliamida, mas não foi possível tirar nenhuma conclusão. Devido ao insucesso dos testes realizados até agora, a degradação da membrana das microcápsulas de poliamida revestidas com TDN requer a necessidade de mais estudos. Devido às suas propriedades, as microcápsulas com óleo encapsulado revestidas com TDN apresentadas neste trabalho, podem ser usadas em diversas aplicações, tais como na microcencapsulação de insecticidas.

Palavras-chave: Microcápsulas com óleo encapsulado, polimerização interfacial, nanopartículas de dióxido de titânio, degradação sob luz ultravioleta

NOTATION AND GLOSSARY

CB - Cetrimonium Bromide

CdB - Conduction Band

CMC - Critical Micelle Concentration

DMSO - Dimethyl Sulfoxide

DMSO-d_6 - Deuterated Dimethyl Sulfoxide

FTIR - Fourier Transform Infrared

^{1}H-NMR - Proton Nuclear Magnetic Resonance

IR – Infra-red

OM - Optical Microscopy

PZC - Point of Zero Charge

PPD - *P*-phenylenediamine

PVA - Polyvinyl Alcohol

KBr - Potassium Bromide

SC - Sebacoyl Chloride

SEM - Scanning Electron Microscopy

TiO_2 – Pure Titanium Dioxide

TDN - Titanium Dioxide Nanoparticles

TGA - Thermogravimetric Analysis

Tween® 20 – Polyoxyethylene Sorbitan Monolaurate

UV - Ultraviolet

VB - Valence Band

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CHAPTER I

INTRODUCTION

1. INTRODUCTION

1.1. MOTIVATION

In recent years, the delivery of drugs and other active substances has become a field of special interest for biomedical aims as it also has in other fields. Microencapsulation is widely used in pharmaceutical, biomedical engineering and agrochemical applications, namely as drug delivery systems, pesticides and insecticides, to provide better health conditions or for industrial activities [1, 2]. Here, the focus is given to the creation of microcapsules for insecticides release.

The simplest and most cost-effective method of delivery has traditionally been unprotected active substance delivery. A proposed solution to this problem is the use of microcapsules to encapsulate active compounds, protecting them from environmental conditions either to avoid side effects of the active ingredient or to prolong its storage life time [1]. Polymer microcapsules are attracting worldwide attention as they are able to perform strong drug delivery systems, ideal for the release processes of active substances [3]. Among them, polyamide microcapsules stand out due to their fast and easy preparation process, with different techniques existing for the production of these microcapsules, such as interfacial polymerization [4].

Titanium dioxide nanoparticles (TDN) have photocatalytic properties, which involve the light-induced catalysis of reducing and oxidizing reactions that can occur with organic molecules adsorbed to the surface of the catalyst. Thus if, TDN is adsorbed on polyamide membrane microcapsules it can promote the degradation of these

capsules under UV irradiation, and consequently the release of the encapsulated substance in the microcapsules [5].

1.2. AIMS

After the description of the problem and the motivation presented above, the definition of the aims to achieve and the thesis overview follows. The aim of this thesis is split into three complementary parts: first, the formation of polyamide microcapsules with an oily core, composed by dodecane, and second, the development of TDN coating on these polyamide microcapsules, and third, an understanding of the microcapsule degradation process under UV irradiation.

In detail, the first part is the formation of polyamide microcapsules with an oily core, dodecane, via interfacial polymerization, with the water phase containing a diamine, PPD, and the organic phase containing a diacyl chloride, SC. The second part is based on the development of polyamide microcapsules coated with TDN, with the help of a cationic emulsifier, CB. Lastly, in the third part, there is the study of the microcapsule membrane degradation process under UV irradiation.

CHAPTER II

THEORETICAL BACKGROUND

2. THEORETICAL BACKGROUND

2.1. MICROENCAPSULATION

Microencapsulation of substances in polymeric or other protective shell materials has become a well-established technology for coating and storage of substances until the time that their activity is needed [6-8]. Microcapsules can be used in various fields, including food, agriculture, and many pharmaceutical and medical products for sustained release of active substances [9, 10].

In recent years, microcapsules have been produced with a much smaller size range. Since about 1980 microcapsules have a size range from 1 μm to as much as 100 μm [11]. Active substance-loaded microcapsules of these dimensions are increasingly used in the storage of volatile substances, and controlled release of toxic drugs [12]. Therefore, atmospheric oxidation or hydrolysis can be prevented, as well as reactions with other components of the environmental atmosphere [7, 11, 13].

Microcapsules can be classified in two main types, regarding their structure: (1) membrane-walled, in which the core material is largely concentrated as a reservoir near the centre, and (2) matrix, in which it is dispersed. Membrane-walled microcapsules can be single-core, in which the core material is surrounded by a single membrane; multi-core, in which many active substances are within the microcapsules wall; double/multi-wall, the core material is inside the microcapsule surrounded by two or more walls; irregular, when the microcapsule wall doesn’t have a regular spherical wall. On the other hand, microcapsules can be embedded in a homogenous or heterogeneous matrix (Figure 1) [11, 14].

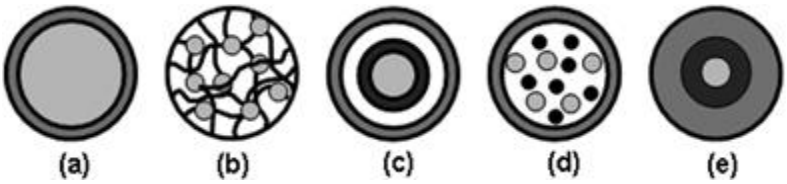


Figure 1 – Microcapsule structure: (a) single-core, (b) heterogeneous matrix, (c) multi-wall, (d) multi-core, and (e) double-wall [15].

The microcapsule wall material has to be selected and determined by the need for a permeable or non-permeable, biodegradable or non-biodegradable shell, depending on the microcapsule's final application. Wall materials can be formed by natural polymers, which can be proteins, nucleic acids and polysaccharides, or by synthetic polymers, such as polyesters and polyamides [16].

Polymers can be synthesized by two different polymerization reactions: addition polymerization, and condensation polymerization. In addition polymerization, polymers are formed by the addition of monomer molecules to each other to form long-chain polymers. On the other hand, condensation polymerization involves the build-up of polymers by the combination of monomer molecules containing reactive functional groups that react, forming new functionalities [17, 18]. Examples of such functional groups are carboxylic acids, which react with alcohols. The condensation reaction of carboxylic acids and alcohols forms esters, and the reaction of carboxylic acids with amines forms polyamides (Figure 2) [19].

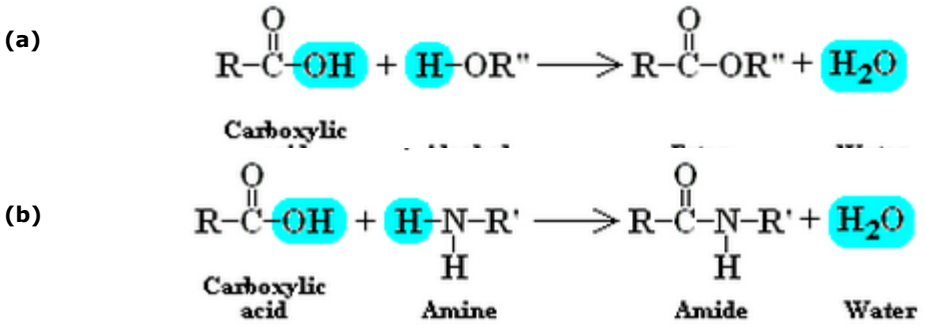


Figure 2 – (a) Formation of esters, from a carboxylic acid and an alcohol functional groups, and (b) formation of amines, from a carboxylic acid and an amine group [19].

Linear polymers can be formed when monomers containing two identical functional groups react with another monomer that contains two other functional groups. Polyethylene terephthalate, a polyester, is one example of a commercial polymer formed by the reaction between dicarboxylic terephtalic acid and dialcohol ethylene glycol (Figure 3) [20]:

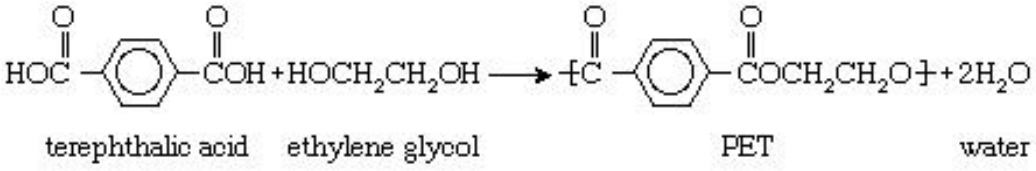


Figure 3 – Polyethylene terephthalate, a polyester, formation by the reaction between dicarboxylic acid terephtalic acid and the dialcohol ethylene glycol [20].

There are many techniques of condensation polymerization. A special classification of condensation polymerization is interfacial polycondensation. In this process, two reactive monomers that are dissolved in two immiscible liquids react by polycondensation reaction

at the interface of the two solutions to form a polymer. In the fast polycondensation reaction, the precipitation of the polymer occurs within minutes, forming a very thin dense film [21]. As the reaction continues, the amine in the aqueous phase crosses the water/organic interface and diffuses through the already formed polyamide layer to react with the acyl chloride on the organic solvent side of the polyamide layer. The growth of the polyamide layer takes place on that side of the interface. The diffusion of the amine towards the inner side of the polyamide increases the thickness of the polyamide film [22, 23].

Interfacial polymerization is a well-known method for the preparation of a variety of polyamides, from aliphatic and aromatic amines in water phase and acyl chlorides in organic phase. One important reaction is that of secaboyl chloride, SC, with *p*-phenylenediamine, PPD, to form a polyamide (Figure 4) [23].

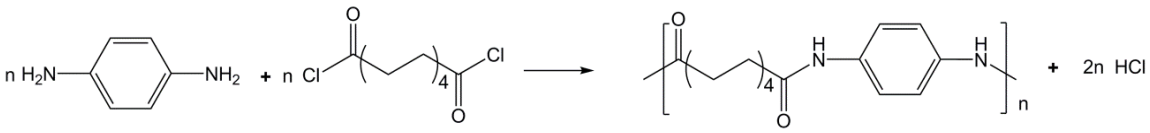


Figure 4– Polyamide formation by the reaction between SC and PPD.

Interfacial polymerization has become a well-established method for the preparation of polymeric microcapsules with very interesting properties [21, 24]. In the case of polyamides they have a high degradation point and high stability [25].

In this assay focus will be on synthetic polymers, namely polyamides, synthesized by interfacial polymerization, between a diamine, PPD, and a diacyl chloride, SC for the preparation of polyamide microcapsules.

2.2. TITANIUM DIOXIDE

Pure titanium dioxide (TiO_2) doesn't occur in nature but is derived from ilmenite or leuxocene ores. It has a wide range of applications. Since the early twentieth century, it has been used as a pigment in paints, coatings, sunscreens, and paper [26].

With the advent of nanotechnology, TDN have found a great deal of applications. Nanotechnology encompasses the understanding of the fundamental physics, chemistry, biology and technology of nanometre-scale objects.[27]. Nanoscale materials such as TDN with such dimension have already found their ways into fields ranging from optoelectronics and sensing to catalysis and medicine, due to their numerous properties, such as unique electronic and chemical properties that arise from their high surface area [28].

In polymer coating with TDN, one very important aspect is the TDN and the protective polyamide layer compatibility. If the small particles have a selective affinity for one of the phases they will be concentrated into this phase during mixing. This partitioning of the particles into one of the two polymer phases is analogous to the partitioning of chemical species in immiscible two-phase solvent systems, often used in interfacial polymerization for microcapsules preparation. The compatibility between the particles and the polymer leads to the dispersion of the TDN in the polymer layer. In solution, the TDN affinity to the polymer has to exceed its affinity to the solvent for the TDN polymer coating to occur [29, 30].

To enhance the polymer-nanoparticle affinity, either components or just one have to be modified with favorably intercoating functional groups. One method for the creation of functionalized polymers is the addition of a charged compound to the polyamide layer. TDN have negative charges on its surface,

Polyamide microcapsules solutions presents a neutral pH and therefore presents a higher pH than the TDN point zero charge (PZC). PZC is the pH at which the TDN surface charge is zero. When pH of the aqueous phase is higher than PZC, TDN present negative charges on its surface [31] (Equation 1). Thus, a mechanism that would favor the positive charges at the polyamide layer, with anion exchange in the aqueous phase, would be using a cation surfactant that partioned into both phases at the interface between the two solvents [32].

Surfactants are amphiphilic molecules that have hydrophilic and hydrophobic segments, so the hydrophilic group will stay positioned in the aqueous phase and the hydrophobic group will stay in the organic phase, positioning themselves in the interface of these two solvents [33]. Hexadecyltrimethylammonium bromide (also known as CB), is a quaternary ammonium salt which has a positively charged nitrogen atom and four alkyl groups linked at the central nitrogen atom [34], with the chemical structure presented in Figure 5. The polar group is the one that contains the positive charge, so this positive charge will stay at the aqueous side of the interface and consequently, at the aqueous side of the microcapsules. Like this, the positive charges are available for electrostatic interactions with the negative charges in the surface of TDN [35-37].

$$\mathrm{TiOH} + \mathrm{OH}^- \longleftrightarrow \mathrm{TiO}^- + \mathrm{H_2O}.$$

Equation 1 – Negative charged TDN surface [31].

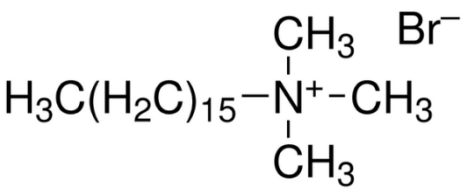


Figure 5 – Chemical structure of CB [38].

In this assay CB will be used for the enhancement of TDN coating of the microcapsules polyamide layer.

2.2.1. PHOTOCATALYTIC PROPERTIES OF TDN:

TDN have a very important property, its photocatalytic activity. In addition to TiO_2, there are many metal oxides and sulfides that have been successfully tested in photocatalytic reactions. Among these are ZnO and Fe_2O_3 [5, 39]. These semiconductors react with photons. When photons have energy equal to or higher than the band gap of the semiconductors, an electron is projected from the valence band (VB) to the conduction band (CdB). The VB is where the electrons do not have free movement, and the higher energy region, the CdB, is where electrons move freely through the crystal. This event generates an electron-hole pair (Equation 2) [31]. For TiO_2 this energy can be supplied by photons with energy in the near ultraviolet (UV) range. This property promotes TiO_2 as a promising candidate in photocatalysis where solar light is used as the energy source [40].

$$TiO_2 + hv \rightarrow h^+_{BV} + e^-_{BC}$$

Equation 2 – Electron-hole pairs light-induced formation, in TiO_2 [31].

VB potencial (h^+) is positive enough to generate hydroxyl radicals ($^{\bullet}OH$) at TiO_2 surface and the conduction band potential (e^-) is negative enough to reduce molecular oxygen as described in Equations 3 and 4 [31].

(3) $$O_2 + e^- \rightarrow {}^{\bullet}O_2^-,$$

(4) $$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+.$$

Equation 3 and 4 – Generation of oxygen and hydroxyl radicals at TiO_2 surface [31].

The hydroxyl radical can attack and oxidize substances present at or near the surface of TiO_2. These reactions are able to degrade toxic compounds into harmless species (e.g. CO_2, H_2O, etc.) [41, 42]. A schematic representation of TDN photocatalytic reactions is presented in Figure 6.

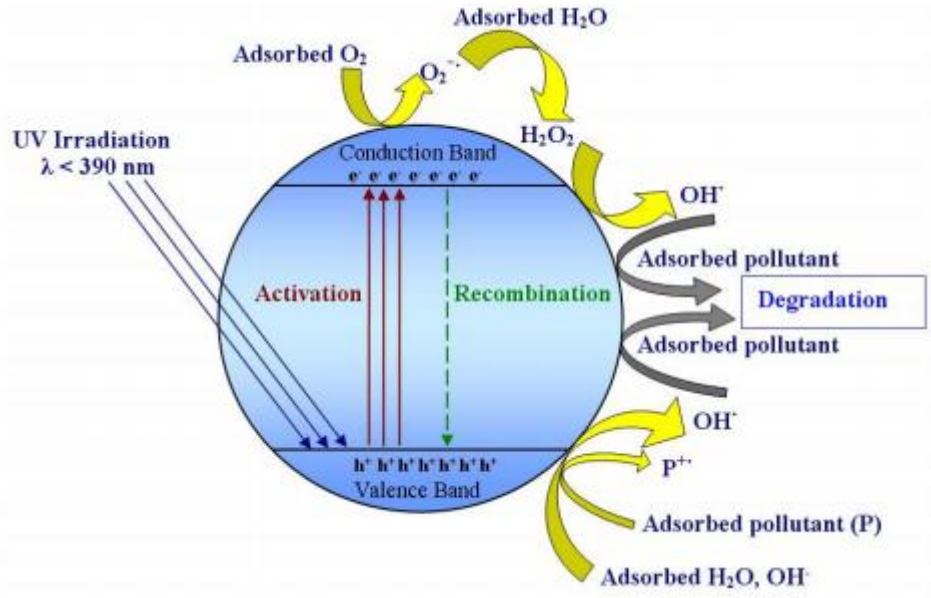


Figure 6 – Generation of photocatalytic active species at the surface of TiO2 nanoparticles. Adapted image from [43].

TDN can be immobilized on many different inorganic substrates. However, TDN coating on polymer substrates is still in its early stages of development Polymers have many properties that make them a suitable material to be coated, such as flexibility, impact resistance and low cost. Thus, coated polymers with photocatalytic properties

can be used in various areas ranging from the construction industries to food packaging, or in insecticides [44, 45].

In this thesis TDN will be used on the polyamide microcapsules coating, in order to promote capsule membrane degradation and, consequently, the release of the oil encapsulated in these microcapsules.

CHAPTER III

EXPERIMENTAL WORK

3. EXPERIMENTAL WORK

3.1. MATERIALS

Sebacoyl chloride (SC) (Sigma-Aldrich, 92%), *p*-phenylenediamine (PPD) (Sigma-Aldrich, 99%), dodecane (Sigma-Aldrich, annhydrous, 99%), poly(vinyl alcohol) (PVA) (Sigma-Aldrich, 99% hydrolyzed), polyoxyethylene sorbitan monolaurate (Tween® 20) (Sigma-Aldrich), calcium carbonate (Sigma-Aldrich), potassium bromide (KBr) (Sigma-Aldrich, 99% trace metals basis), oleic acid (Acros Organics, 97%), hexadecyltrimethylammonium bromide (CB) (Rona Care® Merck, 98%), , 1,1,1,3,3,3-hexafluoro-2-propanol (Sigma-Aldrich, 99%), diethyleneglycol-monobutylether (Sigma-Aldrich, 98%) dimethyl sulfoxide (DMSO) (Fisher Scientific), hexane (Sigma-Aldrich, annhydrous, 99%) and deuterated DMSO (DMSO-d6) (Euriso-top) were used as received.

Titanium Dioxide Nanoparticles (TDN) P25 (25 nm) were synthesized by University of Minho.

3.2. CHARACTHERIZATION TECHNIQUES

In this section the basic techniques used to characterize the products obtained throughout the entire work will be explained.

3.2.1. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

This analytic technique is very useful for the identification and characterization of the functional groups present in a given sample. This identification is based on the detection of the vibrations caused by the interaction between the atoms of the sample and the incident infra-red (IR) radiation [46].

With the incidence of IR radiation on the sample, a spectrum that shows the fraction of radiation transmitted in a particular energy range is obtained, compared to a reference spectrum of energy transmittance recorded previously with no samples. Each functional group exhibits a specific vibration frequency, so in the spectrum this specific vibration corresponds to a distinct energy peak, allowing the identification of the group [46].

Fourier Transform Infrared (FTIR) spectra were carried out in FTIR-4200 spectrophotometer by Jasco recorded at a wavelength comprised between 550 and 4000 cm^{-1} and with 4 cm^{-1} resolution (Figure 7). Potassium Bromide (KBr) mode was used.

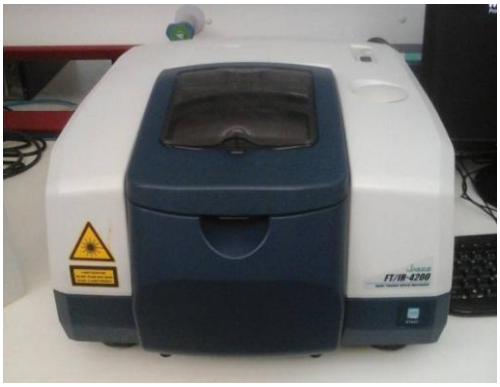


Figure 7 – FTIR spectrophotometer.

3.2.2. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (^{1}H NMR)

^{1}H-NMR spectroscopy is a technique that facilitates the understanding of the chemical behaviour of a given sample when exposed to a powerful magnetic field and irradiated with radiofrequency radiation [46, 47].

When a magnetic field is applied to the sample, the nuclei of a non-null nuclear spin tend to align and to acquire the orientation of the same or the opposite direction of the applied field. At this point, the irradiation of the nuclei with radiofrequency radiation causes their spins to transit to a higher level of energy. The absorbed and emitted energy is then quantified and represented in a spectrum [46].

This spectrum data allows the characterization of the chemical products both in a quantitative and qualitative way.

Proton Nuclear Magnetic Ressonance (^{1}H NMR) spectra were obtained at 25ºC in a Varian Unity 600 MHz Spectrometer using a 3 mm broadband NMR probe, using DMSO as deuterated solvent (DMSO-d_6).

3.2.3. SCANNING ELECTRON MICROSCOPY ANALYSIS (SEM)

SEM is a method for high-resolution imaging of surfaces, using electrons for imaging. The SEM generates a beam of incident electrons positioned onto the sample surface. These incident electrons cause electrons to be emitted from the sample that are referred to as backscattered and secondary electrons. To create a SEM image, the incident electron beam is scanned in a raster pattern across the sample's surface and the emitted electrons are detected for each position in the scanned area by an electron detector[46, 48].

In SEM analyses the samples were coated with gold so they could be seen by the microscope (Figure 8), since they aren't conductive[48].

Some samples were observed placed in a polycarbonate filter and others in a lamella, dried at room temperature and only analyzed once completely dried.

Figure 8 – SEM analysis.

3.2.4. THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA is a technique that analyzes the thermal stability of the samples through the mass variation study, as a function of temperature and/or time, when the samples are subjected to temperature. In addition, it can also be represented its derived that allows analyzing the degradation rate (designated DTG curve). Its main advantages are the study of the samples in a wide range of temperatures, requiring only a small amount of sample, as well as the possibility of changing the surrounding atmosphere [49].

IN TGA analysis it was used a SDT equipment (TA instruments), at a heating rate of 10ºC/min, from room temperature till 600ºC, under a constant nitrogen flow.

3.3. PREPARATION OF POLYAMIDE MICROCAPSULES

The schematic representation of the methods used to prepare the polyamide microcapsules is present in

Figure 9. The general method for the microencapsulation of dodecane into polyamide microcapsules was already reported in the literature [23, 31].

For the preparation of the polyamide microcapsules, the oily phase, composed by dodecane (1 mL, 4.579 mmol), SC (200 µL, 0.938 mmol) and oleic acid (100 µL, 0.317 mmol) were added dropwise into a 25 mL of surfactant aqueous solution (PVA 2% (m/v) and Tween® 20 1% (m/v)) under a vigorous stirring. This oil-in-water emulsion was stirred at 1200 rpm for 3 minutes. The speed agitation dropped to 400 rpm and an aqueous solution of PPD (50 mL, 2.000 g, 0.018 mol was added. The reaction proceeded for 1 hour at room temperature. The resultant polyamide microcapsules were filtered with a polycarbonate filter (diameter – 47 mm, pore size - 2 µm, Whatman), washed with an aqueous solution of ethanol 10% (v/v) and dried at room temperature. This method used is represented in strategy 1, steps 1.1 and 1.2 of Figure 9.

When CB was used at the moment of the microcapsules formation it was previously dissolved in the surfactant aqueous solution (4.22 mg, 0.012 mmol and 6.75 mg, 0.019 mmol). (see strategy 2, steps 2.1 and 2.2 of Figure 9).

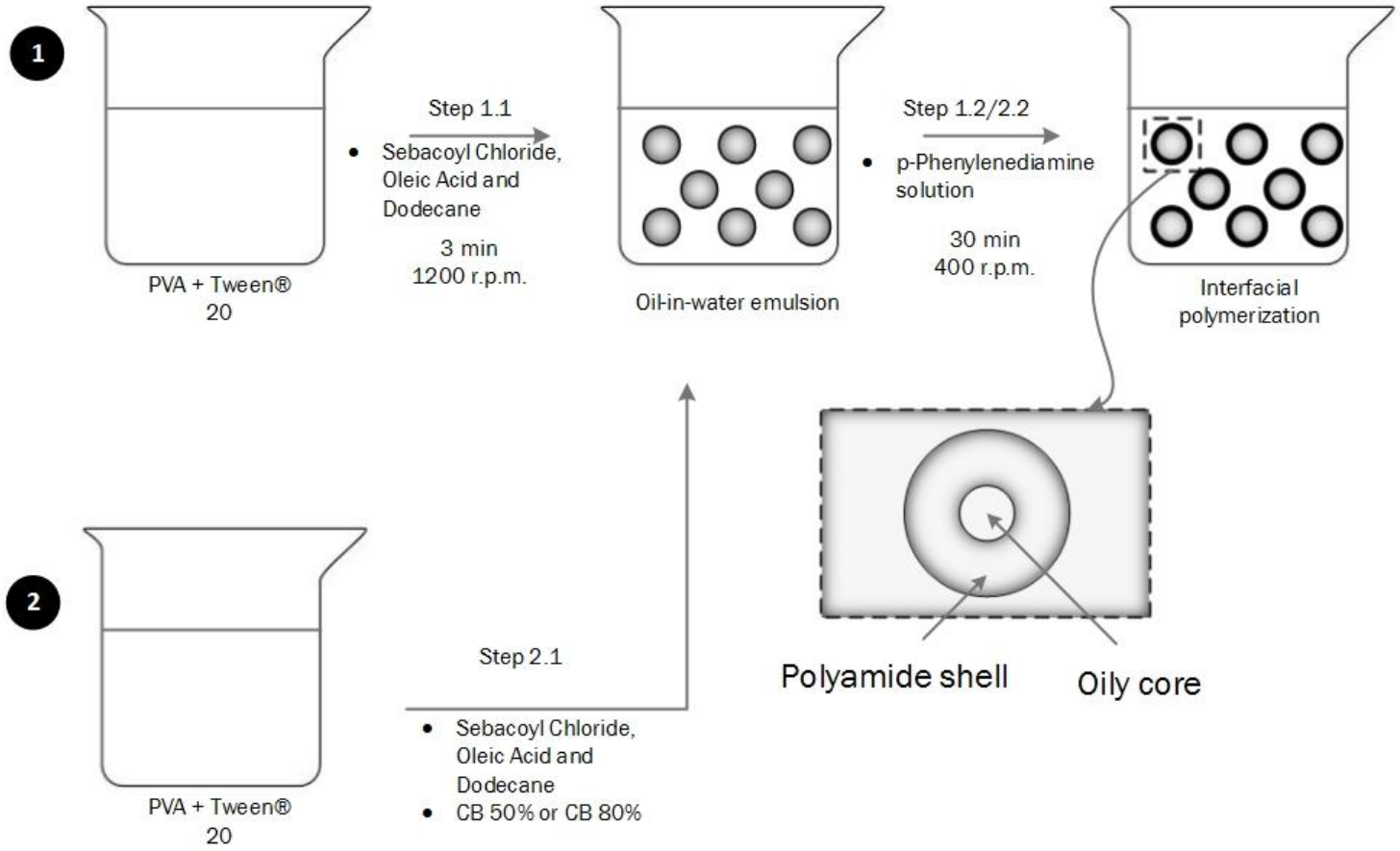


Figure 9 – Two different methods for the preparation of polyamide microcapsules.

PPD was used as hydrophilic monomer because it has very special properties like a rigid structure, due to its aromatic ring, and a high melting point. The hydrophobic monomer, SC, is one of the most commonly applied diacyl chlorides and was chosen due to its solubility in the organic phase, dodecane. The oil encapsulated in the polyamide microcapsules was dodecane. It was used as a proof of concept for hydrophobic organic compounds for microencapsulation applications.

Due to the sensitivity of the method, the reaction conditions were crucial to the formation of the microcapsules and the reproducibility of the method. All of the microcapsule formation assays were performed using the same conditions.

First, for microcapsule synthesis, there is the preparation of a stable oil-in-water emulsion, containing the organic solution of dodecane and lipophilic monomer, in an aqueous medium, in an aqueous/organic phase ratio of 25/1 (v/v).

The polyamide microcapsule synthesis consists of the formation of the capsule membrane at the interface between the oil droplets and the water medium, with the hydrophilic monomer diffusing into the organic phase, reacting with the lipophilic monomer, via interfacial polymerization. In this polycondensation reaction, hydrochloric acid is formed. Thus, an excess of the hydrophilic monomer is added for the solution neutralization, increasing the pH of the aqueous phase, in a PPD/SC ratio of 20:1 (molar).

For the preparation of a stable emulsion, it is very important to know the optimal conditions to use. In this work, an agitation rate of 1200 rpm was used and this value of agitation to produce the capsules, used already in reference [31]. Lower agitation rates have showed in reference [31] to produce bigger droplets which is closely related to the small size of the microcapsules [51, 52].

As reported in earlier studies, emulsion stirring time also affects the microcapsules' size. Longer stirring times decrease the droplets' size, and, consequently, decrease the capsules' diameter [53, 54]. The stirring time chosen for this work was 3 minutes, used as well in reference [23]. This time also has to be determined taking into account acyl chloride hydrolysis, which is a side reaction that decreases the amount of SC available for the interfacial polymerization for polyamide microcapsule formation [23]. Thus, the stirring time affects the polyamide layer formation rate (Figure 10).

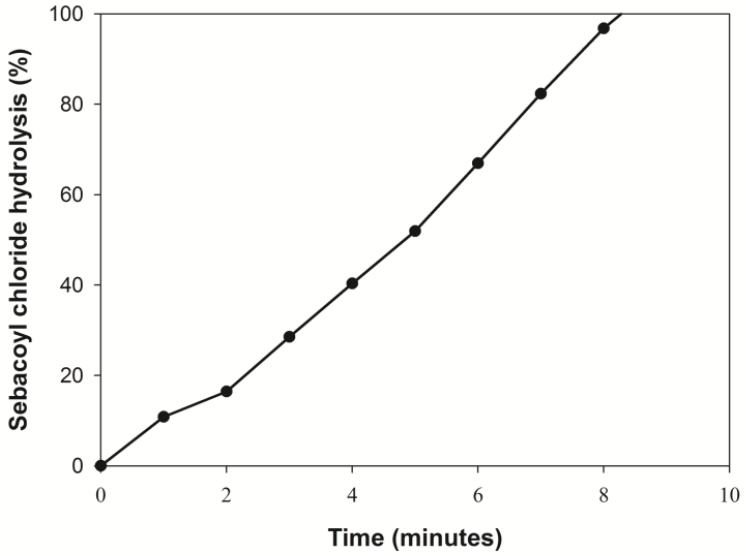


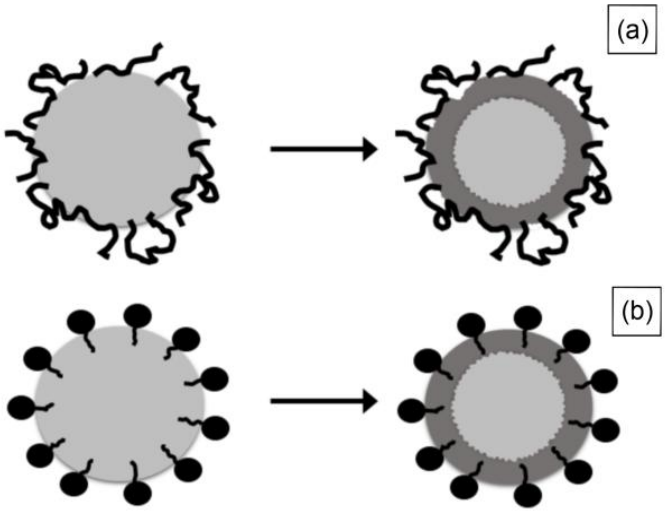
Figure 10 -Hydrolysis of acyl chloride [23].

A propeller-shaped stirrer was used. The oil-in-water mixture results in the oil droplets colliding with one another, resulting in coalescence in larger droplets that leads to a distraction of the spherical particles. For this reason a propeller-shaped stirrer was chosen, which allows high energy input for a stable emulsion formation [52] , used also in reference [23] (Figure 11).

Figure 11 - Propeller shape stirrer.

In the emulsion step, there were used stabiliziers, VA and Tween® 20. PVA acts a protective colloid adsorbed in the oil/water interface, providing a steric stabilization by creating a physical barrier at the oil/water interface. On the other hand, Tween® 20, as an amphiphilic compound, that which has polar and apolar heads facing water and oily phases, respectively, at their interface, provides electrostatic interactions, as is shown in Figure 12 (A) [55, 57, 58]. Tension gradients which are generated by the interfacial stress, due to droplets collision, have the tendency to oppose to this droplets coalescence and restaure the uniform initial state of the droplets. The diffusion of the surfactants into the oil/water interface reduces the droplets collision, by steric and electrostatic interactions, contributing to a stable emulsion preparation (Figure 12 (B)) [59].

(A)



(B)

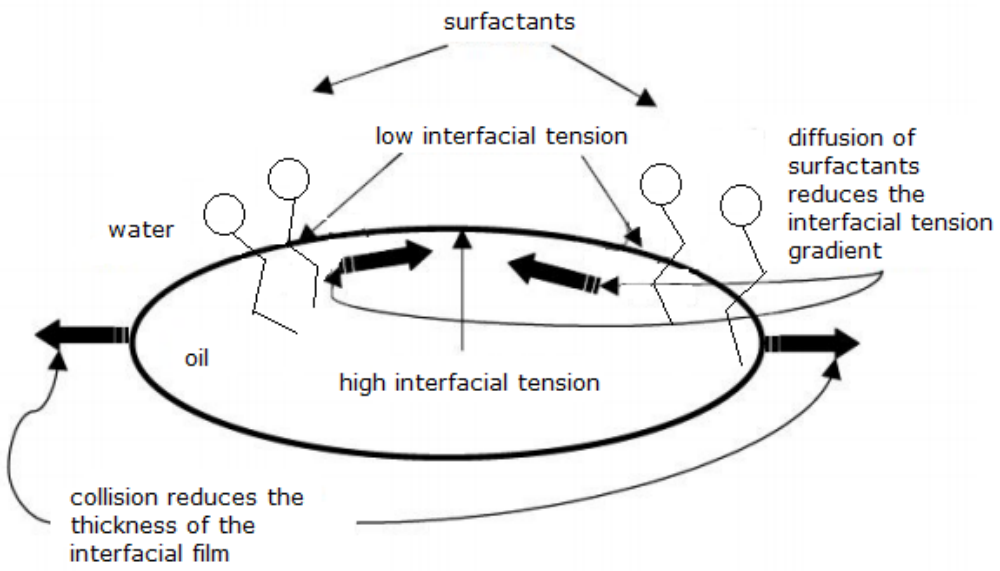


Figure 12 - Schematic representation of stabilizers conformation at the interface- (A) (a) PVA and (b) Tween® 20 [23], and (B) surfactants in an oil-in-water emulsion, adapted image from [62].

3.4. FIXATION OF TDN ON THE POLYAMIDE MICROCAPSULES SURFACE

An aqueous solution of TDN (1 mg/mL) was prepared as follows: firstly, 30 mg of TDN were mixed in 30 mL of water under ultrasounds agitation at 130 Joules and 28 Watts, for 1 minute. The solution was cooled in ice for 3 minutes, ultrasound stirred under the same conditions for one more minute and cooled in ice for more 5 minutes.

For the TDN fixation into the microcapsules surface, 1 mL of the previous TDN solution was added dropwise to the final polyamide microcapsules suspension and mechanical stirred (300 rpm.), for 1 hour. This method is described in Figure 13, which is the continuation of strategy 1, steps 1.1 and 1.2, of Figure 9.

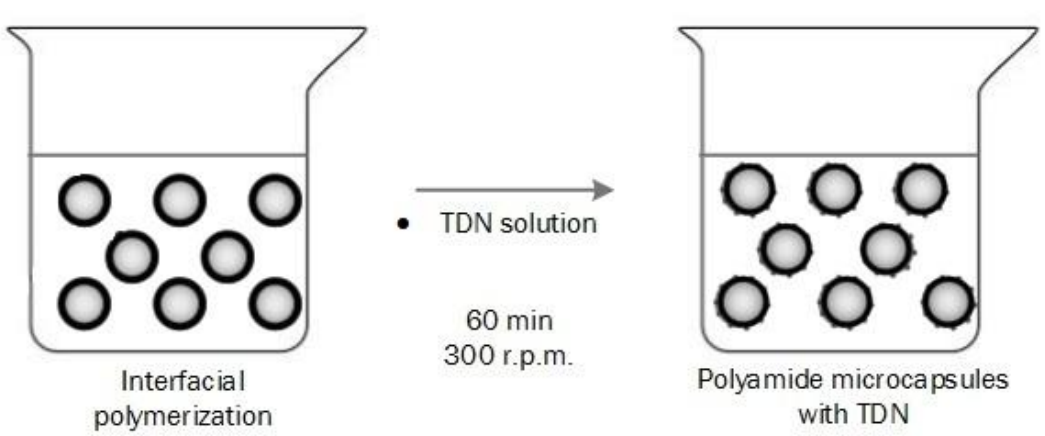


Figure 13 – Method for the TDN addition into the polyamide microcapsules solution.

When CB was used after microcapsule formation it was added to the final polyamide microcapsule suspension as represented in Figure 14, continuing strategy 1, steps 1.1 and 1.2 of Figure 9.

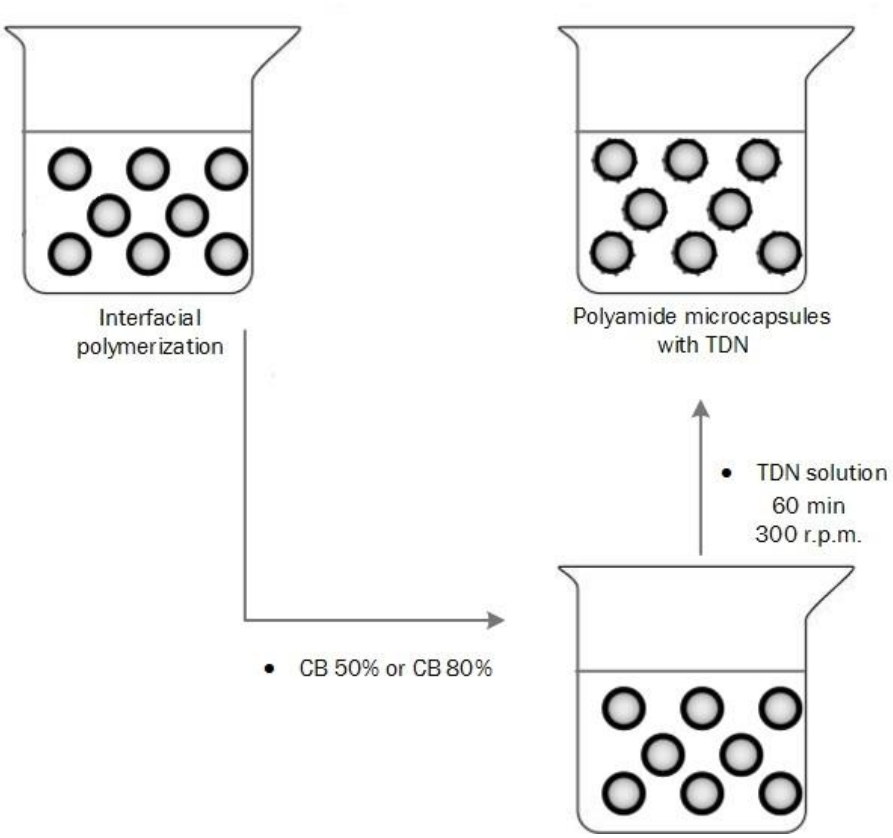


Figure 14 – Method for CB addition after the polyamide microcapsule synthesis with after TDN addition.

3.5. PREPARATION, TDN FIXATION AND IRRADIATION OF THE POLYAMIDE PELLETS

3.5.1. PREPARATION OF POLYAMIDE PELLETS

The schematic representation of the methods used to prepare the polyamide pellets, the TDN fixation on them and their UV-light irradiation are present in Figure 15.

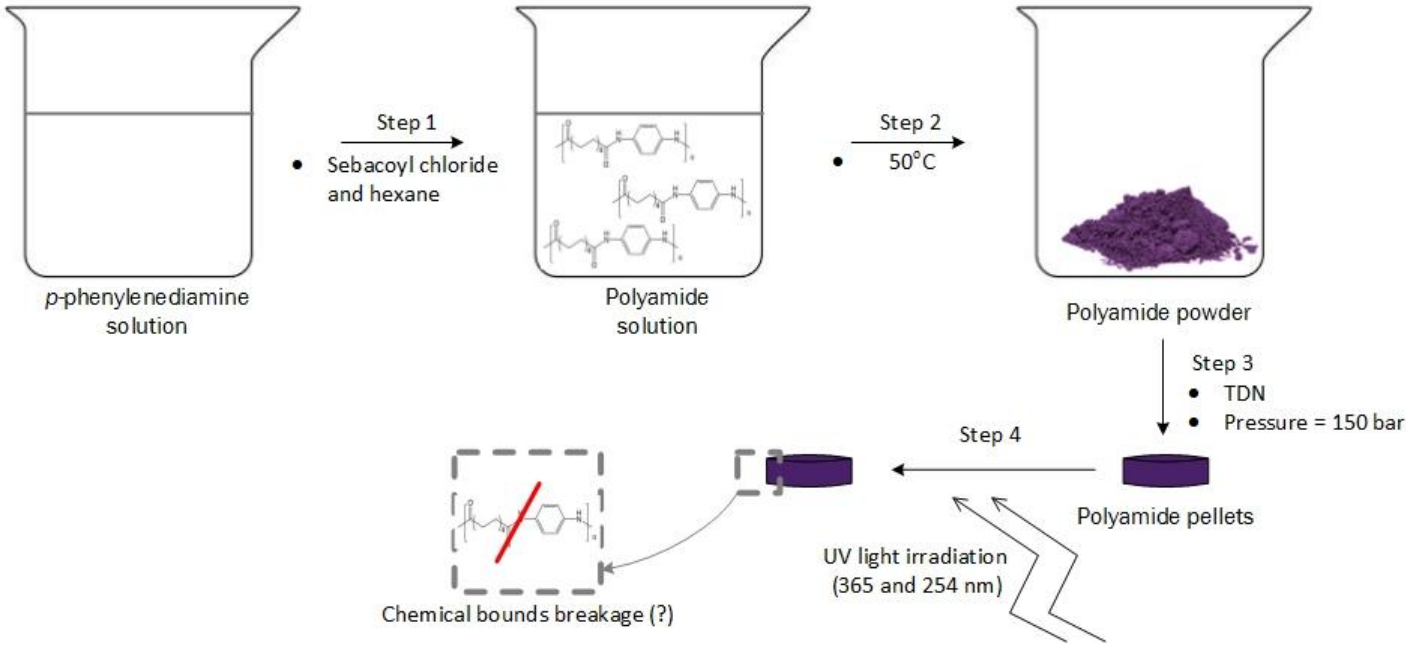


Figure 15 – Method for the preparation of the polyamide pellets with TDN coating and their UV light irradiation.

The polyamide used to prepare the pellets was prepared according to the typical interfacial polymerization. Firstly 25 mL of an aqueous solution of PPD solution (4.00 g – 0.037 mol) and calcium carbonate ($CaCO_3$) (3.983 g) was prepared, and then, a mixture of SC (3 ml – 0.014 mmol) and hexane (10 ml – 0.075 mol) was added very slowly. The reaction proceeded under magnetic stirring for 1

hour at 25ºC. The final product was filtered and washed with an aqueous solution of ethanol 10% (v/v). The polyamide powder was dried at 50ºC.

Polyamide pellets were prepared by pressing 100 mg of the resultant polyamide powder using a stainless steel mould in a hydraulic press (Specas), at 150 bars and room temperature.

3.5.2. FIXATION OF TDN ON THE POLYAMIDE PELLETS

The fixation of TDN to the polyamide pellets was performed using two different strategies. In the first one, 1 ml of the TDN aqueous solution was added, drop-by-drop, on top of the pellets until the pellets were completely coated (5 drops approximately). They were dried over night at room temperature. In the second method, the TDN (1 and 5 mg) was mixed with the polyamide powder (100 mg) and this mixture was pressed using the same press and mould described in the previous section, at 150 bars and room temperature.

3.5.3. IRRADIATION OF THE POLYAMIDE PELLETS

The polyamide pellets were irradiated by UV light using two different UV equipments: mercury vapor lamp (125 Watts) with 365 nm, and a UV irradiation Dr. Grobel, UV-Electronik GmbH chamber with 254 nm during different time intervals.

CHAPTER IV

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

In this chapter all the results obtained throughout this work will be described in detail and discussed.

4.1. PREPARATION OF POLYAMIDE MICROCAPSULES

Polyamide microcapsules were prepared by interfacial polymerization, in an oil-in-water emulsion, between a lipophilic diacyl choride, SC, and a hydrophilic diamine, PPD, as schematized in Figure 4 in the first chapter. The chemical structures of the monomers are presented in Figure 16.

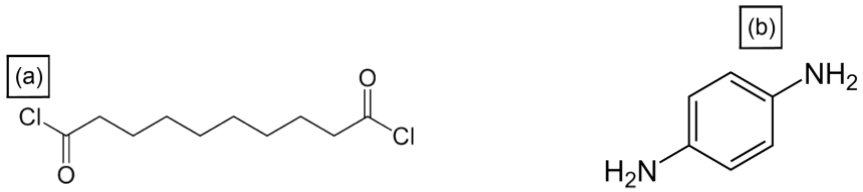


Figure 16 – Chemical structures of the monomers used in the interfacial polymerization, SC and PPD [50].

With optical microscopy (OM) analysis the successful preparation of microcapsules was confirmed (Figure 17). The images at the two possible magnifications display many round-shaped microcapsules with a uniform cell wall, with different diameters. The inspection of the different size fractions showed no visible difference in the product: the capsules were all globular and hardly any impurities could be found [55].

Figure 17 shows that at an emulsion stirring rate of 1200 rpm, microcapsules in the size range of about 20-60 μm were produced

and no clusters and agglomerations are formed between the microcapsules. Thus, a good dispersion of the oil droplets in the aqueous phase, a stable emulsion, with the stirring rate, stirring time and stirrer shape used was performed [56].

To ascertain the surface morphology, size and shell-thickness of the microcapsules formed, SEM characterization was performed, as SEM allows the inspection of the capsule shell at higher magnification.

Based on the SEM characterization result, the polyamide microcapsules revealed that all prepared microcapsules were spherical in shape and possessed a smooth exterior surface (Figure 17 (a) and (b)), as has been obtained in previous studies [23, 31]. Microcapsules also showed a 20-60 μm particle size obtained, confirming the size range observed in Figure 16 (Figure 17 (a)). Figure 17 (b) shows the surface morphology of the microcapsules, with their smooth external surface.

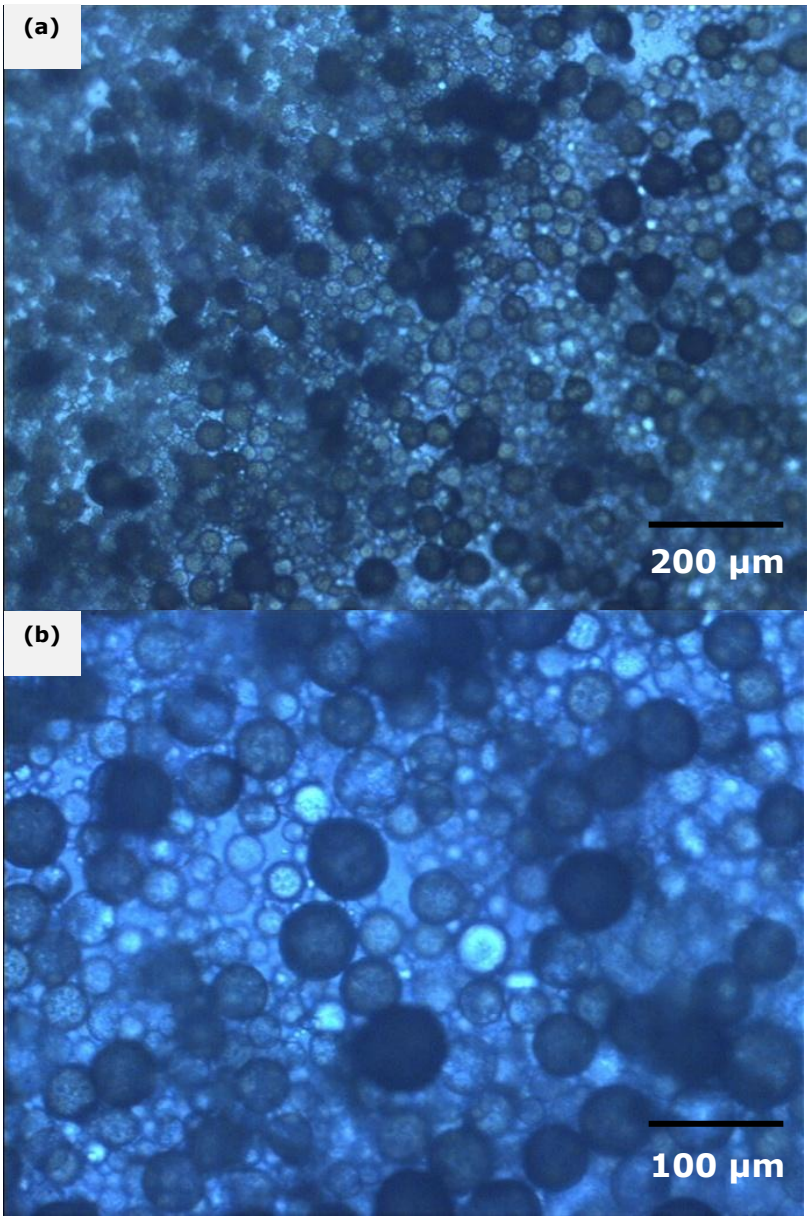


Figure 17 - OM images of polyamide microcapsules.

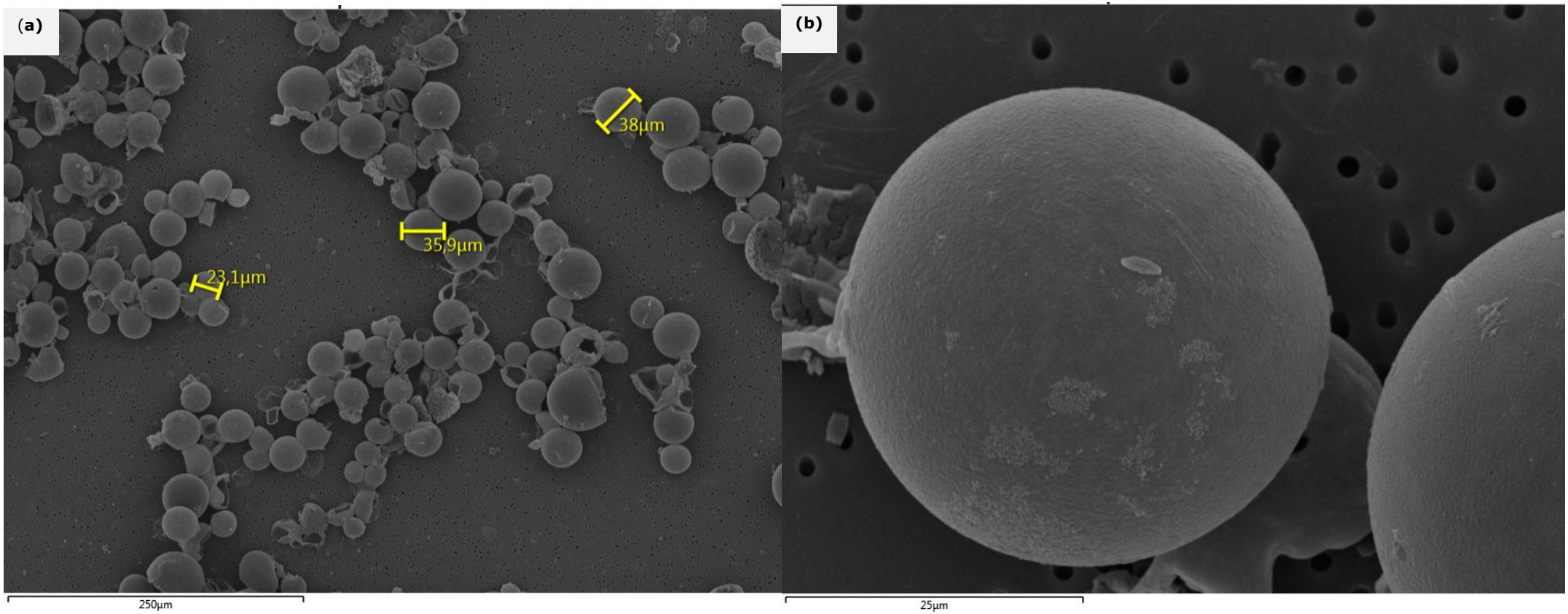


Figure 18 – SEM images of the polyamide microcapsules.

Although some collapsed and deformed spheres were observed, most of them were intact. The ruptured microcapsules showed differences between the external and internal surfaces of the capsules. Figure 19 (a) and (b) show the rough inner shell membrane morphology contrasting with the smooth exterior visible membrane. This continuous exterior membrane is formed as SC reacts with PPD in the aqueous phase, resulting in a polyamide film deposited at the oil/water interface. As was already explained in the second chapter, as the reaction between PPD and SC monomers progresses, the rough interior is formed, as the growth of the membrane occurs towards the organic phase. This inward growth of the polymeric membrane is explained by the polymerization rate that is controlled by the mass transfer of the PPD to the organic phase. Thus, longer polymerization times yield thicker membranes [22]. The smooth external surface is obtained due to the stabilizers used in the polyamide microcapsules synthesis. Oleic acid was also studied and showed to effectively improve membrane stiffness and consequently successful encapsulation of the core-oil [23].

The microcapsules were shown to have a range thickness of 900nm to 3μm (Figure 19 (b)), measured with the help of SEM to the microcapsules that were already ruptured. The supply of reactants in the interfacial polymerization reaction is limited, and, an extremely thin film may be achieved [60]. The membrane thickness depends on the ratio of the core shell material used in the polymerization [61].

Changing the ratio of the amine monomers changes the degree of cross-linking during polymerization. Porosity increases with increasing ratio PPD/SC ratio [63]. With the ratios used in this work, spherical openings, small in size and that resemble pores, are observed on the polyamide microcapsules surface [1]. Figure 20 shows a porous external surface with pores that possess quite a broad size distribution.

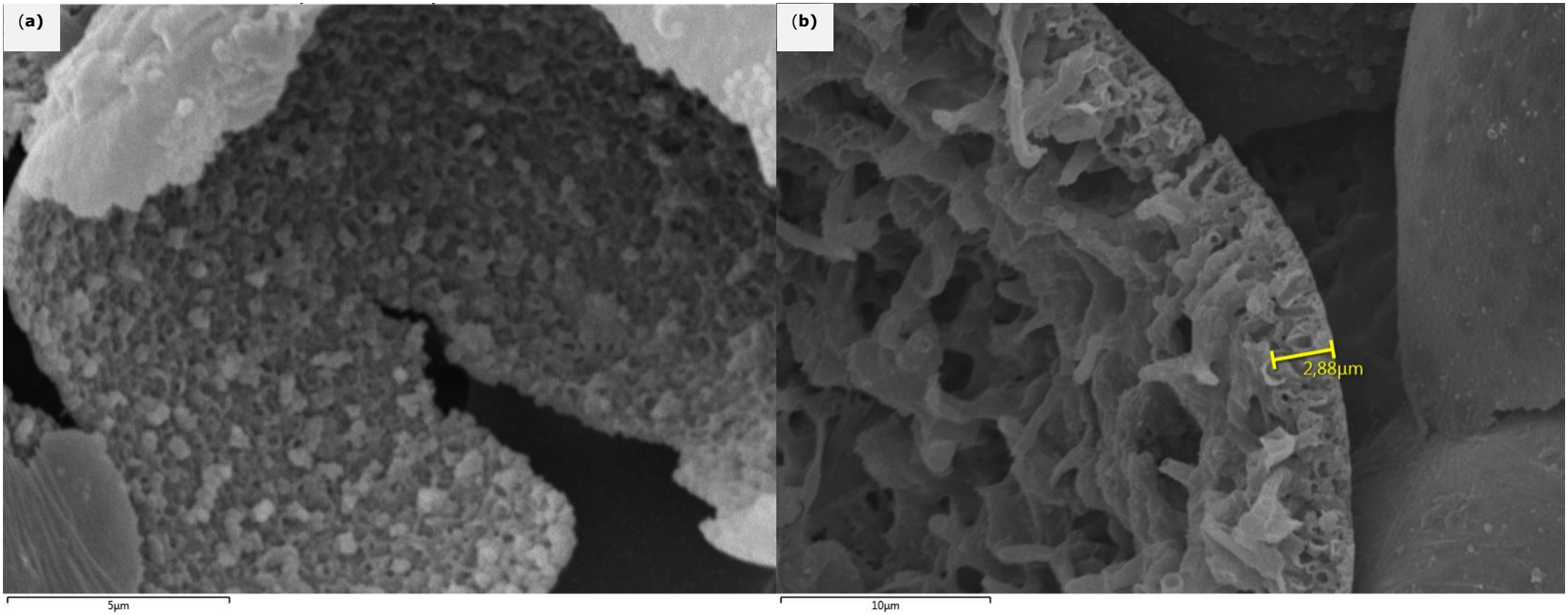


Figure 19 – (a) SEM images of polyamide microcapsules internal and external surfaces and (b) membrane thickness of polyamide capsules.

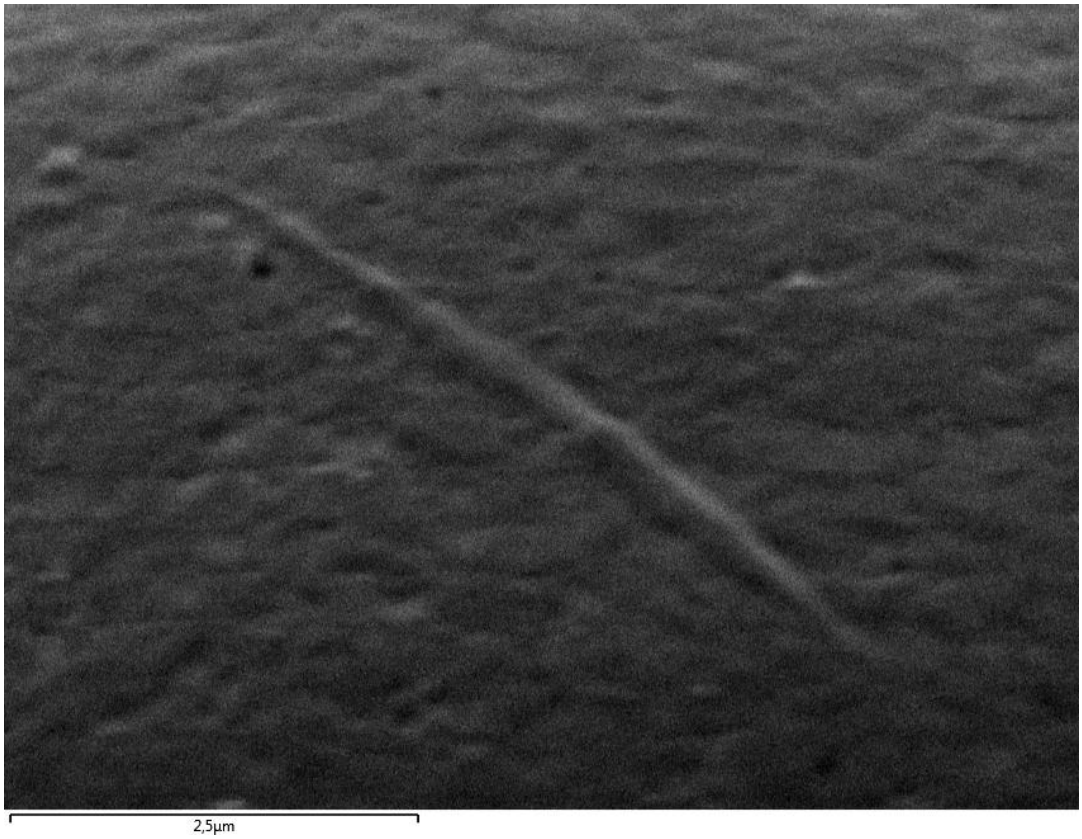


Figure 20 - SEM image of the polyamide microcapsules external membrane.

TGA was performed in order to analyze the thermal stability of the polyamide microcapsules synthesized.

Figure 21 shows that the polyamide microcapsules are stable up to a high temperature, 250ºC, from which there is not a considerable increase in the mass loss, being a stepwise decomposition. The high stability of the polyamide microcapsules can be explained due to the existence of an aromatic ring in the final product by using PPD as a monomer in the polyamide microcapsules synthesis. In the presence of an aromatic ring it is expected a higher thermal stability, which is confirmed in Figure 21 with a not significant initial decrease for low temperatures [64].

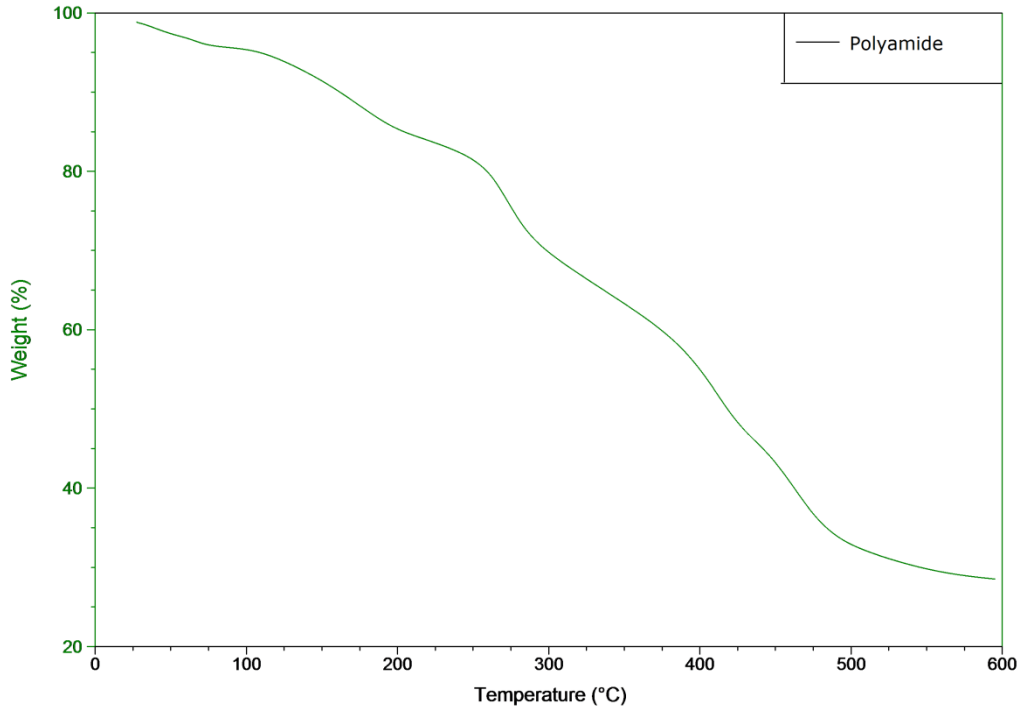


Figure 21 – TGA of the polyamide microcapsules synthesized.

The cationic emulsifier, CB, was used to improve the TDN fixation on the polyamide microcapsules surface.

Two different strategies for CB addition were used. The first one deals with the dissolution of CB in the stabilizer aqueous solution at the moment of the microcapsules synthesis (as described in strategy 2, steps 2.1 and 2.2 in Figure 9). The second one consists of the addition of CB after the microcapsules synthesis (as described in Figure 14, being the continuation of strategy 1, steps 1.1 and 1.2 of Figure 9). In both cases, the concern was to keep the CB concentration under its critical micelle concentration (CMC), specifically in this work at 50% and 80% of its CMC.

The polymeric microcapsules with CB added were also analyzed by OM and SEM analyses.

When CB was added during the polyamide microcapsules formation for enhancement of TDN fixation on the microcapsules

surface, the OM capsules images showed that the capsules maintain their main structure (Figure 22). They remain spherical as showed in Figure 22, when compared to Figure 17, when no CB was added. CB is added during the microcapsule synthesis, so interfacial polymerization occurs with CB already added in the solution, which makes CB an integral part of the microcapsule polyamide layer, being absorbed in the polyamide layer. Thus, any differences are expected in the SEM images in the polyamide microcapsules surface.

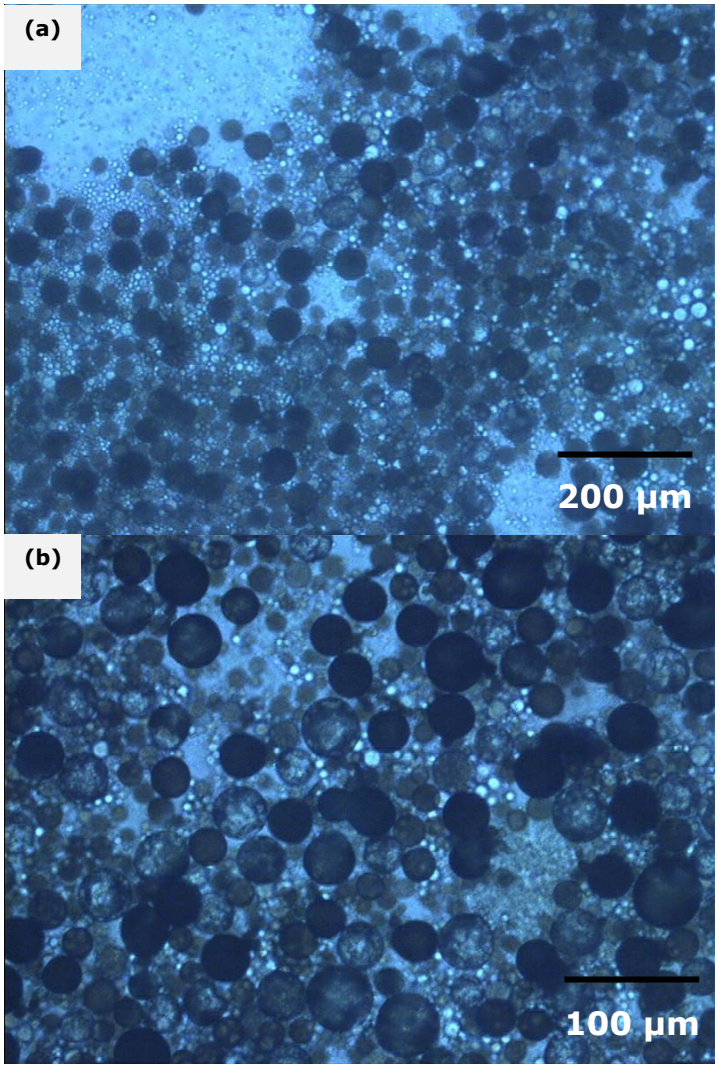


Figure 22 - OM images of polyamide microcapsules with different concentrations of CB added during the polyamide microcapsules synthesis, (a) 50% of CMC of CB and (b) 80% of CMC of CB.

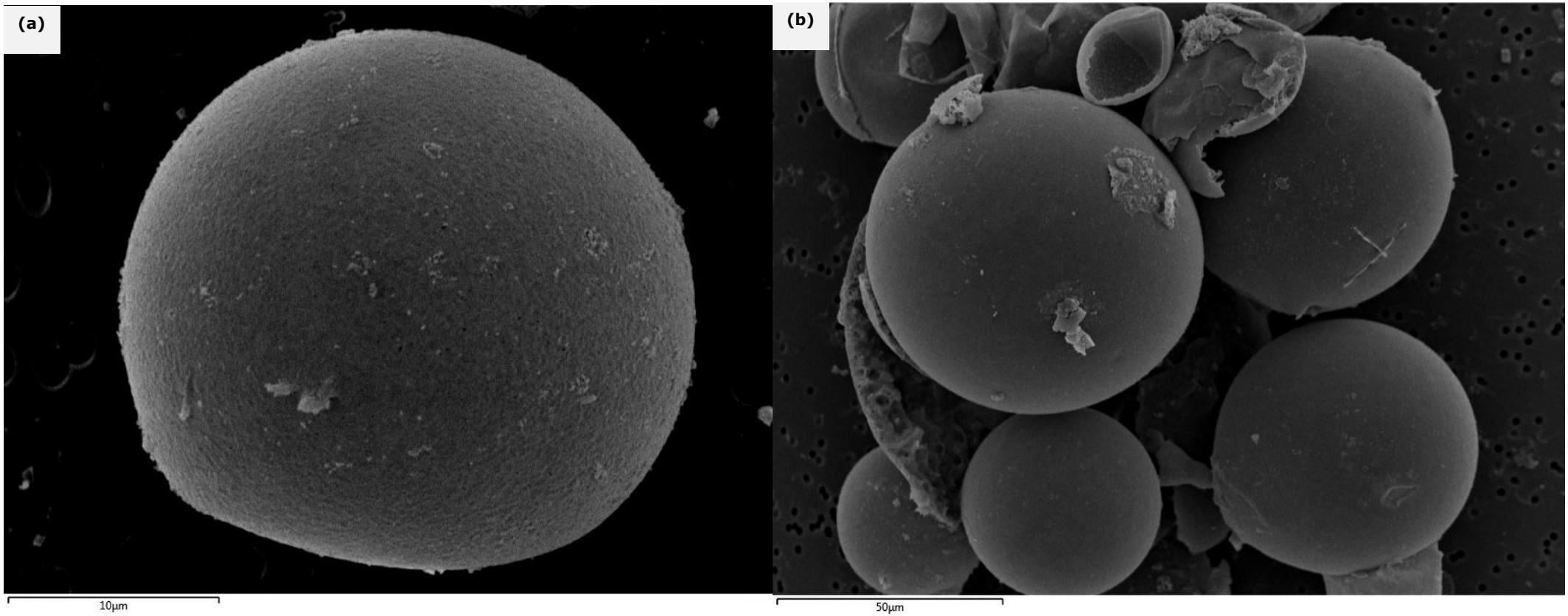


Figure 23 –SEM images of polyamide microcapsules with different concentrations of CB added during the microcapsules formation, (a) 50% of CMC of CB and (b) 80 % of CMC of CB.

When CB was added during the polyamide microcapsules synthesis, the microcapsules were also analyzed by TGA. In Figure 24 it is possible to see the great similarity between the curves which suggests that polyamide with CB addition (50% and 80%) during the microcapsules synthesis exhibits the same thermal stability as polyamide with no CB added. Thus, polyamide with CB added during the polyamide microcapsules synthesis has also a high thermal stability, also up to 250ºC [64].

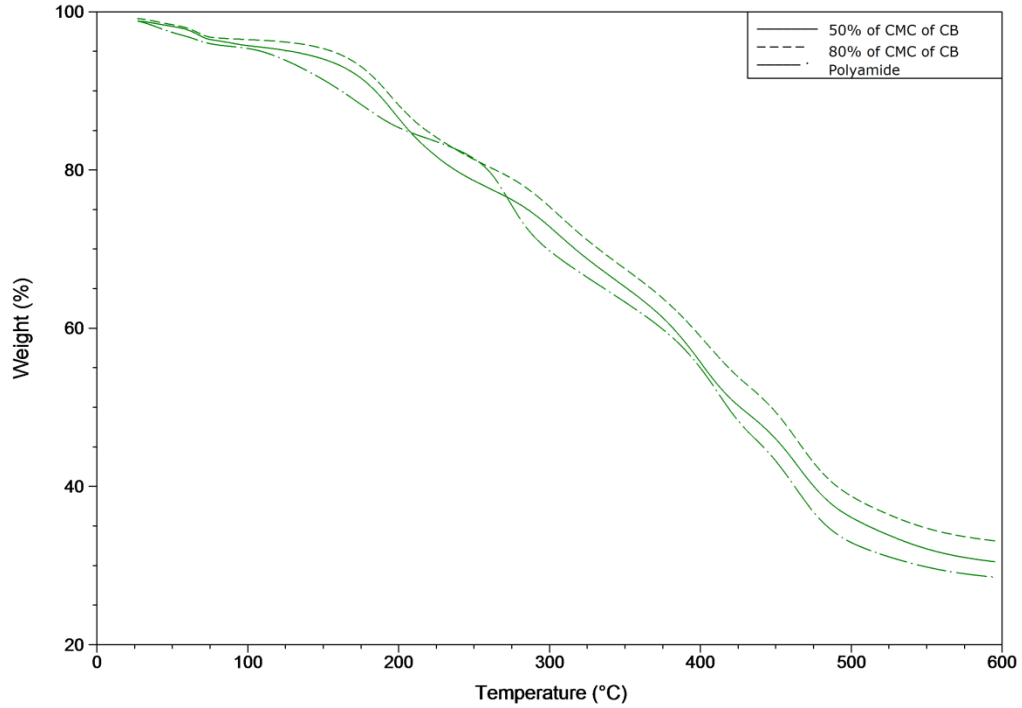


Figure 24 – TGA of the polyamide microcapsules with CB added during the microcapsules synthesis.

4.2. FIXATION OF TDN ON THE POLYAMIDE MICROCAPSULES SURFACE

After the polyamide microcapsules synthesis, an aqueous solution of TDN (1mg/mL) was added to the solution of polyamide microcapsules prepared as described in section 3.3 of the third

chapter. This TDN addition was done to microcapsules without CB, with CB added during the microcapsules synthesis and to capsules with CB added after the polyamide microcapsules synthesis.

The TDN-coated polyamide microcapsules were also observed by OM and SEM analyses (Figure 25 and Figure 26).

When TDN was added to the microcapsules surface, Figure 25 shows that no differences are observed when compared to Figure 18, where there was no addition of TDN. The microcapsules maintain their external smooth surface. Probably some TDN was fixed to the polyamide surface, but it wasn't very significant. Thus, it can't be considered a successful TDN fixation on the polyamide microcapsules surface.

This result indicates that TDN has not great affinity with the polyamide layer of the microcapsules, so it is necessary the microcapsules functionalization with a compound that enhances the TDN fixation. As TDN are particles that have negative charged surface, it would be a better method to add a cationic surfactant with positive charges in the polyamide layer of the microcapsules [32].

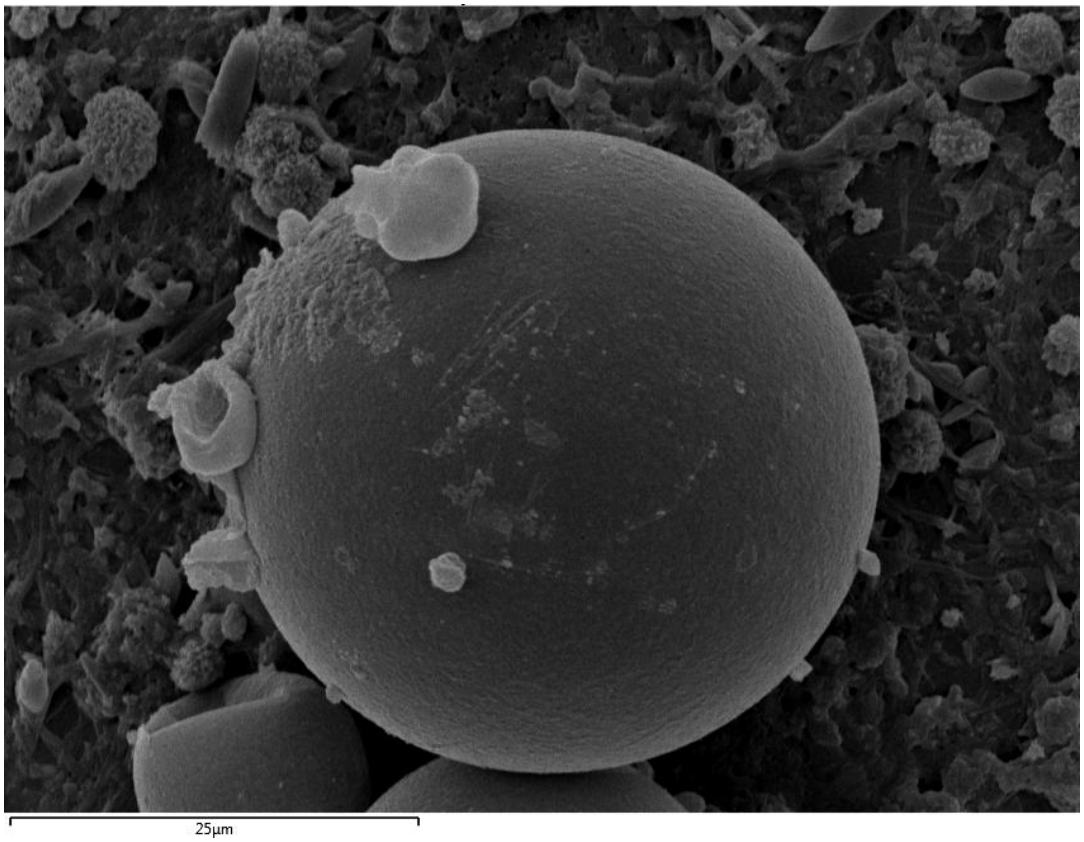


Figure 25 – SEM image of a TDN-coated polyamide microcapsule with no CB addition.

When CB was added during the polyamide microcapsules formation, OM images, in Figure 26 (a) and (b), show that the configuration of the capsules was maintained.

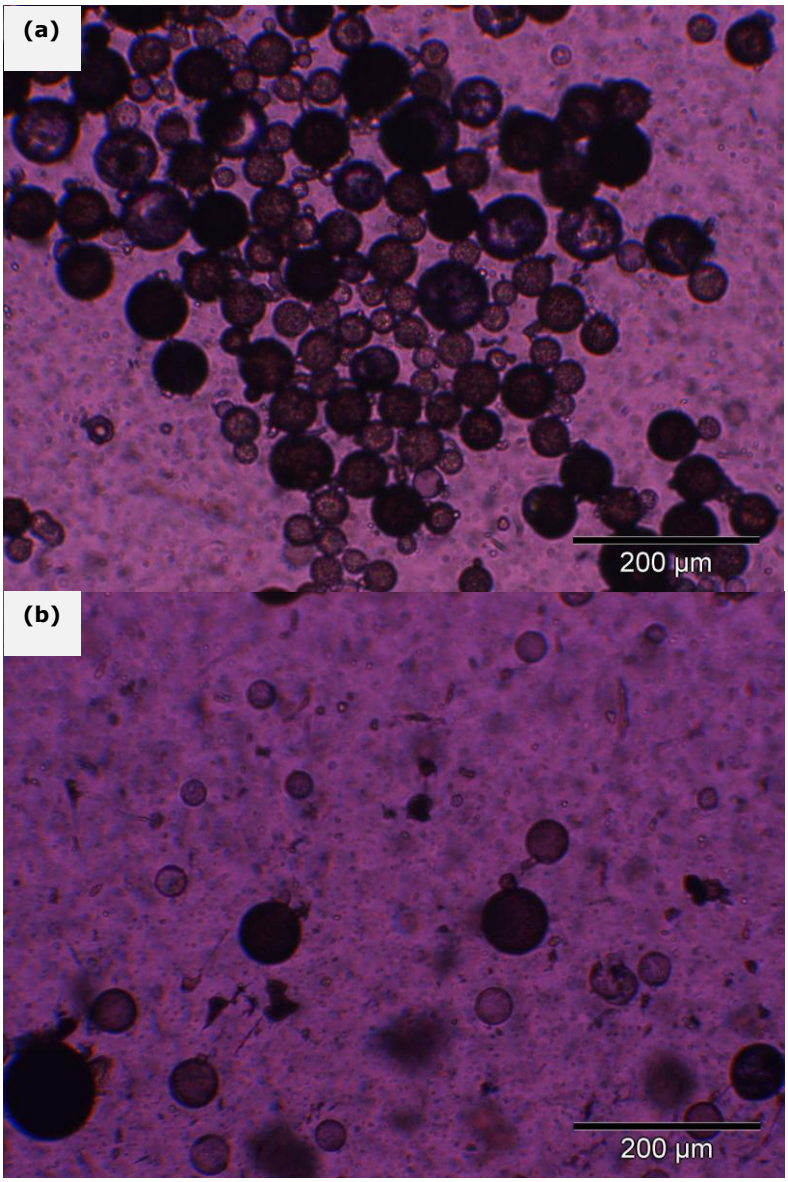


Figure 26 - OM images of polyamide microcapsules TDN-coated with different concentrations of CB added after the polyamide microcapsules synthesis, (a) 50% of CMC of CB and (b) 80% of CMC of CB.

In SEM analysis (Figure 27 (a) and (b)) the microcapsules also show maintenance of their smooth external membrane, when compared to Figure 18. However, analyzing Figure 27 (a) and (b) in more detail, white particles appear quite dispersed on the microcapsules surface. TDN appear to have been fixed on the capsules membrane. To confirm if these white spots are TDN, SEM analysis in higher resolution of these nanoparticles were performed.

In Figure 28, it's evident that TDN have a white color and is presented in agglomerations. Due to their small size and the fact that they agglomerate to each other, TDN are very difficult to observe in separated particles. But, with the configurations and the agglomeration sizes very coherent between Figure 27 and Figure 28, the white spots are very likely to be TDN on the polyamide microcapsules surface.

The fact that TDN are presented on the microcapsules polyamide membrane shows that TDN has affinity to CB. As explained in the second chapter, CB is adsorbed in the polyamide microcapsules surface forming a layer with positive charges. With TDN in the surrounding solution, electrostatic reactions occur between the positive charges of CB and the negative charges of TDN [35-37]. Thus, TDN moves towards the organic phase, and consequently is retained on the microcapsules surface [65]. Figure 27 (b) showed that with higher concentration of CB higher was the TDN fixation on the polyamide layer of the microcapsules. So, 80% of CB showed to be more successful for TDN fixation than 50% of CB.

Another important aspect that has to be noticed is the critical micelle concentration (CMC). CMC is the surfactant concentration at which an appreciable number of micelles are formed [66]. When micelles are present in solution, biomolecular reactions can occur at two places, at the micellar region and in the bulk solution. A decrease in the reactions rate would occur if one of the reactants is incorporate into the micelles such that it is inaccessible to the other reactant for reaction [67]. So in this work, it was chosen to use CB with its concentration lower than its CMC (9.2×10^{-4} mol/L at 25ºC), that showed a successful interaction between CB and TDN.

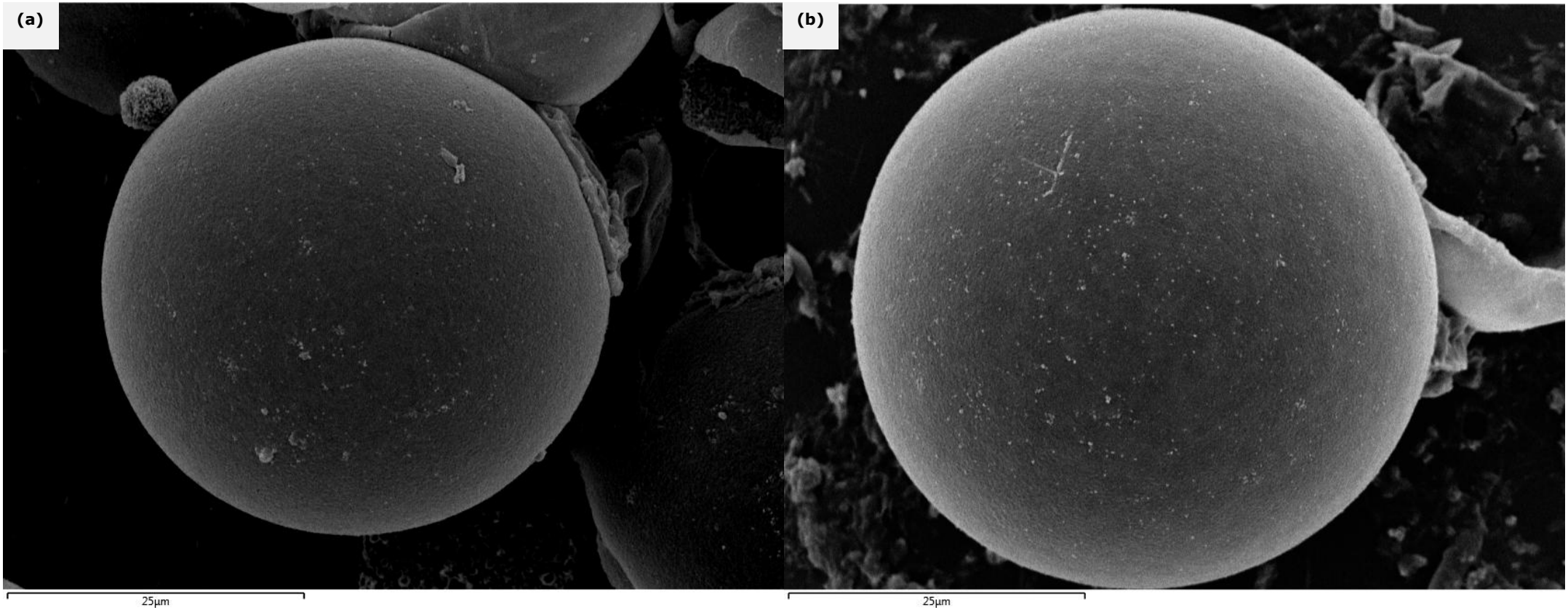


Figure 27 – SEM images of polyamide microcapsules TDN-coated with different concentrations of CB added after the microcapsules formation,(a) and (b) 50% of CMC of CB, and (c) and (d) 80 % of CMC of CB.

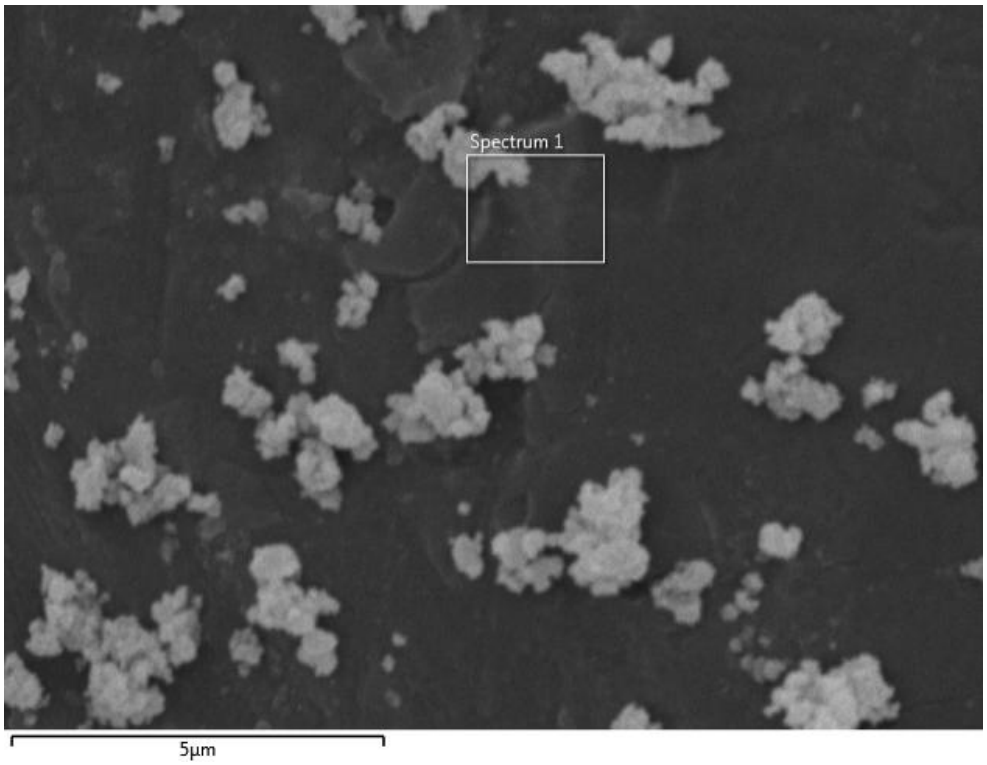


Figure 28 – TDN agglomerations.

When CB was added after the polyamide microcapsules formation, OM images show SEM analysis, Figure 30 (a) and Figure 30 (b) showed that TDN fixation was even higher than the TDN fixation when CB was added during the polyamide microcapsule formation on the surface of the microcapsules. This showed that with the addition of CB after the polyamide microcapsules synthesis, CB was probably adsorbed at a more superficial site of the polyamide layer of the microcapsules than when added during the capsules syntheses. Thus, there are more positive charges available to react with the negative ones on the TDN surface at the polyamide layer surface. Thus, TDN reactions with CB were highly increased, having more amount of TDN fixed on the polyamide microcapsules surface. At this stage, it was observed that the number of TDN particles distributed on the polyamide microcapsules surface is very equal with both CB concentrations. Thus, TDN fixation occurred in a very similar way (Figure 30 (a) and Figure 30 (b)).

SEM images also showed that the microcapsules now have a rougher outer capsule shell layer, with many wrinkled particles on the microcapsules' surface, due to the numerous nanoparticles (TDN) that are fixed and agglomerated on the microcapsules' surface [55].

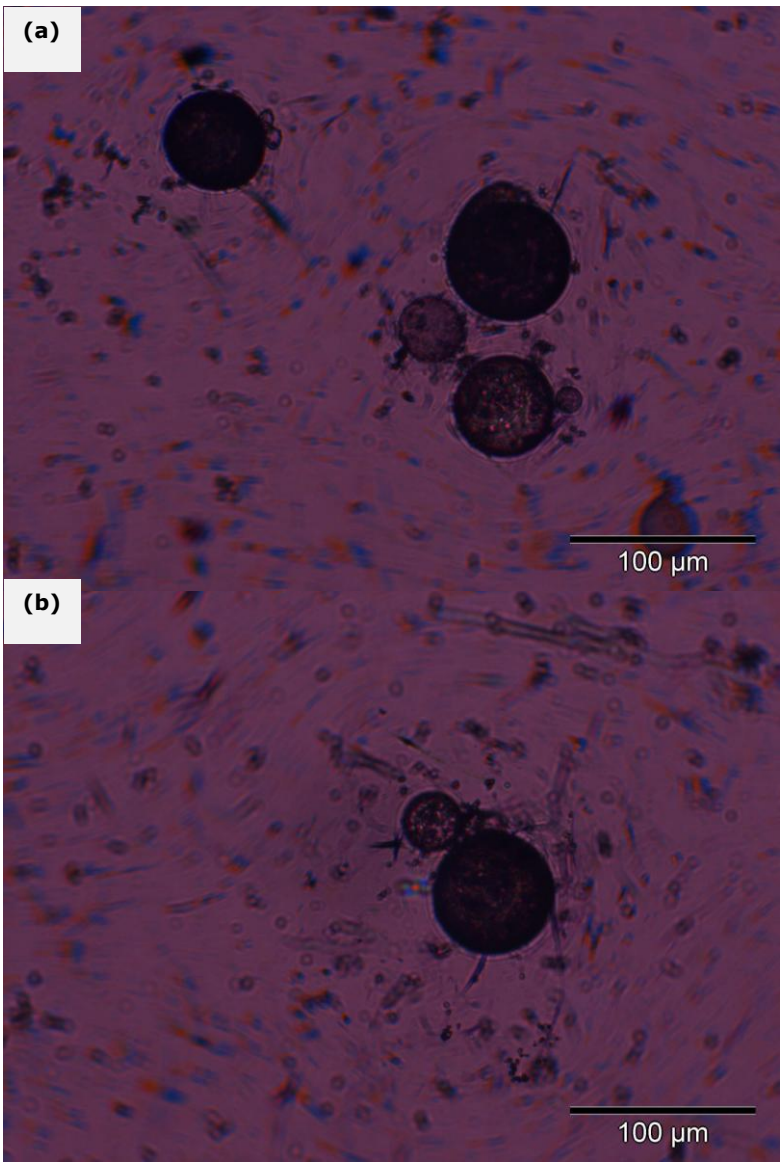


Figure 29 - OM images of polyamide microcapsules TDN-coated with different concentrations of CB added after the polyamide microcapsules synthesis, (a) 50% of CMC of CB and (b) 80% of CMC of CB.

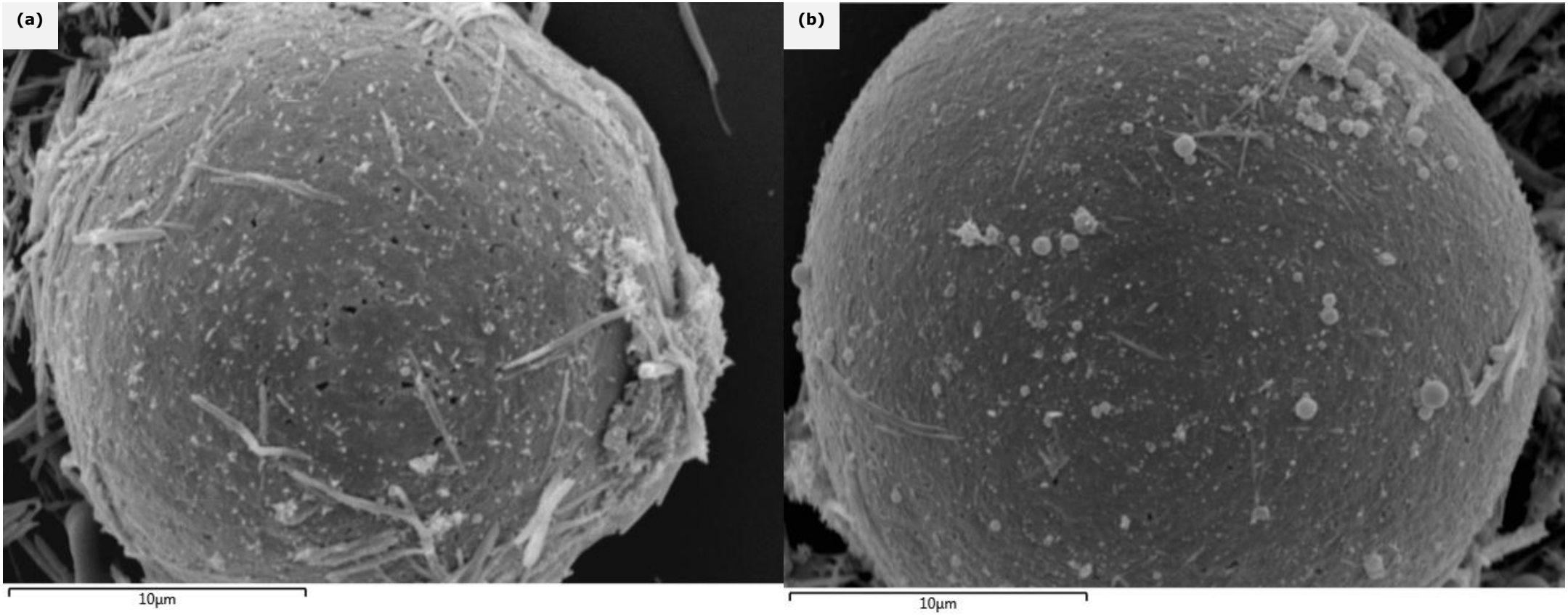


Figure 30 - (a) SEM images of polyamide microcapsules TDN-coated with CB added after the microcapsules synthesis, and with TDN, (a) 50% of CMC of CB and (b) 80% of CMC of CB.

4.3. DEGRADATION PROCESS OF TDN-COATED POLYAMIDE MICROCAPSULES

The use of TDN on the surface of the microcapsules' membrane will promote the membrane degradation upon exposure to UV light, due to its photocatalytic properties. The photochemical reactivity that occurs with TDN when irradiated with UV light is, schematized in Equation 2 of the first chapter. The reaction leads to the oxidation and destruction of the microcapsules surface and consequently the release of the encapsulated oil.

In this stage two different UV lights were used, one with a wavelenght of 365 nm, which was already reported in the literature [68, 69] and a second one with 254 nm (Figure 31). The second wavelenght corresponds to a more energetic UV radiation than the first (354 nm), so the TDN photocatalytic reactions are more likely to occur. Thus, a UV light with 254 nm was used for irradiation of the TDN-coated polyamide microcapsules for their degradation.

In this project in order to save time and resources, a different strategy for the preparation of the polyamide was used. Films of polyamide were chosen instead of making polyamide microcapsules, because only the polyamide chains themselves are needed to evaluate which chemical bounds are broken under UV light irradiation.

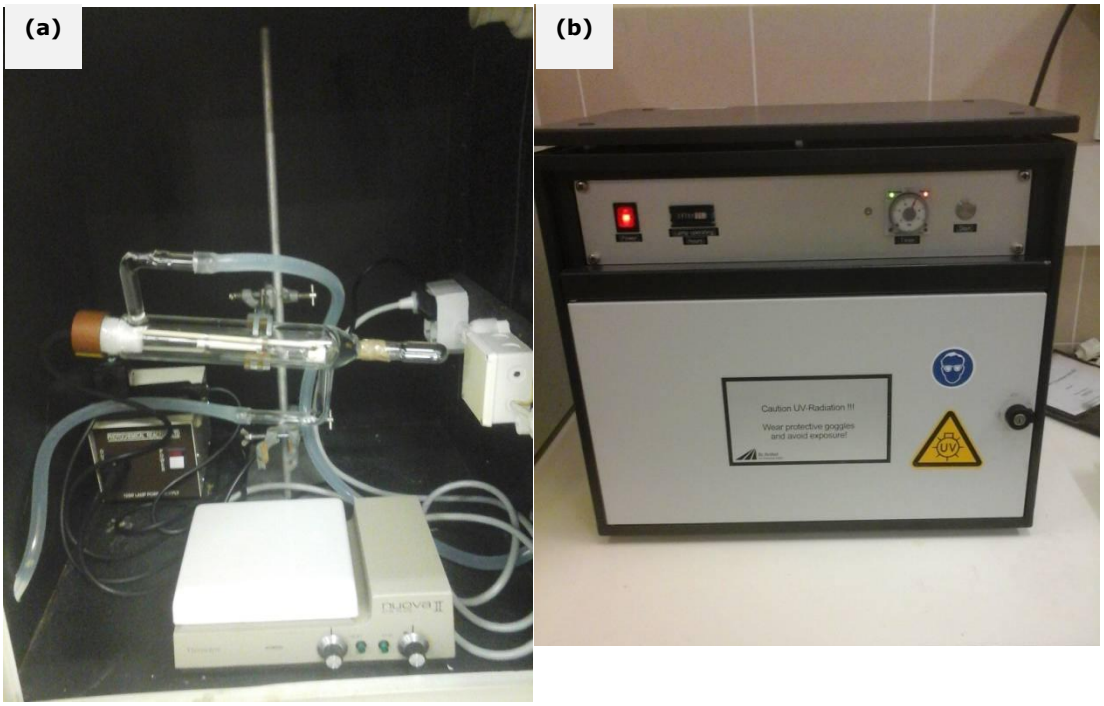


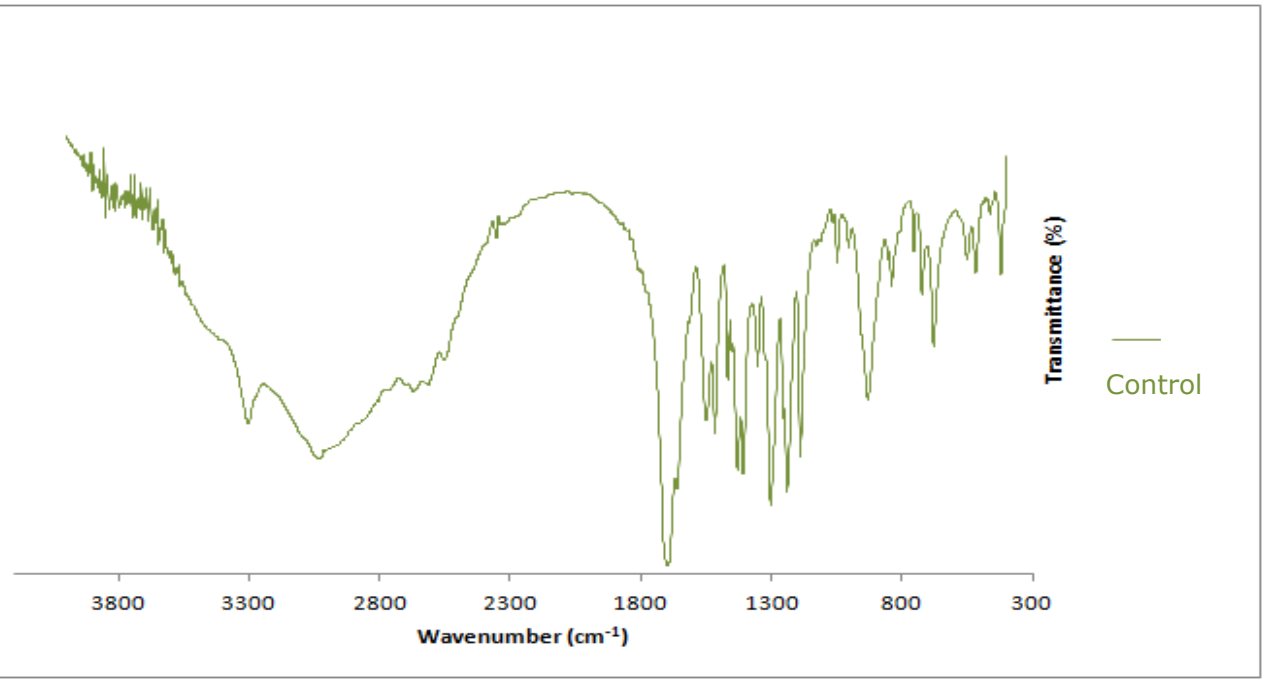
Figure 31 – UV light irradiation chamber with a wavelength of (a) 365 nm and (b) 254 nm.

The polyamide used to prepare the films was synthesized according to the normal interfacial polymerization method. Polyamide was prepared by adding a mixture of SC and hexane, to facilitate the reaction between the two monomers, and PPD. Calcium carbonate was used to neutralize the final solution. Then, this solution was washed with an aqueous solution of ethanol 10% volume/volume ratio (v/v) and then dried at 50ºC. The chemical structure of the polyamide obtained was analyzed by FTIR-KBr and ^{1}H NMR analyses.

The resulting FTIR-KBr spectrum was compared with the spectra presented in the literature [23]. The FTIR-KBr spectra showed the expected peaks at 1690 $cm^{-1}$and 1546 cm^{-1}, which are the characteristic absorption peak of C=O stretching vibration of the secondary amide group, as well as the corresponding N-H stretching vibration, respectively. These two peaks indicate the successful formation of the polyamide. Additional peaks in the area of 3500 and 3060 cm^{-1}displaying –NH stretching vibration of the primary and

secondary amines were also observed. These signals could be related to the excess of amine used. The large band at 3310 cm^{-1} is ascribed to the –C=O characteristic band (Figure 32). This FTIR-KBr spectrum was used as a control for the following FTIR-KBr spectra of the pellets UV light irradiated.

Furthermore, polyamide structure was verified by ^{1}H-NMR spectroscopy (Figure 33). The observed spectrum resembles the spectrum of a polyamide. It showed the characteristics peaks of polyamide at 6.4-7.4 parts per million (ppm), correspondent to the aromatic protons from the *p*-phenylenediamine monomer; 1.47 and 2.17 ppm, correspondent to the protons –C$\mathbf{H_2}$$CH_2$CO and –$CH_2C\mathbf{H_2}$CO, respectively, from the SC unit; and 8.28 and 9.43 ppm, correspondent to the –N**H** protons in the amine group formed by the polymerization reaction between PPD and SC. The characteristic solvent peak (DMSO-d_6) is observed at 2.50 ppm [23].



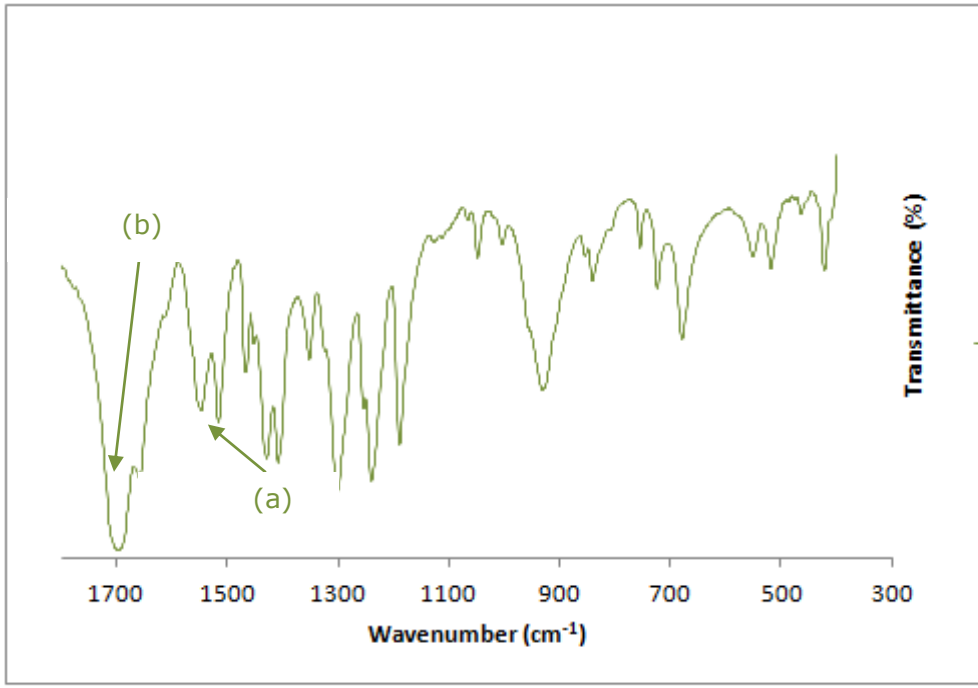


Figure 32 – FTIR-KBr spectra of polyamide powder with (a) the characteristic peak of N-H stretching (1546 cm^{-1}) and (b) the characteristic of –C=O stretching (1690 cm^{-1}).

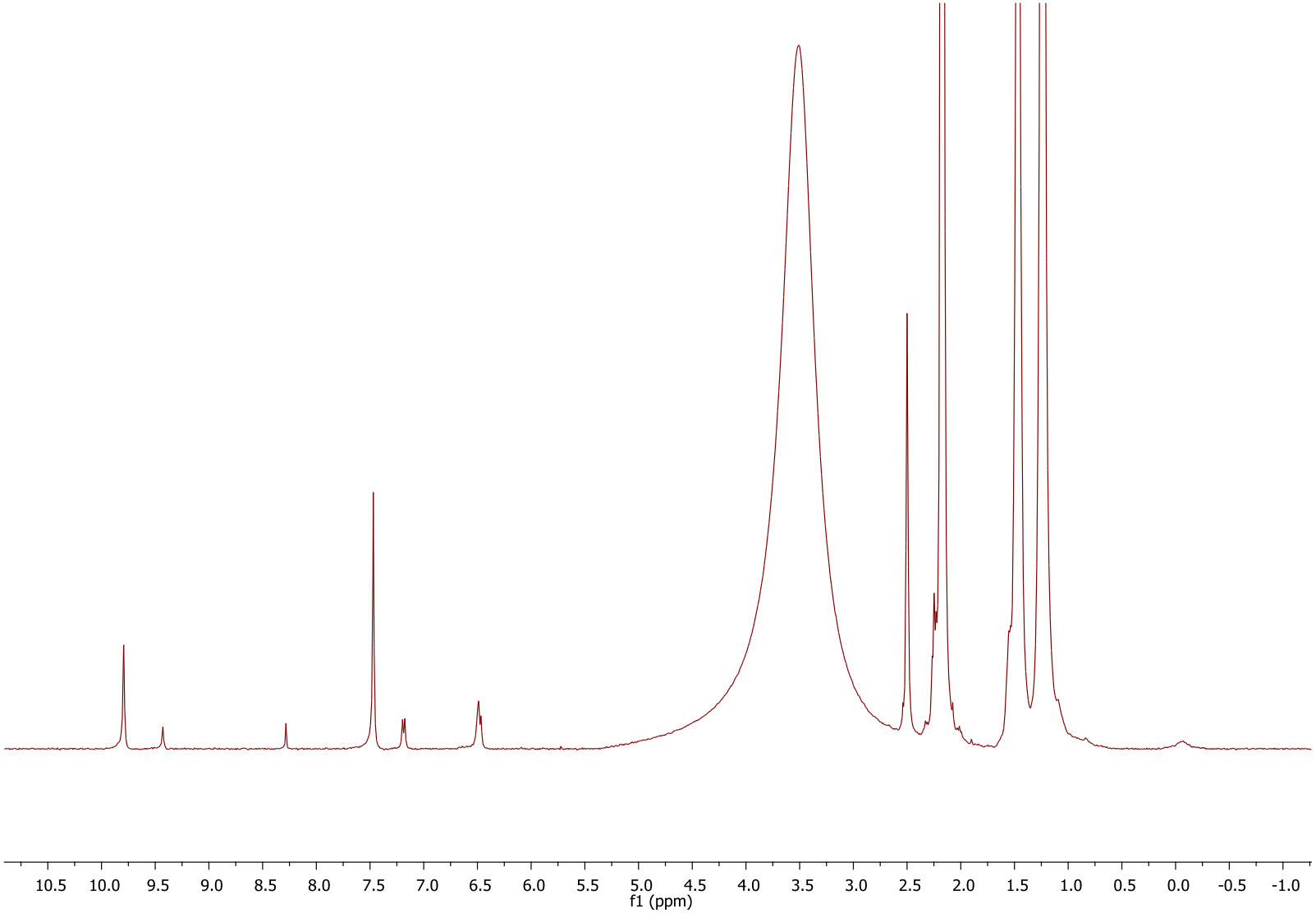


Figure 33 - ^{1}H-NMR spectrum of the polyamide, in DMSO-d_6.

In order to make polyamide films, the solubility of the resultant polyamide powder was tested in different solvents, namely 1,1,1,3,3,3-hexafluoro-2-propanol, a mixture of diethyleneglycol-monobutylether/chloroform/ 1,1,1,3,3,3-hexafluoro-2-propanol and DMSO. The polyamide is only soluble in DMSO. However, DMSO has a high boiling point (189ºC), being very difficult to evaporate it. So, to overcome these limitations, another strategy was performed, where polyamide pellets were obtained in the press and mould showed in Figure 33, with a pressure equal to 150 bars, obtaining very consistent pellets shown in Figure 34.

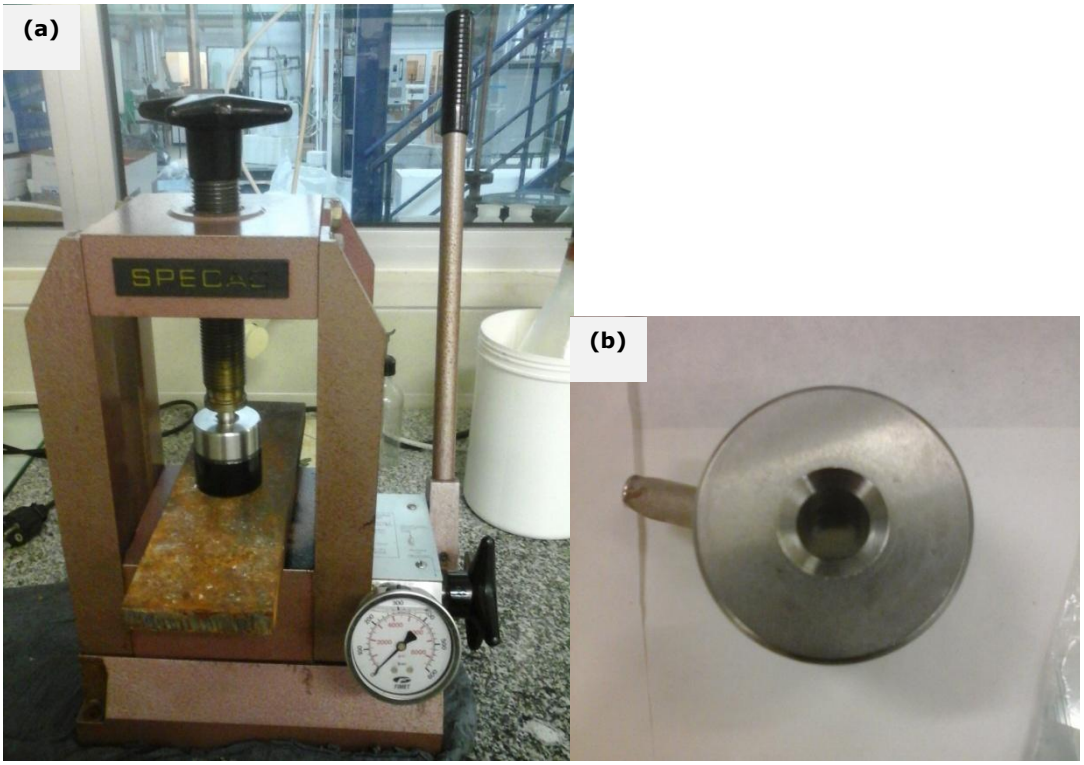


Figure 34 – (a) Hydraulic press and (b) stainless steel mould used to form polyamide pellets.

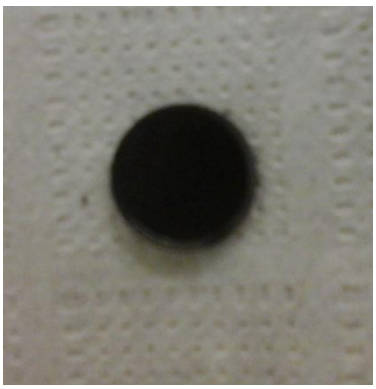


Figure 35 –Polyamide pellet.

The TDN was initially fixed into the top surface of the polyamide pellets. An aqueous solution of TDN (1mg/mL) was added to the polyamide pellets and the water evaporated over night and at room temperature. The polyamide pellets were irradiated under UV light (365 nm) and samples were collect over time and analyzed by FTIR-KBr in order to evaluate the polyamide structure degradation. The FTIR-KBr results of the samples after 30 minutes, 1 hour and 2 hours irradiation are presented in Figure 36.

Analyzing the FTIR-KBr spectrum, in Figure 36, of the polyamide pellets with TDN it is possible to observe that the characteristic peaks assigned to the polyamide structure, are also present in Figure 32. This result showed that the polyamide with TDN-coating was not degradated with UV light irradiation. In Figure 35 peaks from 2970 cm^{-1} to 2830 $cm^{-1}$are also observed, that are the characteristic peaks of TDN, so, TDN was successfully fixed on the polyamide pellets surface.

With this strategy came a second one, where it was tested the addition of TDN to the polyamide pellets surface with TDN being in the form of a powder. Here, the aim was to analyze if the TDN photocatalytic reactions occurred with TDN as a powder, with the same TDN concentration used in the first strategy.

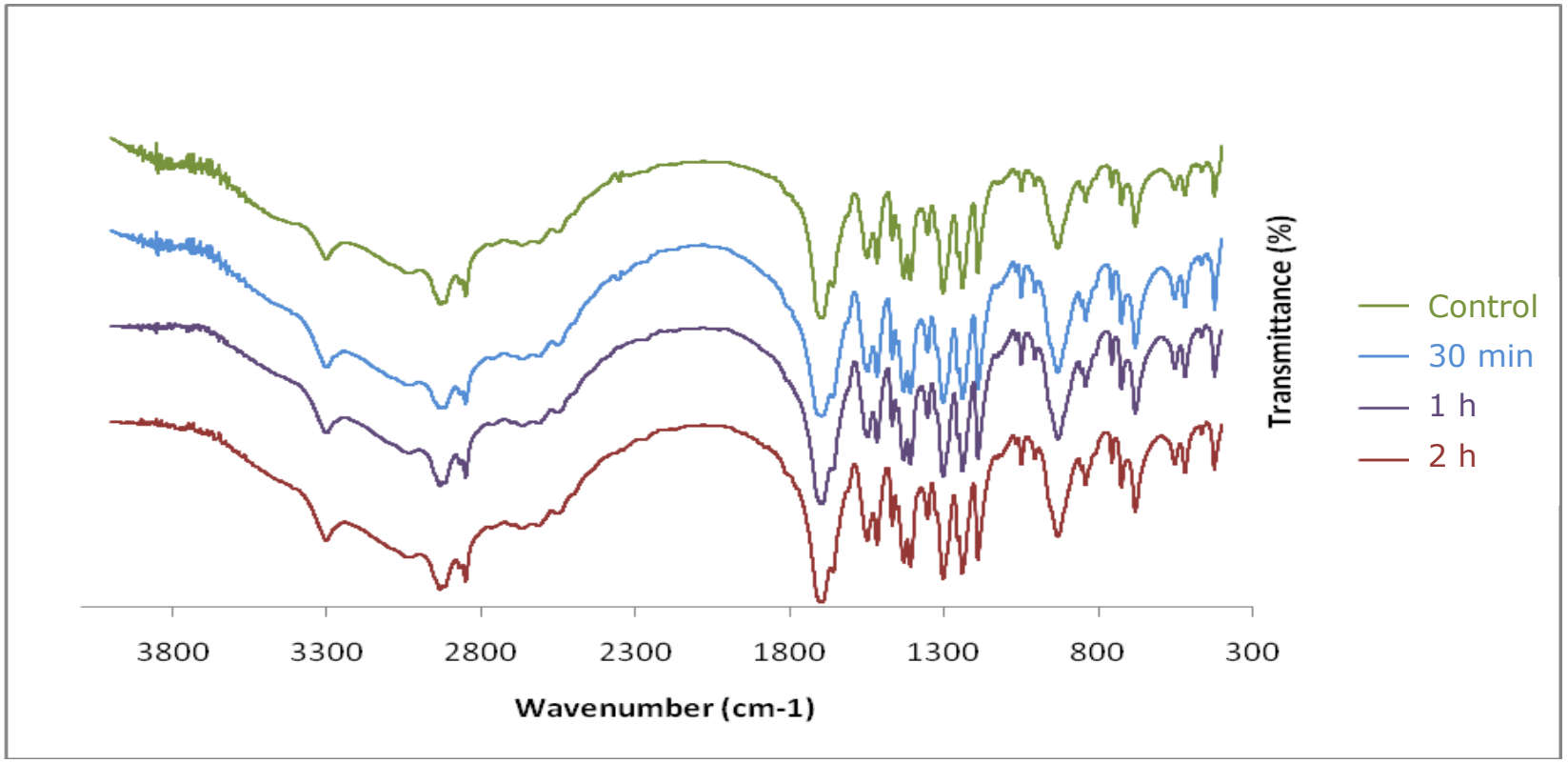


Figure 36 – FTIR-KBr spectra of polyamide pellets with TDN addition as a solution (1 mg/ml), from 4200 cm^{-1} to 300 cm^{-1}.

In the second strategy, TDN was fixed on the polyamide pellets as a powder, with 1mg and 5 mg of TDN added to 100 mg of polyamide powder.

These pellets with 1 mg of TDN on their surface were irradiated with the same UV light (365 nm), used previously, and also irradiated during the same time intervals.

The FTIR-KBr spectrum (Figure 37) also showed the characteristic absorption bands of the polyamide and TDN that appear in Figure 32 and Figure 36. This indicates that no degradation of polyamide structure was observed.

A suitable explanation could be the TDN concentration in the polyamide pellets that could still be very low. With this came the second part of strategy 2, with the purpose of increasing the TDN concentration added on the polyamide pellets. With the increase in the TDN concentration, it would probably be expected the increase of the photocatalytic reactions of TDN and so, the degradation of the polyamide present in the pellets. In this stage, 5 mg of TDN was added on the polyamide pellets surface. These polyamide pellets were irradiated under UV light (365 and 254 nm) and the samples were collected after predetermined intervals.

Figure 37 and Figure 38 show that any differences in the polyamide structure were observed, when compared to Figure 31. So, no polyamide degradation was still observed.

One hypothesis for this to happen is the TDN concentration that probably it is not yet the optimal concentration to be used. TDN concentration cannot be too high because reaching a certain critical point, photocatalytic reactions do not occur, and on the other hand, TDN concentration cannot be too low so that photocatalytic reactions do not occur [70].

Another explanation could be the polyamide pellets thickness that was very high, for the degradation of the polyamide to occur in through the whole pellet [71]. In this second strategy, the irradiation used does not seem to be the reason, as two both UV light were used (365 and 254 nm). However, an additional light could be testes, with for example 775 nm, that was already used in references [72, 73]. Also in this strategy there were used higher irradiation time intervals but it could be tested higher ones [73] .

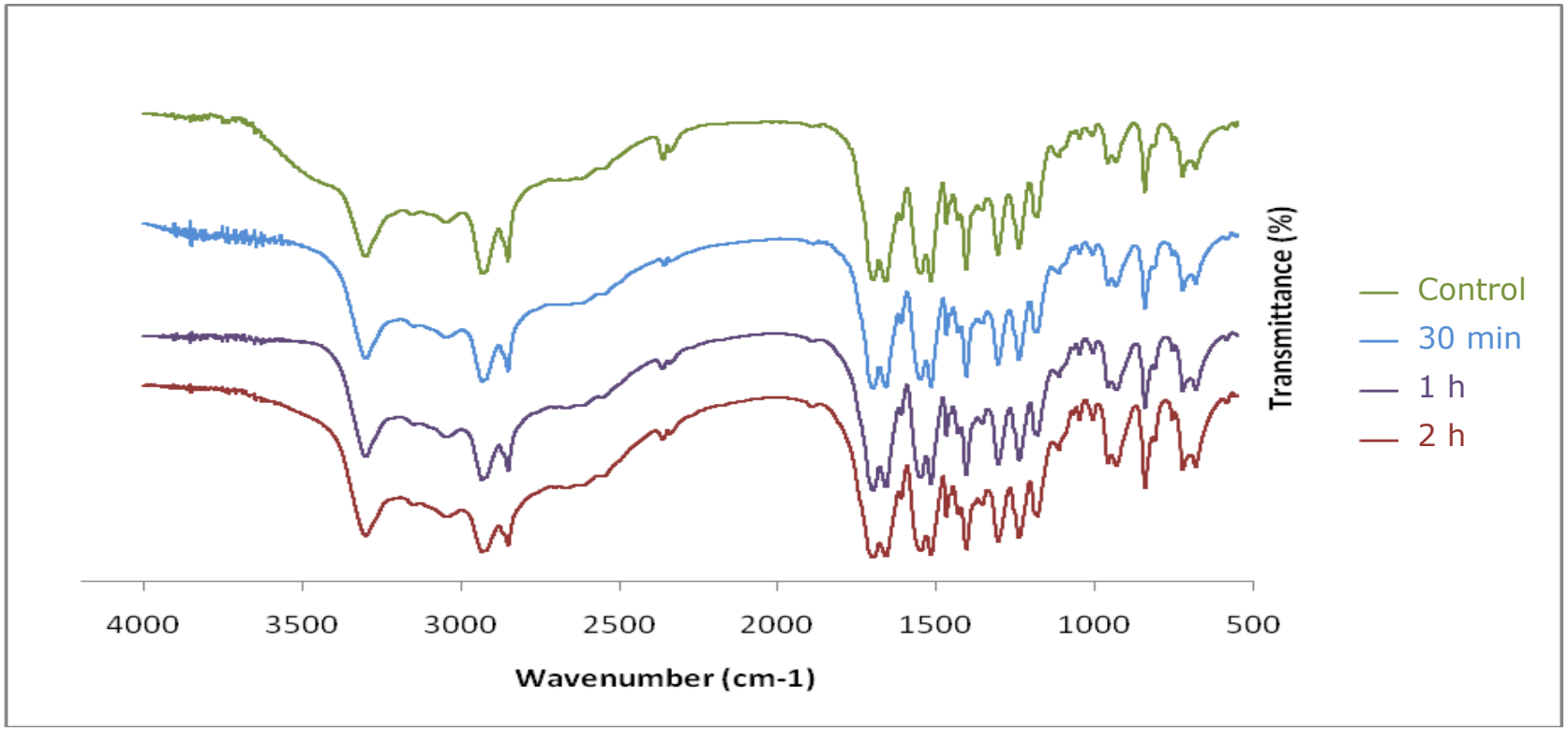


Figure 37 – FTIR-KBr spectra of polyamide pellets with TDN addition as a powder (1 mg) and after irradiation with a wavelenght of 365 nm, during 30 minutes, 1 hour and 2 hours, from 4200 cm^{-1} to 500 cm^{-1}.

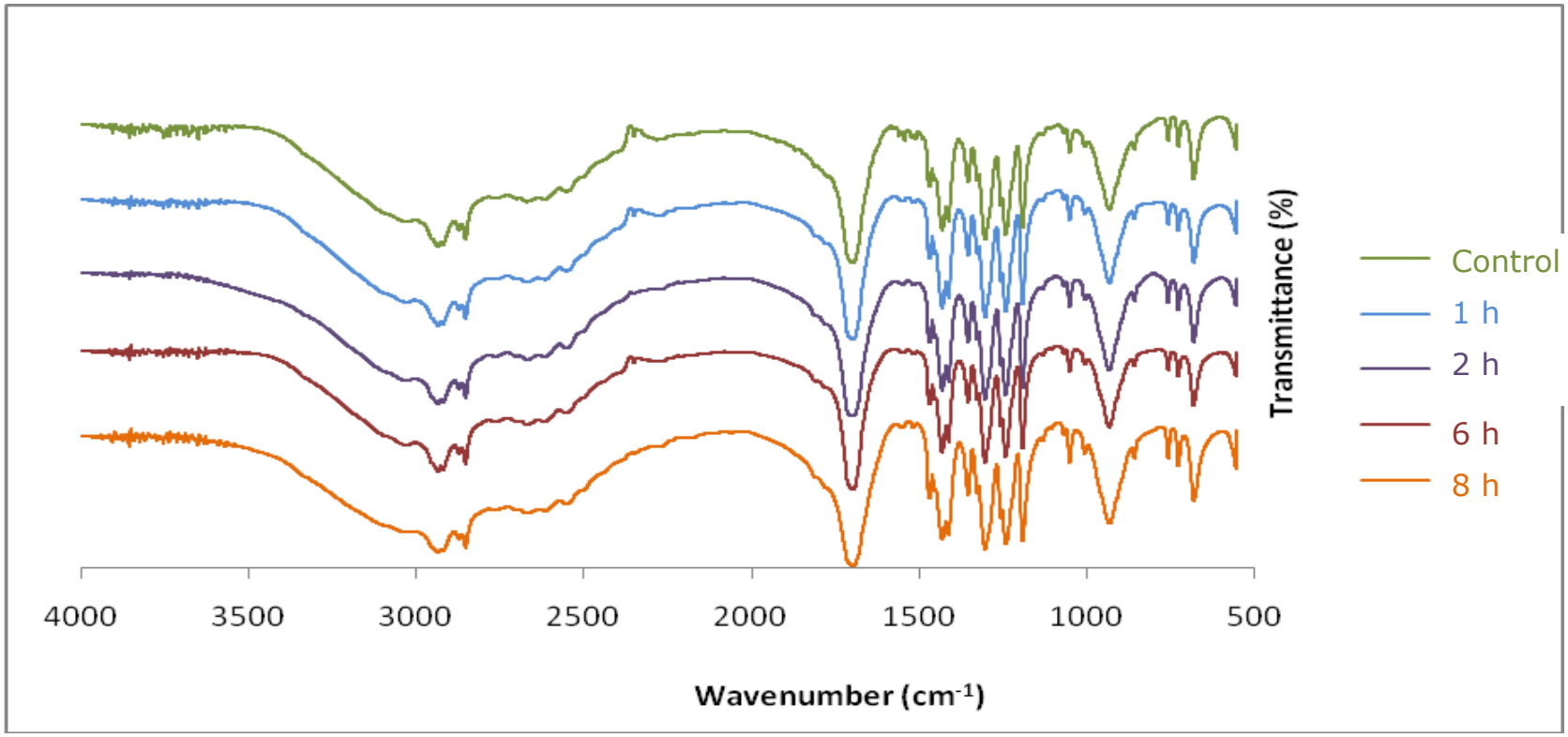


Figure 38 - FTIR-KBr spectrum of polyamide pellets with TDN added as a powder (5 mg) to the polyamide,and irradiated with a wavelenght of 365 nm, during, 1, 2, 6 and 8 hours, from 4000 cm^{-1} to 500 cm^{-1}.

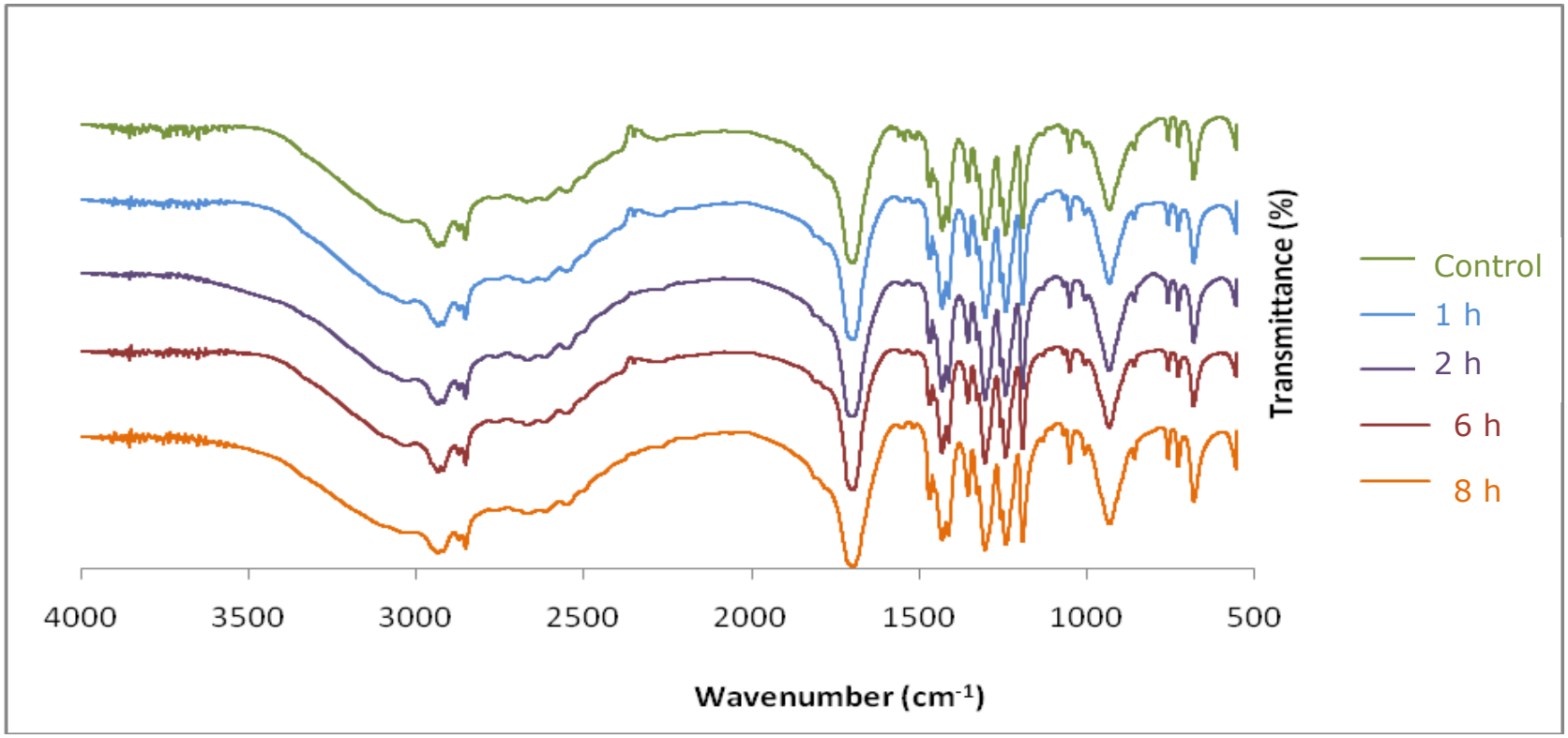


Figure 39 - FTIR-KBr spectrum of polyamide pellets with TDN added as a powder (5 mg) to the polyamide, and irradiated with a wavelength of 254 nm, during, 1, 2, 6 and 8 hours, from 4000 cm^{-1} to 500 cm^{-1}.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

5. CONCLUSIONS AND FUTURE WORK

Microcapsules with dodecane encapsulated were successfully synthesized by interfacial polymerization of a hydrophilic monomer, PPD, and a hydrophobic monomer, SC. Spherical polyamide microcapsules with average diameter in the range of 20-60 μm were manufactured with 1200 agitation rate and proppeler shape stirrer. The average membrane thickness ranged from 900 nm-3 μm. They presented a smooth external membrane and a rougher internal membrane, due to the inner growth of the microcapsules with PPD diffusion into the organic phase.

This work also showed that when CB was added to the polyamide microcapsules surface with its addition during the microcapsules synthesis, the capsules showed to maintain their smooth external membrane but presented TDN fixed on the microcapsules surface, when compared to microcapsules with no CB added and with TDN addition. This TDN fixation increased with higher CB concentration used. On the other hand when CB was added after the polyamide microcapsules synthesis, microcapsules showed to have a rougher external membrane, when compared to the ones with CB added during the microcapsules synthesis, with more TDN on the capsules surface. The TDN fixation also increased with the increase of CB concentration. Thus, in both CB addition strategies TDN was successfully fixed on the polyamide microcapsules surface.

The irradiation of the polyamide pellets prepared with TDN addition as a solution, and as a powder with 1 mg and 5 mg showed no TDN photocatalytic activity, and so no polyamide degradation was observed. This happened with both UV light radiations used (365 and 254 nm) and with different time intervals of irradiation. In this way, the polyamide structure degradation wasn’t successfully achieved.

With this, further studies still need to be done. It would be interesting to study some different chemical compounds, such as copolymers, for their absorption on the polyamide microcapsules surface, for TDN fixation for the microcapsules degradation and consequent dodecane, encapsulated in the capsules, release. It would be also worthy of future study technical performances for the polyamide pellets and their irradiation, namely a different method for a polyamide surface where TDN can be fixed with a lower thickness than the ones presented in this work, the use of an optimal concentration of TDN fixed on the polyamide pellets surface, and the performance of the irradiation tests with different UV-lights and with different time intervals. Another aspect for future studies would be the FTIR-KBr analysis only to the surface of the polyamide pellets instead of the analysis of the whole pellet.

CHAPTER VI

BIBLIOGRAPHY

6. BIBLIOGRAPHY

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